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Review Article

Extraction of Strontium and Cesium by Dicarbollides, Crown Ethers and Functionalized Calixarenes

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Abstract. The two main classes of extractants used for the extraction of cesium and strontium are dicarbollides and crown ethers. Dicarbollides were used on a large scale for the extraction of these two elements from high-activity waste. The basic dicarbollides present drawbacks since they need to be diluted in polar solvent such as nitrobenzene and their efficiency strongly decreases as the acidity of liquid waste increases. Crown ethers enable cesium and strontium to be extracted if the concentration of sodium or the acidity of solutions are not too high. Recently, calixarenes blocked in the 1,3-alternate conformation were used for the selective extraction of cesium, even from high-salt waste matrices.

Key words: dicarbollides, crown ethers, calixarenes, calixarenes crown 6, strontium, cesium.

1. Introduction

In most countries strontium and cesium not extracted in the PUREX process, are incorporated with a majority of fission products in glass matrices. Studies were launched in France, Japan and Russia to recover minor actinides and long-life fission products, particularly [135]cesium (half-life 2.3×10^6 years), in order to destroy them by transmutation or to incorporate them in high integrity matrices.

Generally speaking, the elimination of [90]strontium (half-life 29 years) and [137]cesium (half-life 30 years) from other fission products provides several advantages [1]:

- It can lead to a reduction of vitrified waste volume, due to the fact that fission product and actinide loading can be substantially increased without affecting its stability.
- After 10 years of cooling time, the total heat output is essentially due to these two isotopes. Removing them suppresses the need of redundant cooling of

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fission product solutions and the need for the vitrified high activity waste to be stored for 50 years.

- It leads to a denser disposal in geological formation, due to heat dissipation therefore limited in the disposal. Another advantage is to facilitate the handling and the means of transport of high activity waste.

The separated isotopes can be either used (provide continuous electrical power for strontium, food irradiation, sterilization of medical supplies for cesium), or placed in interim storage.

Medium activity wastes generally contain strontium, cesium and actinide activity which is too effective to be stored in subsurface disposal. From an economical point of view, it can be interesting to remove these long-life elements and then the greatest part of the waste can be disposed of in an existing subsurface site and only a small part containing the long-life nuclides is sent for intermediate storage or disposal.

2. Extractants

Two classes of extractants are used for the removal of strontium and cesium, dicarbollides and crown ethers [2]. More recently, calix[4]arenes were proposed for cesium recovery.

2.1. DICARBOLLIDES

Dicarbollide, a boron cluster species with a π-bonded trivalent cobalt, was first prepared by Hawthorne in 1965 and then extensively studied by Czech scientists (Figure 1a) [3]. Poorly hydrated dicarbollide anions associate with cations to form neutral compounds, sparingly soluble in water, but much more soluble in polar dissociating diluents such as nitrobenzene:

$$M^{n+}_{aq} + nH^+_{org} + nCoB^-_{2\,org} \Leftrightarrow nH^+_{aq} + M^{n+}_{org} + nCoB^-_{2\,org}.$$
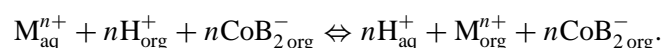
This very lipophilic anion, difficult to protonate, works even in strongly acidic medium and allows cations to be discriminated according to their Gibbs energies of transfer. Cesium which displays the lowest Gibbs energy of transfer to polar organic solvents relative to other cations in high and medium activity wastes, is the most efficiently extracted cation by dicarbollide anion [4].

2.2. CROWN ETHERS

The first crown ethers were synthesized by Pedersen in 1967. These macrocyclic compounds were the first extractants of alkali and alkaline earth cations [5]. The simplest compounds are shown in Figure 2. From these structures more sophisticated extractants were prepared (addition of alkyl chains etc.).
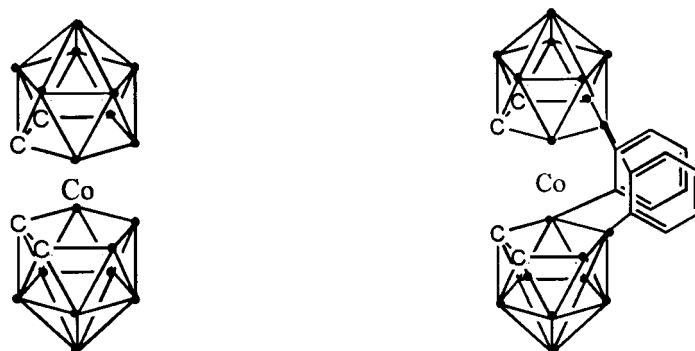
Figure 1. Dicarbollide cobaltate and (*bis*-phenylene) *bis*-dicarbollide cobaltate.
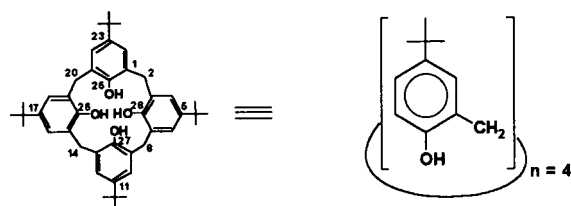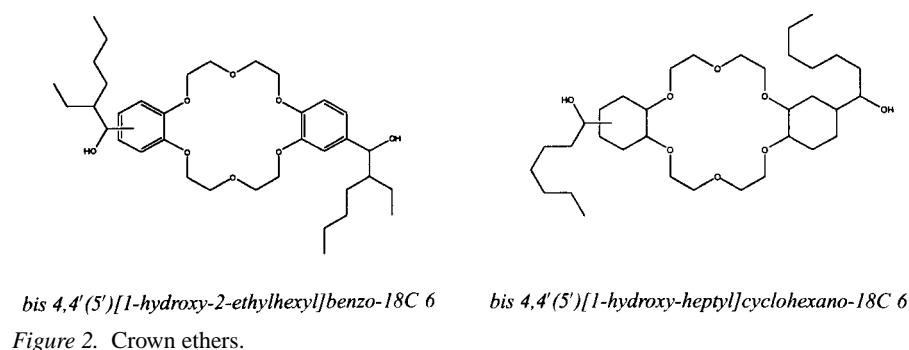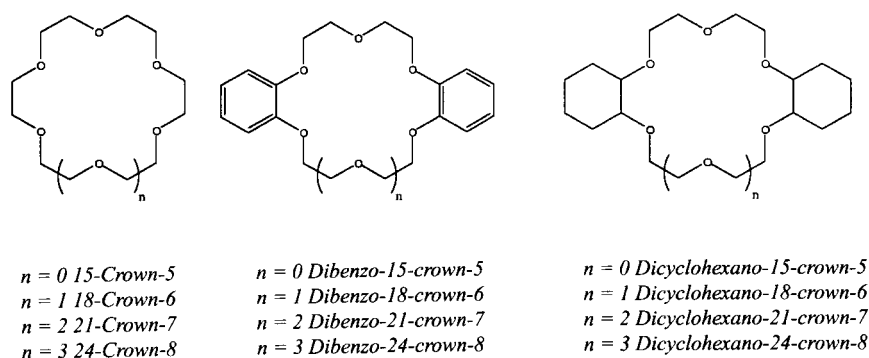
Crown ethers such as 15-crown-5 (15C5) or 18-crown-6 (18C6) are too hydrophilic to be used in liquid–liquid extraction; alkyl or aryl groups must be added to increase their lipophilicity, like dicyclohexano-18-crown-6 (DC18C6) or dibenzo-21-crown-7 (DB21C7). According to McDowell, rigid benzocrown ethers preferentially extract monovalent cations and cyclohexano crowns are more effective for divalent cations [6]. The match between the size of the cation and the size of the crown ether cavity is an important parameter affecting the selectivity; for instance DB15C5, DB18C6 and DB21C7 are respectively matched for the extraction of sodium, potassium and cesium. Another important parameter discussed by Hay is the ligand strain upon complexation or reorganization energy [7].

2.3. CALIX[4]ARENES

The name 'calixarenes' was proposed by Gutsche for the cyclic oligomers obtained by condensation of formaldehyde with *p*-alkyl phenols [8–10]. 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 3). The suffix arene indicates the presence of aryl groups in the molecule.

p-tert-Butylcalix[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 4).

Izatt *et al.* were the first to use *p-tert*-butylcalixarenes and *p-tert*-pentylcalixarenes for the transport of alkali metal cations and especially of cesium through bulk liquid membranes. These calixarenes being insoluble in most of the diluents, the transport experiments were carried out by dissolving them in a mixture of dichloromethane 25% v/v and carbon tetrachloride 75% v/v. Transport by the butyl (or pentyl) calixarenes is selective for cesium over other alkali cations, the selectivity increases as the size of the calixarenes decreases: calix[8]arene < calix[6]arene < calix[4]arene. One must point out that the highest fluxes are ob-

n = 0 15-Crown-5   n = 0 Dibenzo-15-crown-5   n = 0 Dicyclohexano-15-crown-5
n = 1 18-Crown-6   n = 1 Dibenzo-18-crown-6   n = 1 Dicyclohexano-18-crown-6
n = 2 21-Crown-7   n = 2 Dibenzo-21-crown-7   n = 2 Dicyclohexano-21-crown-7
n = 3 24-Crown-8   n = 3 Dibenzo-24-crown-8   n = 3 Dicyclohexano-24-crown-8

bis 4,4' (5')[1-hydroxy-2-ethylhexyl]benzo-18C 6   *bis 4,4' (5')[1-hydroxy-heptyl]cyclohexano-18C 6*

Figure 2. Crown ethers.

Figure 3. p-tert-butyl-calix[4]arenes.

tained with hexamers and octamers and that these carriers are efficient only for pH higher than 12 [11–13].

Calixarenes offer several advantages as carriers:

- low water solubility,
- formation of neutral complexes with cations through loss of a proton,
- potentiality of coupling cation transport and reverse proton transport.

Calix[4]arene-crowns-*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. 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-*bis*-(crown-*n*)). The crowns can include one or two benzene units (Figure 6).
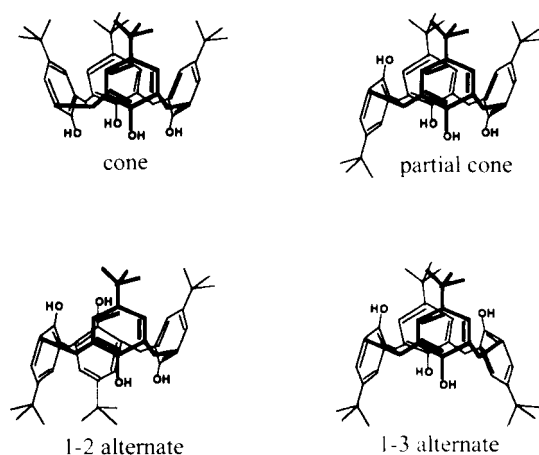
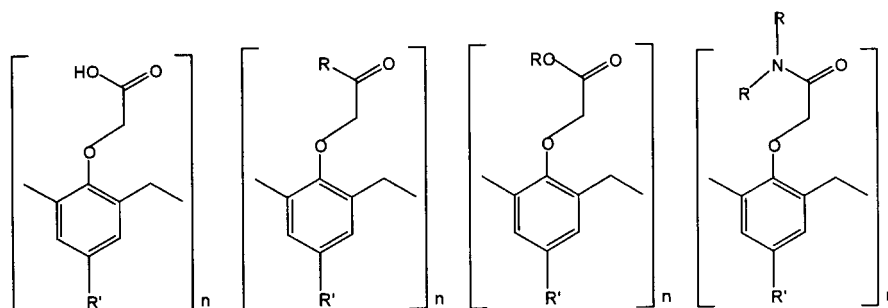*Figure 4.* Conformations of *p-tert*-butyl-calix[4]arene.

Figure 5. Functionalized calixarenes on the wide rim: Carboxylate, ketone, ester, amide, R = alkyl, R$'$ = H, *t*-butyl.

3. Dicarbollides

From 1976, Czech scientists extensively studied the extraction of cesium from acidic medium (0.5 M HNO$_3$) by dicarbollide anion $\{[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Co\}$ [14–19] diluted in polar nitrobenzene and its stripping by nitric acid at a concentration higher than 3 M. Generally, hexachloro and hexabromo derivatives are used, the substitution by these halides increases the stability of the compounds in acidic medium and the partitioning coefficients of the dicarbollide between organic and aqueous phases. Moreover the substitution of cobalt by iron or nickel affects adversely the extractant stability [20].

Strontium extraction is also possible from the same medium by adding polyethylene glycol (PEG: HO—(C$_2$H$_4$O)$_n$—H) to the dicarbollide and particularly, the lipophilic *p*-nonylphenyl nonaethylene glycol (Slovafol 909 HO—(C$_2$H$_4$O)$_9$—C$_6$H$_4$—C$_9$H$_{19}$). The oxygen atoms of the PEG remove some of the water molecules surrounding the cation and improves its transfer into nitrobenzene. One has to
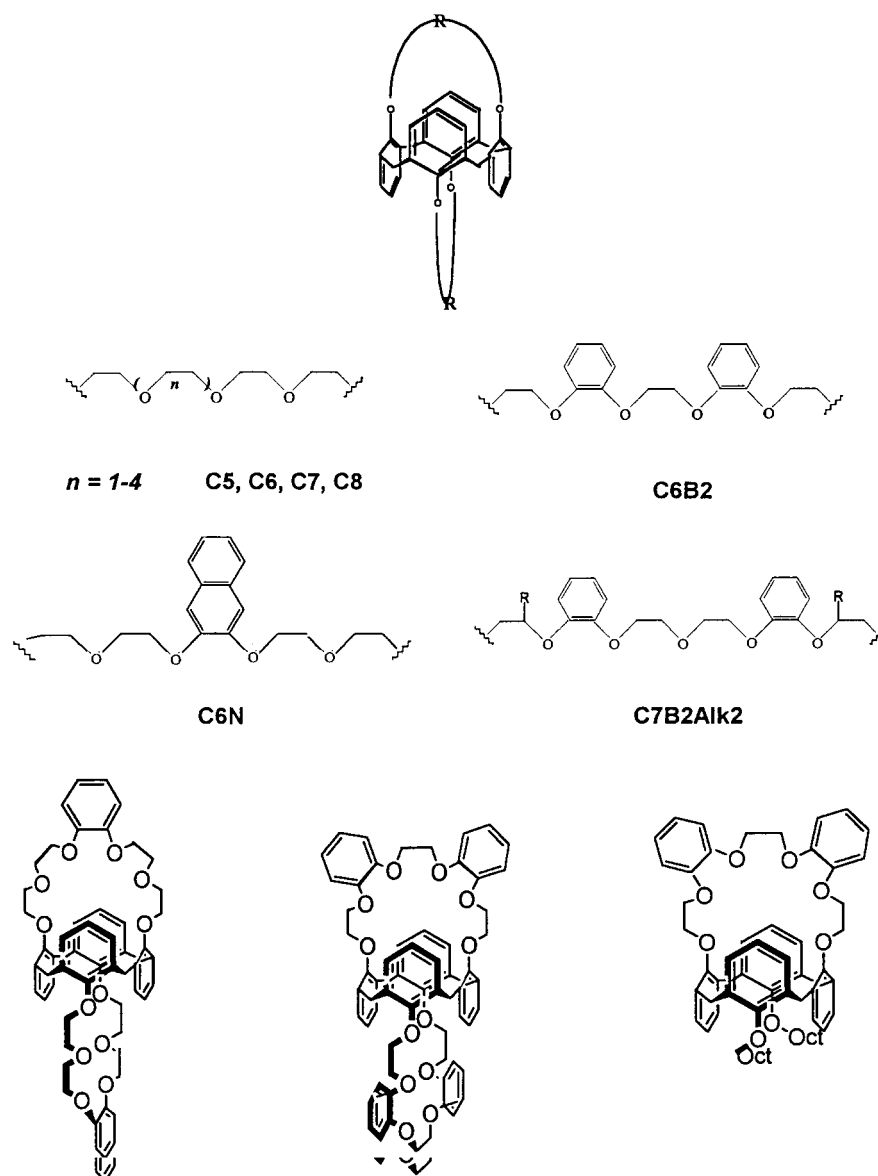
Figure 6. Calix[4]arene-*bis*-(benzocrown-6)-calix[4]arene-*bis*-(dibenzocrown-6)   dialkoxy
calix[4]arene dibenzocrown-6.

point out that PEG does not significantly improve cesium extraction. In fact, some
selectivity for cesium versus sodium is sacrificed.

Dicarbollides which display good stability towards irradiation, have some im-
portant drawbacks: they are only effective in harmful diluents such as nitrobenzene
and they contain halides which can be released during the reprocessing operations

and lead to corrosion of the facilities. Studies were launched to overcome these drawbacks.

Diethylene glycol ditetrafluoropropyl, a diluent, containing no nitro groups, is proposed for chlorinated cobalt dicarbollide. Adding Slovafol to the extractant and diluent makes cesium and strontium extractable from nitric acid solutions up to 2 M [21].

Tetramethyl-dicarbollide and tetrahexyl-dicarbollide were prepared according to the method described by Hawthorne in 1967. Tetrahexyl-dicarbollide diluted in aromatic hydrocarbon solvents displays comparable distribution coefficients to that obtained with classical dicarbollide diluted in nitrobenzene and is more lipophilic. Also, losses in the aqueous phase were negligible [22–24].

The distribution coefficient of cation M^{n+} is linked to the equilibrium constant by the relation:

$$D_{M^{n+}_-} = K_{eq} \frac{[H^+CoB_2^-]^n}{[H^+]^n}.$$

The equilibrium constant values were 800, 0.5 and 1.7 for cesium, sodium and strontium, respectively.

Tests carried out with tetrahexyl-dicarbollide diluted in diethylbenzene for the removal of cesium and strontium from alkaline media showed that the distribution coefficient measured for 0.01 M NaOH ($D = 50$) was slightly diminished by increasing the NaOH concentration. The strontium distribution coefficients, obtained with the same organic phase, range from 30 to 7, as the NaOH concentration increases from 0.01 to 1 M.

Under the auspices of the European Community Commission, studies were carried out by Czech scientists (Rais, Selucky, Hermanek, Plesek, Casensky et al.), at the University of Barcelona (Teixidor), University of Lyon (Mongeot) and CEA, Cadarache (Dozol) for the synthesis of carborane or dicarbollide derivatives and their extracting abilities [25]. Three new performing families of dicarbollide derivatives have been synthesized:

1. by introducing a phenyl group on one or two carbon atoms of each carborane units;
2. by introducing a CH_3 group and a $(CH_2)_3OR$ group on the two carbon atoms of each carborane unit. For the first class of compounds and for the latter, where $R = (CH_2)_3CH_3$, cesium and strontium distribution coefficients are enhanced for acidic pH (1 or 3) [26, 27];
3. particularly interesting results were achieved with (*bis*-phenylene)-*bis*-dicarbollide cobaltate or 'bisphenylenecosan', especially when it was diluted in dibutyl methane sulphamide (DIBUMESAM) [28]. With this diluent, an increase of cesium distribution coefficients of about three orders of magnitude was observed when dicarbollide was replaced by *bis*-phenylenecosan. However, after repeated extraction/stripping cycles, the strong decrease of cesium distribution coefficients was attributable to a nitration of the phenylene units.

The extraction of cesium by the chlorinated cobalt dicarbollide (0.06 M) diluted in a mixture of nitrobenzene and carbon tetrachloride and that of strontium by the same organic phase with addition of 1 vol.% of Slovafol 909, was tested on raffinates arising from the first cycle of VVER spent fuel reprocessed without any adjustment. The recovery of the nuclides was 99.8%, the decontamination factors were higher than 500 [29].

4. Crown Ethers

Since the beginning of the 1980s fundamental studies on the extraction of alkali and alkaline earth cations were extensively carried out at the Oak Ridge National Laboratory. Kinard and McDowell [30] tried to improve the extraction of alkali and alkaline earth cations in non-polar diluents by mixing crown ethers with known extractants. In order to avoid the need to transfer the anion from the aqueous phase to the organic phase, they proposed in this phase, to dissolve aqueous insoluble cation exchangers such as versatic acid, didodecylnaphtalenesulfonic acid (HDDNS) or di-(2-ethylhexyl) phosphoric acid (HDEHP). With these additives, the specificity of crown ethers relative to the size of the cavity of the crown ether, was maintained and important synergistic factors were obtained. They also illustrated that *tert*-butyl benzo-substituted crown ethers were effective synergists for alkali cations in contrast to *tert*-butyl cyclohexano-substituted crown ethers, which display a high degree of synergism towards alkaline earth cations. This difference of selectivity is explained by the electron withdrawing role and the higher rigidity of the aromatic substituents [30–32].

To improve the cesium extraction, McDowell and co-workers presented several strategies:

- 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; and
- transforming the crown ethers into cation exchangers by adding lipophilic acid or by attaching an acid moiety to the crown ether.

McDowell predicted that the most powerful cesium extractant should be di-*tert*-butylbenzo-21C7. This crown ether (5×10^{-2} M), used with didodecylnaphthalene sulfonic acid and diluted in toluene, displayed distribution coefficients higher than 100 when contacted with an aqueous phase 0.1 M HNO_3. It should be noted that the distribution coefficients sharply decreased as acidity increased [33, 34].

The extraction of cesium nitrate has been measured for different 21C7 crown ethers: classical DB21C7, DC21C7, *bis*-[4(5),4′(5′)-*tert*-butylbenzo]-21-crown-7 and *bis*-[4,4′-*tert*-butylbenzo]-21-crown-7 (see Figure 2). The different benzo-crown ethers present the same behaviour, in contrast, DC21C7 is a better extractant of cesium. Taking into account the selectivity for cesium over sodium of different 18C6, 21C7 and 24C8 moderates, the previous conclusions, dicyclo hexanocrown

ethers, show a poor selectivity, explained by the flexibility of these compounds and by their higher basicity which favours the sodium cation, which is 'harder' than cesium. As expected the highest selectivities are achieved with 21C7 and more specially the least lipophilic DB21C7. The extraction of alkali cations using benzo or t-alkyl-benzo-21C7 or -24C8 shows that addition of benzo substituents onto 24C8 enhances both the distribution coefficients and the selectivity for the larger cations, tetrabenzo-24C8 exhibits the highest distribution coefficients, but the selectivity is lower than that obtained with dibenzo 21C7 [35–38].

DC18C6 possesses five stereoisomers, cis-syn-cis (A), cis-anti-cis (B) and trans-syn-trans (C) are the most effective for the extraction of cations. A is the most efficient extractant (D_{Sr} = 24.8 for DC18C6 0.05 M in chloroform). With C, the maximum extraction is obtained at a higher acidity, but the distribution coefficient is only 14.3. For the extraction of strontium and cesium from nitric acid solutions, the following organic phases are chosen respectively, DC18C6 (0.1 M in chloroform), DB21C7 (0.1 M in nitrobenzene). Phosphomolybdic acid must be added to DB21C7 to allow cesium to be quantitatively extracted [39, 40].

From 1979, Gerow, Schuler *et al.* [41–43] envisaged the extraction of cesium and strontium from acidic high activity liquid waste with two new crown ethers, the chosen diluent was a mixture of TBP and kerosene compatible with the PUREX process used at the Savannah River Plant. One has to point out that it was the first time that a solution was proposed for the removal of cesium and strontium from a very acidic medium (HNO$_3$ 3 M). For an aqueous phase containing nitric acid (3 M) and cesium (0.006 M), a distribution coefficient of 1.6 was achieved by using *bis*-(4,4′(5′)-[1-hydroxy-2-ethylhexyl]-benzo)-18-crown-6 (0.02 M) in the mixture nonyl-naphthalenesulfonic acid (0.1 M) or 5% – TBP (27%) – kerosene (68%). Cesium can be stripped from the aqueous phase by nitric acid (1 M) in several steps. A strontium distribution coefficient of 1.98 was obtained by contacting an aqueous phase containing nitric acid (3 M) and strontium (0.003 M) with an organic phase containing *bis*-(4,4′(5′)-[1-hydroxyheptyl]cyclohexano)-18-crown-6 (0.02 M) in the same mixture. Strontium can be recovered from the organic phase by multiple stripping steps with dilute nitric acid [41–43]. Tests conducted with the two crown ethers showed satisfactory stability towards irradiation.

Blasius [44, 45] chose DB21C7, from among several other crown ethers, to remove cesium from two medium activity wastes mainly containing sodium nitrate and nitric acid (MAW 1: HNO$_3$ (1 M), NaNO$_3$ (0.5 M), MAW 2: HNO$_3$ (0.8 M), NaNO$_3$ (3.4M)). Only DB21C7, used in high dielectric constant diluents such as nitromethane (D = 2.03), nitrobenzene (D = 1.03), substantially extracted cesium. Even at higher concentration (5 × 10^{-2} M), the distribution coefficients were too low for practical applications. A way to increase cesium extraction was the addition of voluminous and polarizable anions such as molybdophosphate, tetraphenyl borate, hexachloro antimonate .... Some of these compounds are not useful: tetraphenyl borate is hydrolyzed, molybdophosphate leads to precipitates. The addition of hexachloroantimonate to DB21C7 diluted in

nitrobenzene allowed cesium to be quantitatively removed from MAW1. The extraction of strontium from MAW1 was possible with DC18C6 (0.0137 M) diluted in 1,1,2,2-tetrachloroethane. With a mixer settler apparatus, a strontium decontamination factor of about 100 is achieved for the simulated evaporator concentrate [46].

Radioactive liquid wastes arising from reprocessing operations are concentrated by evaporation, distillate is discharged into the environment, removal of ^{90}Sr, ^{137}Cs and actinides enables these wastes to be decategorized and to be directed to a subsurface repository; only a small part containing these long lived elements is sent to an interim storage or disposal. In these operations all cations, radioactive or not, are concentrated, so evaporator concentrates contain large amounts of sodium (3–4 M) and other cations such as magnesium, calcium, aluminium at lower concentrations. From 1988, studies were launched for the selective extraction of these long lived elements by using DC18C6 and *tert*-butylbenzo-21C7 or decylbenzo-21C7 for the respective removal of strontium and cesium. Most of the studies were devoted to finding a diluent or a mixture of diluents for these crown ethers, fulfilling some requirements needed by the implementation of supported liquid membranes (SLM): sparingly soluble diluents in order to obtain a good stability of the membrane, diluents (decanol, isotridecanol, *p*-diisopropylbenzene, hexylbenzene, and mixtures of these alcohols with these alkylbenzenes) favouring the extraction of cations and preventing the transfer of nitric acid which competes with the cations and leads to a decrease of the driving force of the SLM [47–52].

Transport experiments implementing SLMs were conducted in a hot cell with a few liters of genuine concentrate from the Cogema Marcoule reprocessing plant. The removal of strontium is obtained by a hollow fiber SLM including DC18C6 (0.5 M) diluted in the mixture decanol/hexylbenzene, the performances are mediocre: the decontamination factor (initial activity/activity after treatment) and the concentration factor (initial volume of waste/volume of waste containing strontium after treatment) are respectively 50 and 32. Moreover, the membrane cannot be reused, DC18C6 not being sufficiently lipophilic. The transport of cesium by *tert*-benzo-21C7 (0.5 M) diluted in decanol (0.8 M) hexylbenzene, is incomplete, the selectivity of the crown ether being too low, the carrier is saturated by the sodium cations (3–4 M), which are much more abundant than cesium ($<10^{-4}$ M). Previously, tests were carried out on simulated wastes with a membrane containing both extractants (DC18C6 and *tert*-butylbenzo-21C7), the transfer of cations is sensibly lowered by the increase of the membrane viscosity due to the presence of the two crown ethers in this one [53].

In 1990, Horwitz *et al.* [54–56] chose DC18C6 and its dimethyl or di-*tert*-butyl derivatives, diluted in different oxygenated, aliphatic diluents, for the extraction of strontium from acidic solutions, demonstrated that the highest strontium distribution coefficients were obtained with *n*-pentanol and *n*-hexanol and correlated the extraction of this cation with the water content of the diluent. The presence of water in the diluent does not need the complete removal of the hydration shell of

the nitrate associated to strontium for its transfer in the organic phase. Following these studies, Horwitz proposed the SREX process (**Str**ontium **Ex**traction) with di-*tert*-butyl-cyclohexano-18C6, diluted in 1-octanol (0.2 M) for the extraction of strontium from acidic solution (>HNO$_3$ 1 M). Tests carried out with this organic phase showed a good chemical and radiochemical stability and that 99.7% of strontium was extracted in three extraction stages. The process was applied to store sodium-bearing wastes from Idaho Chemical Processing. Tests demonstrated that in spite of interferences with alkali and alkaline earth cations present in these wastes (sodium, potassium, calcium), strontium can be effectively extracted from these wastes. With a new organic phase (di-*tert*-butyl-cyclohexano-18C6 0.15 M diluted in 1.2 M TBP/Isopar L), a flowsheet for the simultaneous extraction of strontium and lead and their subsequent separation during the stripping phases was designed, using sixteen centrifugal contactors. Results obtained with centrifugal contactors confirmed the laboratory results and also a relatively poor selectivity of the extractant which simultaneously extracts lead, mercury (which build up in the organic phase because of an insufficient stripping) zirconium and potassium [57–62].

Dietz tested several crown ethers, dicyclohexano-18C6, di-*tert*-butyl-benzo-18C6, di-*tert*-butyl-benzo-21C7 and di-*tert*-butyl-benzo-24C8 for cesium extraction from very acidic solutions (HNO$_3$ 4 M), the most efficient (D$_{Cs}$ = 4) was the di-*tert*-butyl-benzo-21C7 (0.1 M) diluted in methylpentanone and, as for strontium, evidenced the role of the dissolved water in the diluent. In subsequent works, Dietz obtained the highest selectivity for cesium over sodium with 21C7 derivatives, but the most efficient extractant was 4,4′-(5′)-di-[(1-hydroxy-ethylhexyl)-benzo]-18C6 associated with TBP (0.2 M) which, contacted with an acidic solution (HNO$_3$ 4 M), gave a distribution coefficient of 30. Dietz concluded that none of the tested compounds provided the ideal combination of extraction efficiency, selectivity, stability and solubility [63, 64].

The previous studies ended up at an 'advanced integrated system' combining the CSEX and SREX processes for the extraction of cesium and strontium. The two crown ethers (*bis*-4,4′(5′)[(2-hydroxy-alkyl)-benzo]-18-crown-6 and *bis*-4,4′(5′)[(*tert*-butyl)cyclohexano]-18-crown-6) are diluted in the mixture phase modifier/diluent: 1.2-M TBP-5% (v/v) lauryl nitrile – Isopar-L. The process enables 99.99% of cesium and strontium to be recovered from acidic liquid wastes (3.78 M) containing mainly aluminium (0.486 M), calcium (0.778 M), zirconium (0.225 M) and to a lesser extent sodium (0.015 M). One of the advantages is to combine the two extraction steps into a single process which reduces the amount of equipment [65].

The efficiency of di-*tert*-butyl-cyclohexano-18C6, diluted in octanol was confirmed by tests carried out on solutions arising from the acidic (HNO$_3$ 3.75 M) dissolution of sludges stored in one of the high activity waste tanks at the Hanford site. The decategorisation is carried out in three steps: extraction of lanthanides and actinides by CMPO-(Octyl-phenyl-N,N-diisobutyl carbamoyl methyl phosphine

oxide), extraction of strontium by di-*tert*-butyl-DC18C6 and removal of cesium by a process implementing ammonium molybdophosphate and a phenol formaldehyde organic ion exchanger. The strontium decontamination factors exceeded 7800 [66, 67].

For the extraction of strontium and cesium, Kumar respectively chose DC18C6 diluted in alcohols and DB18C6 derivatives diluted in nitrobenzene (dibenzo-18C6, di-*tert*-butylbenzo-18C6, 4,4'(5')-di-acetyl-benzo-18C6, 4,4'(5')-dihexanoyl-benzo-18C6, 4,4'(5')-dinonaoyl-dibenzo-18C6). Kumar *et al.* established a relation between the strontium distribution coefficients and the water content of the organic phase. The highest strontium distribution coefficients were achieved with the mixture of alcohols butanol 80%-octanol 20%. The cesium distribution coefficients are moderate, the most effective cesium extractant is di-*tert*-benzo-18C6. Phosphotungstic acid enhances the extraction of cesium, but its low solubility in nitrobenzene restricts its use [68, 69].

As mentioned by Blasius, large anions such as phosphotungstate enhance the cesium extraction, however Lin observes a strong decrease of the extraction of cesium in the presence of a large amount of sodium nitrate. Nevertheless the extracting ability is satisfactory for solutions containing less than 2 mole L^{-1}. Extraction by the following organic phase (DB21C7 0.012 M, phosphotungstate 0.004M in nitrobenzene) allows 90% to be extracted from a solution containing HNO_3 (0.5 M) and $NaNO_3$ 2 M [70].

Vanura investigated the synergetic extraction of strontium and cesium by mixing dicarbollide with several crown ethers. Extraction of strontium from nitric acid performed with 15C5/dicarbollide diluted in nitrobenzene from perchloric acid with dibenzo-18C6/dicarbollide also diluted in nitrobenzene enabled us to determine the extraction constants of these complex systems [71, 72]. In contrast to DB24C8 and DC24C8, DB15C5, DB18C6 and DB21C7 enhance cesium extraction by one order of magnitude. The highest distribution coefficients and selectivities for strontium over calcium are obtained with 15-crown-5 and with 15-benzo- and dibenzo-crown-5, 12C4 and 18C6 are less efficient and selective extractants of these cations [73].

5. Calixarenes

Measurements of complexing abilities of different functionalized calixarenes in the cone conformation performed by Arnaud-Neu *et al.* [74, 75], established that calix[4]arenes bearing ester or ketone moieties displayed high affinity for alkali cations, specially for sodium. Unlike these compounds, tetramers functionalized with diethylamide groups exhibit very strong complexing abilities for calcium, strontium and to a lesser extent for barium. The selectivity for calcium over magnesium of this calixarene is the highest for a neutral ligand. The suppression of the *p-tert*-butyl groups for diethylamide calix[6]arenes strongly increases the complexation of cesium and strontium. The unsubstituted hexaethylester calix[6]arene

and the *p-tert*-butyl-hexaethylester calix[6]arene which show a strong ability to complex cesium and to a lesser extent rubidium were proposed to be incorporated in the membrane of an ion selective electrode [76].

In a search for better extractants than crown ethers, efforts were devoted to crown ethers built on the calixarene molecular platform in the framework of a project supported by CEC and coordinated by CEA Cadarache [77]. The project included specialized teams in different areas:

- Synthesis of crown ethers or calixarenes (Universities of Barcelona (Lopez Calahorra), Belfast (McKervey), Mainz (Böhmer), Parma (Ungaro), Strasbourg (Vileus)),
- Transport of cations by macrocycles (University of Twente (Reinhoudt)),
- Extraction and complexation constant determination (ECPM Strasbourg (Arnaud, Schwing), CEA Cadarache (Dozol)),
- Computational chemistry (University of Strasbourg (Wipff)), CEA Cadarache (Lamare)),
- Tests on simulated and real waste (CEA Cadarache).

Since the synthesis of a crown compound with two opposite phenolic groups linked by a pentaethyleneglycol chain, many calix[4]arenes with crown ether moieties were produced and proved to be efficient for the complexation of alkali and alkaline earth cations due to the presence of the crown ether link [78]. The selectivities of the complexation were strongly dependent on the conformation of the calixarenes. Ungaro and Vicens blocked the calixarene crown into a 1,3-alternate conformation by adding respectively, either two alkyl chains or a second polyethylene glycol on the two remaining phenolic units.

From the studies of the fifteen calix crowns synthesized (Table I), the main conclusions are [79–85]:

- In spite of the presence of two cavities, the stoichiometry of the complexes cesium calixarene-*bis*-crown diluted in NPHE is 1:1, except under exceptionally forcing conditions [86].
- For alkoxy-crown-6 and *bis*-crown-6, the extraction is mainly dependent on conformation. The conformationally mobile methoxy-calixarene-crown-6 (the methoxy group can rotate through the annulus of the calixarene) displays a much lower efficiency and selectivity than the calixarenes blocked in the 1,3-alternate conformation. The exceptional selectivity shown by calixarene-crown-6 for cesium can be explained by the stabilisation of the complexes calixarene-cesium by the bonding interactions with the four benzene units of the calix[4]arene [87–90].
- The extraction is to a lesser extent linked to the crown's size, the best results are obtained for two classes of calixarenes with polyethyleneglycol bridges containing six oxygen atoms, distribution coefficients of calixarenes bearing five or seven oxygen atoms are much lower than that of *bis*-crown-6. It should be noted that a small modification of the size of the crown, obtained for instance by replacing in the crown *o*-benzo by *p*-benzo, generates a strong decrease

Table I. Distribution coefficients of cesium and sodium. Selectivity Cs/Na. Aqueous feed solution: MNO_3 5×10^{-4} M $-$ HNO_3 1 M. Organic solution: 10^{-2} M extractant in 1,2-nitrophenyl hexyl ether ($o/a = 1$, $t = 25$ °C)

Compounds	D_{Na}	D_{Cs}	α(Cs/Na)
Calix[4] arene dimethoxy-crown-6	3×10^{-3}	4×10^{-2}	
Calix[4] arene hydroxy-ethoxy-crown-6	4×10^{-3}	4.2	>4200
Calix[4] arene dipropoxy-crown-6	2×10^{-3}	19.5	9750
Calix[4] arene diisopropoxy-crown-6	$<10^{-3}$	28.5	>28500
Calix[4] arene di-*n*-octyloxy-crown-6	$<10^{-3}$	33	>33000
Calix[4] arene di-*n*-octyloxy-(dibenzo-crown-6)	$<10^{-3}$	31	>31000
Calix[4] arene dimethoxy-crown-7	4×10^{-3}	7×10^{-3}	
Calix[4] arene *bis*-crown-5	2×10^{-3}	0.4	
Calix[4] arene *bis*-crown-6	1.3×10^{-2}	19.5	1500
Calix[4] arene *bis*-crown-7	$<10^{-3}$	0.3	–
Calix[4] arene *bis*-*p*-benzo-crown-6	$<10^{-3}$	2×10^{-2}	–
Calix[4] arene *bis*-*o*-benzo-crown 6	1.7×10^{-3}	32.5	19000
Calix[4] arene *bis*-(dibenzocrown-6)	$<10^{-3}$	23	>23000
Calix[4] arene *bis*-naphthyl-crown 6	$<10^{-3}$	29.5>	>29000
Calix[4] arene *bis*-diphenyl-crown-6	$<10^{-3}$	7×10^{-2}	–
n-decylbenzo-21-crown-7	1.2×10^{-3}	0.3	250
Tert-butylbenzo-21-crown-7	1.2×10^{-3}	0.3	250

of distribution coefficients. These observations highlight the importance of the complementarity between the crown and the cesium cation [80].

For all tested calixarenes, it can be seen that cesium distribution coefficients increase as acidity increases. A maximum is reached for an acidity of about 2 M, then they decrease. However the behaviour of all the calixarenes is not identical, calixarene-*bis*-crown displays the lowest distribution coefficients whatever the acidity of the aqueous phase. The distribution coefficients of the two alkyl calixarenes mono crown, relatively high in low acidity medium, slowly increase until the maximum. The presence of benzo or naphthyl groups on the crown enhances the extraction of cesium: around the maximum, distribution coefficients higher than 100 are reached. One must notice that the presence of a second benzene group on the crown increases this efficiency further: high distribution coefficient values are obtained (between 200 and 300) for an acidity ranging between 2 and 4 M [91].

This trend is also observed for extraction of cesium from an acidic medium containing large amounts of sodium. The selectivity for cesium over sodium is difficult to determine due to the low amount of sodium extracted. A way to indirectly estimate the selectivity of calixarenes is to evaluate the cesium extraction in competition with large amounts of sodium, a strong increase of the cesium distribution
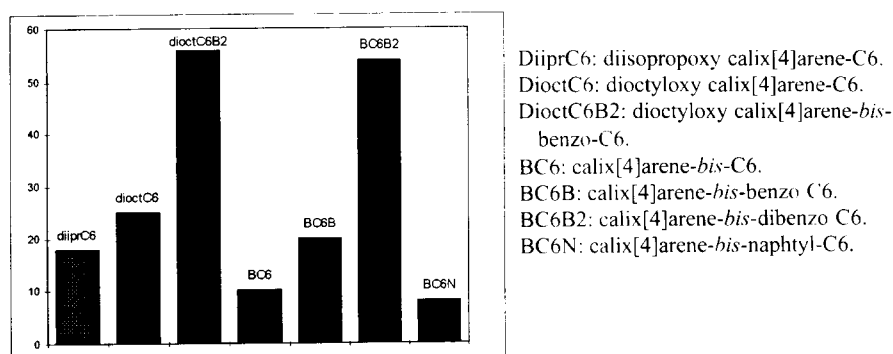
DiiprC6: diisopropoxy calix[4]arene-C6.
DioctC6: dioctyloxy calix[4]arene-C6.
DioctC6B2: dioctyloxy calix[4]arene-*bis*-
    benzo-C6.
BC6: calix[4]arene-*bis*-C6.
BC6B: calix[4]arene-*bis*-benzo C6.
BC6B2: calix[4]arene-*bis*-dibenzo C6.
BC6N: calix[4]arene-*bis*-naphtyl-C6.

Figure 7. Distribution coefficients of cesium in competitive extraction with sodium. 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 extractant in 1,2-nitrophenyl hexyl ether ($o/a = 1$, $t = 25\,^{\circ}$C).

coefficients is observed for dibenzo-crown calixarene and to a lesser extent for benzo or naphthyl calixarenes (Figure 7).

Several transport experiments through supported liquid membranes were performed on different carrier (calixarene crown 6) concentrations. At a concentration of 0.05 M diluted in NPOE, quantitative transport of cesium was performed within 24 h with very low transport of sodium [92]. The emphasised lipophilic character of the calixarenes and the use of nitrophenylalkylether enable stable membranes to be prepared, except for the *bis*-crown-calixarene-crown-6, and to be reused several times [93]. Two types of measurements (distribution coefficients, transport through SLMs) were carried out on a real waste. The high activity liquid waste was a dissolution of a MOX Fuel (Burn up 34 650 MWJ/tU) where uranium and plutonium have been previously extracted by TBP (classical PUREX process). The experiments were performed in the Carmen hot cell of CEA Fontenay aux roses [94].

Several calixarenes were used: *bis*-crown-6-calix[4]arene, diisopropoxy-crown-6-calix[4]arene and di-(nitrophenoxyoctyloxy)-crown-6-calix[4]arene. The latter, conjointly synthesized by the Universities of Parma (Ungaro) and Twente (Reinhoudt), was a very interesting compound due to its very high lipophilicity and to its great solubility in nitrophenylalkylether. The high selectivity of this class of calixarene was confirmed by this test: for all radionuclides (actinides or fission products: [106]Ru, [154]Eu, [125]Sb, [144]Ce), the decontamination factors were higher than 100 and ranged from 12 to 60 for iron, molybdenum, zirconium, cerium, neodymium.

Calix[4]arene-*bis*-crown, diisopropoxy-calix[4]arene-crown-6 and di-NPOE-calix[4]arene-crown-6 used as carriers in supported liquid membranes (0.1 M NPHE) respectively transported 58.3%, 77.5% and 86.3% of cesium through SLM. Only cesium was significantly transported during these tests, higher cesium activities could have been transported by increasing the duration of the experiments.

Efforts were made to explain and predict the important selectivity of dialkoxy-calixarenes-crown-6 by computer simulations. The Cs/Na selectivity was discussed in terms of calixarene conformation (cone, partial cone and 1,3-alternate) and solvent effects. The Cs/Na selectivity appeared to be conformationally dependent: in the gas phase (or in dry chloroform) the three conformers preferred sodium. On the contrary in water, cesium was calculated to be bound preferentially over sodium for the 1,3 alternate conformer only. Wipff concludes that this selectivity for cesium is related to solvation effects rather than to interactions with the π electrons of benzene units [95–97].

Simulations on *bis*-crown-calixarenes were extensively reviewed and pointed out the importance of solvation effects on the selectivity in the alkali series [98]. Lamare studied by Molecular Dynamics the relative stability of alkali cation complexes of 1,3-alternate calix[4]arenes with substituted crowns in an explicit water phase. An efficient complexant must provide co-ordination sites in place of the first hydration shell of the cation, so the best match must be achieved between the sites of complexation of the ligand and the cation. The calculations demonstrate the excellent complementarity of calixarene (*bis*-benzo-crown-6)/cesium (the cation is almost equidistant from the six oxygen atoms) and to a lesser extent for calixarene-*bis*-crown-6 for which the distances are larger. On the contrary, calixarene (*bis*-crown-7) does not display a good complementarity between cesium and the oxygen atoms of its crown [99]. Calculations on the sodium nitrate complex of calixarene (*bis*-crown-6) have shown that the sodium cation is co-complexed with a water molecule [100]. Simulations on calixarene dibenzo-crown-6, before their synthesis, have shown that their affinity towards alkali cations was comparable to those of calixarenes exempt from benzene units or including one benzene moiety on the crown. Calixarene dibenzo-crown-6 displays a higher selectivity for cesium over sodium due to a lesser extraction of sodium. This decrease of sodium extraction is explained by the greater difficulty for the cation to be complexed without total dehydration in a more lipophilic complexation site [101].

Haverlock tested calixarene-*bis*-naphthyl-crown-6 for the removal of cesium from a solution simulating a Hanford tank supernatant. With this calixarene diluted at a concentration 10^{-2} M in four different diluents, the selectivity of cesium over sodium exceeded 10^4. The Cs/Na selectivity determined under the same conditions with *bis*-(*tert*-butylbenzo)-21C7 was at best 200. In spite of a relatively important Cs/K selectivity in the range 122–935, the high concentration of potassium limited the extraction of cesium [102].

Kim [103–107] synthesized dialkyl-calixarene-dibenzo-crown-n (with $n = 7$ and 8) and also calixarene-dibenzo-crown-n with two butyl groups attached on the crown ether linkage (cf. Figure 6). The efficiency and the selectivity of these compounds were determined by using alkali transport through a bulk liquid membrane: The flux values increased from lithium to cesium while they decreased when calixarene-*bis*-crown-8 was used instead of calixarene-*bis*-crown-7. It was confirmed that the presence of *tert*-butyl in the para position to phenolic oxygen
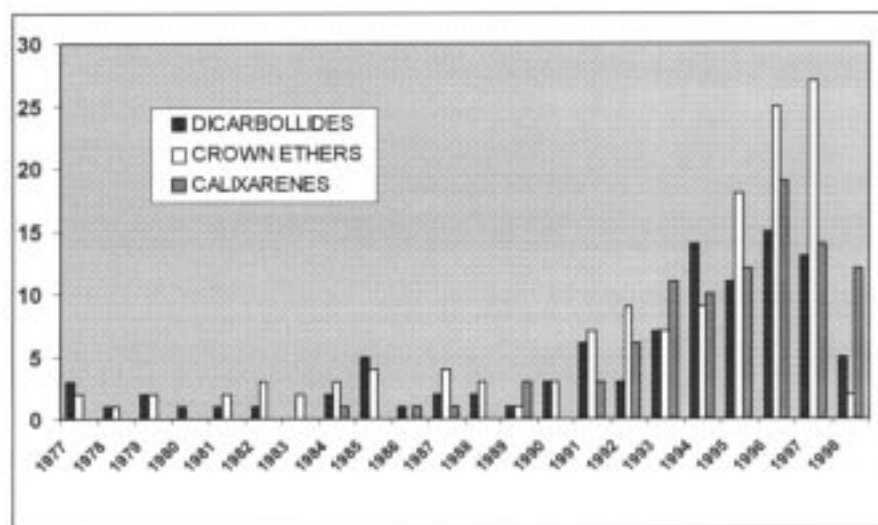
Figure 8. Number of publications between 1977 and 1998.

prevented the extraction of alkali cations. The increase of complexation ability is attributed to the flatness and lipophilicity induced by the presence of benzo units on the crown.

6. Sources

For this survey, the databases consulted by computer were INIS and Chemical Abstracts respectively provided by AIEA and the American Chemical Society. These databases were consulted initially in 1967 for Chemical Abstracts and 1970 for INIS.

The strategy was not exactly the same for the three classes of extractant.

Dicarbollides: Investigations were not limited in INIS and restricted to **nuclear** and **waste** in Chemical Abstracts.

Crown ethers: Because of the large number of publications, investigations were limited to **nuclear**.

Calixarenes: No limitations. Investigations were carried out with **extraction, complexation**, **nuclear** and **waste**.

Then the double references were suppressed. On the remaining corpus, the number of references per year was identified (Figure 8).

7. Conclusions

Dicarbollides enable cesium and strontium (by adding polyethyleneglycol for the latter) to be simultaneously removed from acidic waste matrices. They were prepared on a large scale by Czechs and used by Russians for the recovery of cesium

and strontium from high activity waste. Modifying the basic dicarbollide allows these dicarbollides to be diluted in diluents less hazardous than nitrobenzene, for instance it can be diluted in aromatic hydrocarbon. However, this lipophilic anion behaves as a cation exchanger, its efficiency decreases as acidity is increased and the selectivity for cesium over sodium is insufficient for the extraction of cesium from media containing large sodium amounts.

Dicyclohexano-18C6 and its derivatives are undeniably the most used extractants of strontium. Tests carried out in the framework of the SREX process demonstrated the ability of DC18C6 to remove strontium from acidic solutions or even in the presence of alkali or alkaline earth cations. The main drawbacks of these crown ethers are a moderate selectivity for strontium over alkali and alkaline earth leading to a decrease in the efficiency of the extraction. Moreover the use of TBP decreases the selectivity of this extractant, strontium, potassium, lead and also mercury, and zirconium are removed.

Most of the studies carried out on the cesium extraction conclude that benzo-21C7 derivatives are the most selective extractants of cesium. However, these compounds require a synergetic agent for cesium removal from very acidic media and display a low selectivity for cesium over other alkali metal cations specially over sodium.

Dialkoxy-calix[4]arene-crown-6 and calix[4]arene-*bis*-crown-6, much more efficient and selective than dicarbollides and crown ethers are promising cesium extractants, some developments (synthesis on a large scale, chemical and radiochemical stability etc.) in progress need to be concluded before it is possible to use them industrially.

Acknowledgements

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