SELECTIVE EXTRACTION AND TRANSPORT OF CESIUM WITH CALIX[4]ARENES CROWN FROM RADIOACTIVE LIQUID WASTES

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Cesium possesses two long lived isotopes ^{135}Cs and ^{137}Cs, the first one of which the half live is very long must be selectively separated either for transmutation, either for encapsulation in a very specific matrix. As for ^{137}Cs, it is interesting to remove it with strontium and actinides in order to decategorize immediate level radioactive wast. Cesium must be removed with a very high selectively in the first case from very acidic medium (HNO_3 3-4 M) in the second one from acidic high sodium nitrate concentration liquid waste. Calix[4]arenes crown or bis crown in the 1,3 alternate conformation exhibit a tremendous efficiency and selectivity for cesium. These exceptional performances, much higher than those obtained with the best crown ethers, were obtained on simulated wastes and confirmed in two hot tests by liquid-liquid extraction and by implementing supported liquid membranes.

1 - INTRODUCTION

Nuclear Fuel reprocessing operations produce both high and medium level activity liquid wastes. Studies are launched, in the framework of SPIN programm to selectively remove actinides or long lived fission products like [135]Cs in order to distroy them by transmutation or to dispose of them in very stable matrices. On the other hand medium level activity wastes are treated by evaporation this treatment leads to large volume of concentrates composed mainly of inactive salts. It is desirable to remove the long-lived radionuclides (actinides, ^{90}Sr and ^{137}Cs) from the concentrates, this allows these decontaminated wastes to be directed to surface repositories, only a small volume containing these radionuclides being disposed of in geological formation. We have to point out that in both cases, high or medium activity liquid wastes, it is interesting to selectively and efficiently remove cesium isotopes.

2 - EXTRACTION OF CESIUM BY ION EXCHANGERS OR EXTRACTANTS

For several decades, inorganic ion exchangers or absorbers were used to remove cesium, recent reviews concluded, from the study of these compounds that Cristalline Silico Titanates (CSTs) were the most promising (if reuse of material was not required) followed by ammonium molybdo phosphate, ferrocyanides and other phosphates [1][2]. However the authors concluded that elution, if possible, had to be studied in order to minimize the volume of waste produced.

Two classes of extractants were particularly studied for the extraction of cesium : Dicarbollides and crown ethers. Czechs carried out extensive studies for the synthesis and extraction properties of dicarbollides [3]. These lipophilic anions withstood protonation in very acidic medium and removed cesium effectively in nitric solution up to 3 M, the stripping occuring at higher acidity (5 M), but the extraction abilities sharply decreased in presence of sodium nitrate. Crown ethers, were also proposed for the extraction of cesium, bis (tert butyl benzo) 21 crown 7 or bis (hydroxyheptyl) 18 C 6 synergized by organic soluble anions like dinonyl (or didodecyl) naphtalene sulphonic acid were able to remove cesium from very acidic solutions but not in presence of high sodium concentration due to the high coextraction of sodium [4] [5]. *Blasius* showed that, among the classical crown ethers, DB 21 crown 7 was the only crown ether providing the required selectivity towards sodium, however to accomplish an extraction from sodium nitrate medium, the crown ether had to be combined with heteropolyacids or hexachloroantimony acid [6]. Lipophilic tert butyl (or decyl) benzo 21 crown 7 failed to quantitatively remove cesium from simulated acidic high sodium concentrates, we directed our efforts towards a new promising class of macrocycles functionalized calixarenes [7].

3 - CALIXARENES

Calix[4]arenes are macrocycles made up of phenolic units (generally n = 4 to 8) linked by methylene bridges. Butyl[4]calixarene, the cyclic tetramer, is an important building block because it can be synthesized in large amounts from inexpensive starting materials, it can be functionalized either using the phenolic oxygens, either by it's para position. Moreover calix[4]arene is conformationally mobile and can assume four conformations : cone, partial cone, 1-2 alternate, 1-3 alternate (Fig. 1). The analogy of calix[4]arene in cone conformation with a beaker (calix in greek) led *D. Gutsche* to call them calixarenes. The functionalization associated with the conformational properties led to a large variety of « tailored » macrocycles.

cone   **partial cone**   **1,2-alternate**   **1,3-alternate**
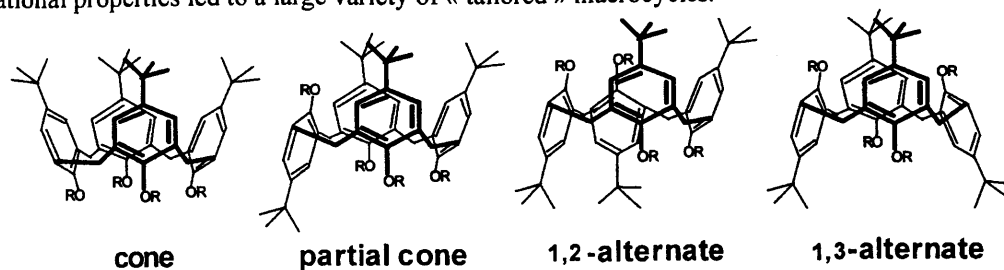
Figure 1
calix[4]arene conformations

In search for better extractants than crown ethers, efforts were devoted to crown ethers built on calixarene molecular platform. Since the synthesis of a crown compound with two opposite phenolic groups linked by a penta ethylene glycol 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 [8]. The selectivities of the complexation were strongly dependent on the conformation of the calixarenes. R. Ungaro and J. Vicens, blocked the calixarene crown into a 1,3 alternated conformation by adding respectively, either two alkyl chains either a second polyethylene glycol on the two remaining phenolic units.

Thirteen calix crowns have been studied, the extraction results are given in Table 1, the main conclusions are :

For alkyoxy crown 6 and bis crown 6, the extraction is mainly dependent on conformation, the compounds in the 1,3 conformation displays the highest cesium distribution coefficients and very low sodium distribution coefficients hence the highest Cs/Na selectivity [10].

The extraction is at a lesser extent linked to the crown's size, the highest results are obtained for two classes of calixarenes with polyethylene glycol bridges containing six oxygens.

The exceptional selectivity of these two classes of calixarenes for cesium, much higher than those of the most efficient crown ethers, can be explained by the stabilization of the complexes calixarene-cesium by the bonding interactions with the four phenyl units of the calix[4]arene [11].

Table 1

Extraction of cesium and sodium - Selectivity Cs/Na

Aqueous feed solution, 5.0×10^{-4} M M^+ (NO_3^-) in 1 M HNO_3 ;

Organic solution, 10^{-2} M extracting agent in 1,2-nitrophenyl hexyl ether

	D_{Na}	D_{Cs}	$\alpha(Cs/Na)$
1,3-calix[4] dimethoxy crown 6	3.10^{-3}	$4\ 10^{-2}$	
1,3-calix[4] hydroxy ethoxy crown 6	$4\ 10^{-3}$	4,2	≥ 4200
1,3-calix[4] dipropoxy crown 6	$2\ 10^{-3}$	19.5	≥ 19500
1,3-calix[4] di isopropoxy crown 6	$< 10^{-3}$	28.5	$\geq 28\ 500$
1,3-calix[4] di n oxtyloxy crown 6	$< 10^{-3}$	33	≥ 33000
1,3-calix[4] di methoxy crown 7	$4\ 10^{-3}$	$7\ 10^{-3}$	
1,3-calix[4] biscrown 5	2×10^{-3}	0.4	
1,3-calix[4] biscrown 6	1.3×10^{-2}	19.5	1500
1,3-calix[4] biscrown 7	$< 10^{-3}$	0.3	
1,3-calix[4] bis-p-benzo-crown 6	$< 10^{-3}$	2×10^{-2}	
1,3-calix[4] bis-o-benzo-crown 6	1.7×10^{-3}	32.5	≥ 19000
1,3-calix[4] bisnaphthyl-crown 6	$< 10^{-3}$	29.5	≥ 29000
1,3-calix[4] bisdiphenyl-crown 6	$< 10^{-3}$	7×10^{-2}	
n-decylbenzo-21-crown 7	1.2×10^{-3}	0.3	250
tert-butylbenzo-21crown 7	$1.2 \times 10{-3}$	0;3	250

4 - TRANSPORT OF CATIONS THROUGH SUPPORTED LIQUID MEMBRANES

4.1. Supported Liquid Membranes

The selective extractants used for extraction are often very expensive and thus limit the use of the techniques mentioned previously ; work was therefore carried out in this study on the use of selective extractants with liquid membranes technology.

Supported liquid membranes (SLM) are made up of two-aqueous phases separated by an organic phase. The aqueous phase, called the feed phase, contains the radioelements to be extracted by means of the organic phase. They are then carried to the other aqueous phase, called the stripping phase. The organic phase, constituted by an extractant dissolved in a diluent, impregnates a microporous support placed between both aqueous phases. The driving force of the process is attributable to the difference of the nitrate concentrations in the feed phase [NaNO$_3$ (4 M), HNO$_3$ (1 M)] and in the stripping phase (no nitrate). The transport mechanism that takes place is called co-transport, as the cation and the extractant transit through the membrane in the same direction.

The use of neutral carriers, such as a calix[4]arene crowns, leads to a coupled co-transport of cations and nitrate anions through the SLM [12]. When concentrates or acidic solutions are used as feed solution, and demineralized water as stripping solution, the concentration gradient of the nitrate anions will force the transport of cesium against their own concentration gradient thus leading to their concentration in the stripping solution.

4.2- Permeability Determination

The transport of ^{137}Cs from synthetic aqueous solutions of NaNO$_3$ (4 M) and HNO$_3$ (1 M), was followed by regular measurement of the decrease of radioactivity in the feed solution by γ spectrometry analysis. This allowed graphical determination of the constant permeabilities P (cm.h^{-1}) of cesium permeation through the SLM by plotting the logarithm of the ratio $C/C°$ vs.time, as described in the model of mass transfer proposed by *Danesi* [13]

$$\ln \frac{C}{C°} = -\frac{\varepsilon.S}{V}.P.t$$

where
C is concentration of the cation in the feed solution at time t (mol.l^{-1}) ;
$C°$ is initial concentration of the cation in the feed solution (mol.l^{-1}) ;
ε is volumic porosity of the SLM %) ;
S is membrane surface area (cm^2) ;
V is volume of feed and stripping solutions (cm^3)
t is time (h).

Transport experiments were carried out with the most promising compounds ; their permeability are given in the Table 2.

Table 2

^{137}Cs Transport Experiments through Flat Sheet-Supported Liquid Membranes : Permeability Determination after 6 h of Permeation

Aqueous feed solution, NaNO$_3$ (4 M) and HNO$_3$ (1 M) ; aqueous strip solution, deionized water ; organic solution, 10^{-2} M carrier in 1,2-nitrophenyl octyl ether.

P_{Cs} (cm.h^{-1})

1,3-calix[4] hydroxy ethoxy crown 6	0.4
1,3-calix[4] dipropoxy crown 6	1.6
1,3-calix[4] di iso propoxy crown 6	1.3
1,3-calix[4] di n octyloxy crown 6	1.9
1,3-calix[4] biscrown 5	9×10^{-2}
1,3-calix[4] biscrown 6	1.3
1,3-calix[4] biscrown 7	4×10^{-2}
1,3-calix[4] bis-p-benzo-crown 6	3×10^{-3}
1,3-calix[4] bis-o-benzo-crown 6	2.8
1,3-calix[4] bisnaphthyl-crown 6	2.7
1,3-calix[4] bisdiphenyl-crown 6	0.1
n-decylbenzo-21-crown 7	9×10^{-2}

5 - TESTS ON REAL LIQUID WASTES

Two types of measurements (distribution coefficients, transport through SLMs) were carried out on two real wastes. The experiments were performed respectively in the *CARMEN* hot cell of CEA/DCC/DRDD on an acidic HA liquid waste provided by this Department and in the facilities of COGEMA Marcoule /Service on a M.A. concentrate provided by COGEMA Marcoule.

Several calixarenes were tested in the experiment carried out in CARMEN cell (bis crown-6-calix[4arene, 1,3 diisoproposy-2-4-crown-6 calix[4]arene and 1,3-di(2 nitrophenoxy octyloxy)-2,4- crown-6-calix[4]arene this calixarene has been conjointly synthesized by the Universities of Parma (Pr UNGARO) and Twente (Pr REINHOUDT), the latter was a very interesting compound due to its very high lipophilicity and to its great solubility in NPHE or NPOE but available in low amount. 1,3 di octyloxy-2-4-crown-6 calix[4]arene was used for decontaminating the concentrates.

compound 1	compound 2	compound 3	compound 4
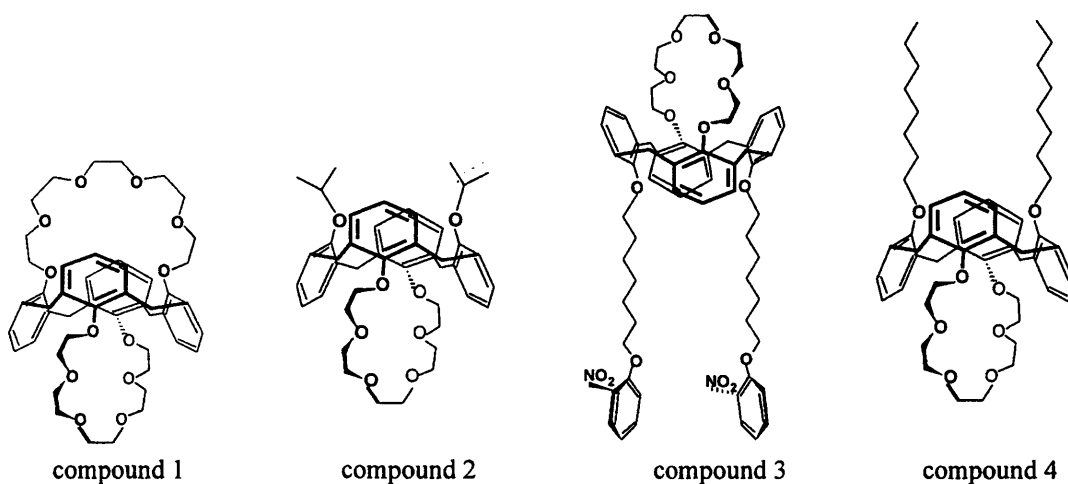
Figure 2

Structure of crown 6 calix[4]arenes

Compound 1 : bis crown-6-calix[4]arene
Compound 2 : 1,3-diisopropoxy-2,4-crown-6-calix[4]arene
Compound 3 : 1,3-di(2-nitrophenoxy octyloxy)-2,4-crown-6-calix[4]arene
Compound 4 : 1,3-dioctyl oxy-2,4-crown-6-calix[4]arene

5.1- Test on HA liquid waste

The H.A. liquid waste is 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). Composition of the waste is summarized in Table 3.

Table 3

Chemical and radiochemical composition of the real raffinate to reprocess

	Concentration (mol/l)	Activity (Ci/l)
Acidity	4	
Fe	4.5×10^{-4}	
Zr	5.1×10^{-3}	
Mo	4.9×10^{-3}	
Nd	4.9×10^{-3}	
Ce	3×10^{-3}	
Pu	$< 2 \times 10^{-5}$	
U	$< 4.2 \times 10^{-5}$	
Tc	$< 5. \times 10^{-5}$	
Np	$< 2.1 \times 10^{-5}$	
Cs	4.15×10^{-3}	
^{106}Ru		0.73
^{125}Sb		0.21
^{134}Cs		2.78
^{137}Cs		17.9
^{144}Ce		0.42
^{154}Eu		1.07
^{241}Am		1.22 (17.8 %)
^{244}Cm		5.57 (81.3 %)
^{242}Cm		0.024

Distribution coefficient measurements were carried out by putting into contact a calixarene crown 6, 0.1 M, diluted in NPHE, with the real waste, cesium distribution coefficients higher than 60 were obtained, then this cation was easily stripped in demineralized water (Table 4). Moreover the high selectivity of this class of calixarene, observed with synthetic waste was confirmed by this test : for all radionuclides (actinides or fission products : ^{106}Ru, ^{154}Eu, ^{125}Sb, ^{144}Ce) the decontamination factors (Ratio of initial activity of the elements in waste to activity of these elements in organic phase) were higher than 100 and ranging from 12 to 60 for Fe, Mo, Zr, Ce, Nd. (Table 5).

Table 4

Calixarènes	Cesium distribution coefficients (D_{Cs})			
	Extraction		Back-extraction	
	*	**	*	**
Compound 1	55±5	50±5	10±1	10±1
	55±5	46±5	11±1.1	12.5±1.2
Compoind 2	61±6	55±5	10±1	10±1
	71±7	78±8	6.7±0.7	7.2±0.7

* *aqueous phases mass-balance*
** *measurements of organic and aqueous phases*

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Table 5

of liquid-liquid extraction of a real raffinate (Table 1) by crown calixarenes.
Cesium distribution coefficients and cesium decontamination factors towards other elements

Calixarènes	Decontamination factors of cesium towards M, $DF_{(Cs/M)}$:										
	βγ emitters				Chemical elements				Actinides		
	^{106}Ru	^{125}Sb	^{144}Ce	^{154}Eu	Mo	Zr	Fe	Nd	Ce	α tot	Cm
Compound 1	9	>100	>100	>100	9	15	~60	24	19	~50	~50
	7	>100	>100	>100	11	11	22	17	20	~50	~50
Compound 2	73	>100	>100	>100	22	12	25	44	17	>100	>100
	36	>100	>100	>100	117	13	13	64	30	>100	>100

Calixarene 0.1 M in 1,2-NPHE, t = 30°C, stirring speed 1000 rpm, back-extraction : demineralized water.
note : two Dcs measurements were performed.
$D_{Cs} = [DCs]_{org}/[Cs]_{aq} \cdot DF_{(Cs/M)} = D_{Cs}/D_M$.

A small percentage of nitric acid was coextracted (5 to 7 %) which is an interesting factor knowing that we observed a competitive extraction of nitric acid and cesium cation.

Calix[4]arene bis crown, diisopropoxy calix[4]arene crown 6 and di NPOE calix[4]arene (not available in sufficient amount to perform distribution coefficient measurements) were used as carriers in supported liquid membranes (0.1 M NPHE). Respectively 58.3 %, 77.5 % and 86.3 % of cesium was transported from liquid waste to the demineralized water, higher cesium activities could have been transported by increasing the duration of an experiment (Table 6). Only cesium was significantly transported during these tests, Molybdenum and Zirconium were detected in stripping phase at very low level when diisopropoxy calix[4]arene crown 6 was used, with di NPOE calix[4]arene crown 6 Molybdenum, Zirconium, Iron, Neodynium, Cerium were detected at a very low level. The decontamination (concentration of element in feed solution/concentration of elements in stripping solution) factors obtained were higher than 100 for all elements or radionuclides (Table 7).

Table 6

Extracted cesium percentage during transport experiments

Compound	Extracted cesium (%)	
	after 4 h	at the end of the rest
Compound 1	30.4	58.3 (13 h)*
Compound 2	55.7	77.5 (8h40)*
Compound 3	63.1	86.3 (9 h)*

* the transport test lasted (xh)

It is obvious that bis-crown-6-calix[4]arene was the less efficient molecule. This molecule is the less lipophilic one. Because of the high ratio (aqueous phases/organic phase) used in SLM experiments (~3000-4000), the loss of extractant molecule in the aqueous media is far from negligible.
Further transport kinetics of bis-crown-6-calix[4]arene were slower.

Cesium decontamination factors were highly satisfactory (Table 7). No other element (except Rubidium) was extracted at a higher level than 1-2 %.

Table 7

Cesium decontamination factors obtained during transport experiments

Calixarenes	Time (h)	βγ emitters				Chemical elements					Actinides	
		^{106}Ru	^{125}Sb	^{144}Ce	^{154}Eu	Mo	Zr	Fe	Nd	Ce	α tot	Cm
compound 1	13	>50	>50	>50	>50	>100	>100	>100	>100	>100	>100	>100
compound 2	8.7	>50	>50	>50	>50	>100	>100	>100	>100	>100	>100	>100
compound 3	9	>50	>50	>50	>50	>100	>100	>100	>100	>100	98	98

(header spanning: Decontaminaiton factors of cesium towards M, $DF_{(Cs/M)}$:)

Permeability coefficient and membrane fluxes were calculated. The results are indicated in the Tables 8 and 9.

According to Danesi's model, flux of cations were calculated from experiments carried out with the real waste and simulated waste for different nitric acid concentrations (2-6 M). A decrease of cation flux was observed with an increase of the acidity due to an higher transport of HNO_3. At a HNO_3 4 M conentration, the cesium flux was 10 % lowered real waste, this flux was included within the range of reproducibility of fluxes.

Table 8

Permeability coefficients obtained for Cs during transport experiments

Calixarenes	S_{eff} (cm^2)	time (h)	Cesium permeability (cm.h^{-1})	
			Feed compartment	back-extraction compartment
compound 1	12.6	13	0.66	0.72
compound 2	12.2	8.7	2.39	2.06
compound 3	12	9	2.19	2.67

Table 9

Membrane fluxes obtained for Cs during the transport experiments

Calixarenes	S_{eff} (cm^2)	time (h)	Membrane flux (mol.cm^{-2}.h^{-1})	
			Feed compartment	back-extraction compartment
compound 1	12.6	13	2.6×10^{-6}	3.1×10^{-6}
compound 2	12.2	8.7	6.7×10^{-6}	7.6×10^{-6}
compound 3	12	9	6×10^{-6}	6.7×10^{-6}

1,3-diisopropoxt-2,4 crown-6-calix[4]arene and 1,3-di(2-nitrophenoxy octyloxy)-2,4 crown-6-calix[4]arene gave better results than bis-crown-6-calix[4]arene (less lipophilic).

1,3- di (n octyloxy)-2,4 crown-6-calix[4]arene was diluted in 1,2 nitrophenyl hexyl ether (5.10^{-2} M) for the distribution coefficient measurements and transport experiments. The composition of the concentrate is given in Table 10.

Distribution coefficients of cesium exhibited 1,3-di-n-octyloxy-2,4- crown-6-calix[4]arene (Table 11) high affinity. The extraction and back-extraction percentages agreed with those obtained the high level liquid waste was decontaminated and were fairly satisfactory.

Table 11

Chemical and radiochemical composition of the real raffinate to reprocess [1]

Cations	g.l⁻¹	M	Anions	g.l⁻¹	M
Na	60	2.61	NO_3^-	340	
K	4.5	0.117	PO_4^{3-}	$1.7\ 10^{-3}$	
Mg	14.9	0.620	Cl^-	<0.1	
Ca	0.38	0.0095			
Al	0.5	0.0137			
Cr	0.05	0.000693			
Fe	0.98	0.0175			
U	1.3	0.00546			
Mo	<0.02	$<2.1\ 10^{-4}$			
Zn	0.07	$1.07\ 10^{-3}$			
Zr	<0.01	$<1.1\ 10^{-4}$			

Acidity : 1.05 M

Radioelements	Mbq.l⁻¹	mCi.l⁻¹
Pu 239 to 242	1.7	0.046
Pu 238 + Am 241	8.14	0.22
Cm 244	1.33	0.036
Cm 242	6.66	0.18
Sr 89 + 90	648	17.5
Co 60	3	0.1
Ru 106	720	19.5
Sb 125	40	1.1
Cs 134	180	4.9
Cs 137	3200	86.5
Ce 144	350	9.5
Pr 144	350	9.5
Eu 154	9	0.2

Table 11

Cs decontamination of the real effluent by liquid-iquid extraction

	Extraction		Back-extraction	
	D_{Cs}	% Extraction	D_{Cs}	% back-extraction
134Cs	15.8	91.1	4.37	17.3
137Cs	14.3	89.2	4.27	18.1

feed solution : TBP washed effluent, organic solution : calixarene octyl 5.10⁻² M/NPHE, back-extraction : demineralized water.

Only residual plutonium after TBP washing and potassium are noticeably co-extracted. Sodium is not extracted at all and the Cs/Na selectivity is confirmed. Potassium is co-extracted but does not prevent Cs extraction.

The real effluent was introduced after TBP washing and acidification to 1 M HNO₃ in the central compartment of the double membrane system. (The 2 membranes contain the calixarene octyl 5.10^{-2} M diluted in NPHE). This two membrane device was used to reduce the duration of transport.

After 9 hours, practically all the cesium was transferred. Other elements were left in the feed solution. The tremendous selectivity of crown 6 calix[4]arenes was demonstrated by the decontamination factors higher than 50 or 100 (Table 12), except in the case of residual plutonium. The symetric behaviour of feed and strip concentrations confirmed that there was no cesium retention inside the membranes.

Permeabilities, reported in the Table 13, pointed out the transport's efficiency..

Table 12

Real effluent Cs decontamination by SLM. Solutions after 9 hours contact.
Decontamination factors of Cs

Element X	D.F
239-242Pu	2.5
238Pu + 241Am	148 ≅ >100
244Cm	154 ≅ >100
242Cm	803 ≅ >100
134Cs	-
137Cs	-
Na	>100
K	>105 ≅ >100
Mg	380 ≅ >100
Ca	58.7
Al	40.7
Fe	>1750 ≅ >100
Zn	>302 ≅ >100

Feed solution : real effluent after TBP washing and acidified to 1 M (HNO₃) , organic solution :
crown calixarenes 5.10^{-2} M/NPHE, back-extraction solution : demineralized water, double membrane system.

Table 13

Cs transport from a real effluent. Permeabilities according to Danesi
(calculated for the 4 first hours of the transport)

	Cs 137	Cs 134
Right	1.65	1.70
Left	1.62	1.71
Right + Left	3.27	3.41

Feed solution : real effluent after TBP washing and acidified to 1 M (HNO₃),organic solution : crown
calixarene 5.10^{-2} M/NPHE, back-extraction solution : demineralized water, double membrane system

CONCLUSION

Studies carried out with several calixarenes display the interest of using calix[4]crowns. These compounds are much more efficient than crown ether for the extraction of cesium from acidic medium and exhibit a tremendous selectivity cesium/sodium, moreover the extraction is reversible, cesium can be recovered in demineralized water, this property allows volume of waste to be strongly decreased. Some preliminary tests indicating a good stability towards irradiation of calix[4]arene crown 6 must be confirmed. Calix[4]arenes seem very promising for the removal of ^{137}Cs from liquid containing sodium salts at high concentration and also for the selective separation of ^{135}Cs before transmutation or disposal in a specific matrix.

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BIBLIOGRAPHIE

[1]   R.J. ORTH, K.P. BROOKS, D.E. KURATH, P.N.L. 9874 UC 721.

[2]   S.F. MARSH; Z.V. SUITRA, S.M. BOWEN, L.A. 12654.

[3]   J. RAIS, J. PLESEK, P. SELUCKY, M. KYRS, L. KADLECOWA, J. Radioanal. Nucl. Chem., 1988,97,13.

[4]   I.H. GEROW, J.E. SMITH, M.W. DAVIS Jr, Sep. Sci., 1981, 16(5) 519-548.

[5]   W.J. Mc DOWELL, G. N. CASE, J.A. Mc DONOUGH, R.A. BARTSCH, Anal. Chem., 1992, 64, 3013-3017.

[6]   E. BLASIUS, K.H. NILLES, Radiochim. Acta, 1984, 35, 173-182.

[7]   J.F. DOZOL, J. CASAS, A. SASTRE, Sep. Sci. 1995, 30(3), 435-448.

[8]   C. ALFIERI, E. DRADI, A. POCHINI, R. UNGARO, G.D. ANDREETTI, J. Chem. Soc. Chem. Commun., 1983, 1075.

[9]   (a) C.D. GUTSCHE, Acc. Chem. Res. 1983, 16,161. (b) C.D. GUTSCHE, Top. Curr. Chem.1984,123,1 (c)R. UNGARO, A. POCHINI, I, Frontiers in Supramolecular Organic Chemistry and Photochemistry, H.J. SCHNEIDER, H. DURR, Eds., Verlagsgesellschaft : Weinheim, 1990, pp 57-81. (d) A. ARDUINI, M. FABBI, P. MINARI, A. POCHINI, A.R. SICURI, R. UNGARO, In Supramolecular Chemistry, V. BALZANI, L. DE COLA, Eds.; Klumer Academic Publishers : Dordrecht, The Netherlands, 1992, pp 31-50. (e) Z. ASFARI, J. WEISS, J. VICENS, Synlett 1993, 719. (f) S. SHINKAI. Tetrahedron, 1993, 49, 8933. (g) Z. ASFARI, J. WEISS, S. PAPPALARDO, J. VICENS. Pure Appl. Chem. 1993, 65,585. (h) V. BOHMER, Angew. Chem., Int. Ed. Engl. 1995, 34, 713.

[10]   (a) R.UNGARO, A. CASNATI, F. UGOZZOLI, A. POCHINI, J.F. DOZOL, C. HILL, H.ROUQUETTE. Angew. Chem. Int. Ed. Engl., 1993, 33, N° 14, 1506-1509.
       (b) Z. ASFARI, C. BRESSOT, J. VICENS, C. HILL, J.F. DOZOL, H. ROUQUETTE, S.EYMARD V. LAMARE, B. TOURNOIS, Anal. Chem., 1995, 67, 3133-3139.

[11]   (a) A. IKEDA, H. TSUZUKI, S. SHINKAI, Tetrahedron Lett. 1994, 8417. (b) A. IKEDA, S. SHINKAI
J. Am. Chem. Soc. 1994, 116, 3102. (c)A. IKEDA, S. SHINKAI. Tetrahedron Lett. 1992, 7385
(d) K. IWAMOTO, S. SHINKAI, J. Org. Chem. 1992, 57,7066. (e) F. FUJIMOTO, N. NISHIYAMA,
H. SHINKAI, J. Chem. Soc., Perkin Trans. 2 1992, 643. (f) K. ARAKI, H. SHIMIZU, Chem. Lett,
1993.

[12]   C. HILL, J.F. DOZOL, H. ROUQUETTE, S. EYMARD, B. TOURNOIS. J. Membrane Sci., 1996,
114, 73-80.