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

Use of Calix[4]-bis-2,3-naphthocrown-6 for Separation of Cesium from Pressurized Heavy Water Reactor Simulated High Level Waste Solutions (PHWR-SHLW)

D. R. Raut[a]; P. K. Mohapatra[a]; S. A. Ansari[a]; V. K. Manchanda[a]
[a] Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai, India

To cite this Article Raut, D. R. , Mohapatra, P. K. , Ansari, S. A. and Manchanda, V. K.(2009) 'Use of Calix[4]-bis-2,3-naphthocrown-6 for Separation of Cesium from Pressurized Heavy Water Reactor Simulated High Level Waste Solutions (PHWR-SHLW)', Separation Science and Technology, 44: 15, 3664 — 3678

To link to this Article: DOI: 10.1080/01496390903183352

URL: http://dx.doi.org/10.1080/01496390903183352

Separation Science and Technology, 44: 3664–3678, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390903183352

Taylor & Francis
Taylor & Francis Group

Use of Calix[4]-bis-2,3-naphthocrown-6 for Separation of Cesium from Pressurized Heavy Water Reactor Simulated High Level Waste Solutions (PHWR-SHLW)

D. R. Raut, P. K. Mohapatra, S. A. Ansari, and V. K. Manchanda
Radiochemistry Division, Bhabha Atomic Research Centre,
Trombay, Mumbai, India

Abstract: Distribution studies on Cs(I) were carried out from pressurized heavy water reactor (PHWR) simulated high level waste (SHLW) solution using calix[4]-bis-2,3-naphtho-crown-6 as the ligand. A mixture of 1:1 nitrobenzene and toluene was evaluated as a suitable diluent. The distribution ratio of Cs(I) increased with the aqueous feed acidity upto 3 M HNO_3 and decreased thereafter due to extraction of hydronium ions. The maximum D_{Cs} value at $\sim$3 M HNO_3 suggested the possible application of the system for the recovery of radio-cesium from high level waste solution. The addition of 0.4% (v/v) Alamine 336 (a tertiary amine) facilitated the quantitative stripping of Cs(I) with distilled water. Quantitative extraction of Cs(I) from SHLW containing 0.32 g/L of Cs was observed in five contacts at $O/A = 1/2$ with 2.5×10^{-3} M calix[4]-bis-2,3-naphtho-crown-6. Similarly, quantitative stripping of Cs(I) from the loaded organic phase was achieved in two contacts with distilled water at a volume ratio (O/A) of 2. Selectivity studies carried out using several radiotracers such as ^{143}Ce, ^{140}La, ^{140}Ba, ^{137}Cs, ^{103}Ru, ^{99}Mo, ^{99m}Tc, ^{97}Zr, ^{91}Sr, etc. indicated excellent selectivity for Cs. The reagent exhibited excellent chemical stability up to a period of six months.

Keywords: Calix-crown, cesium, nuclear waste management, solvent extraction

Received 12 March 2009; accepted 12 May 2009.

Address correspondence to P. K. Mohapatra, Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India. Fax: +91-22-25505151. E-mail: mpatra@barc.gov.in

INTRODUCTION

One of the accepted strategies for the remediation of high level nuclear waste (HLW) involves vitrification in glass matrices followed by burial in deep geological repository. However, long-lived fission products such as ^{137}Cs ($t_{1/2} = 30.1$ y) with high heat out put (0.417 W/g) pose threat to the vitrified blocks due to possible long term deformations. The removal of radio cesium from HLW makes not only the handling of the latter easier but also recovered ^{137}Cs can be put to several applications as a radiation source such as in food preservation, sterilization of medical products, branchy therapy, blood irradiation, treatment of sewage sludge, etc. (1). The use of ^{137}Cs in place of ^{60}Co ($t_{1/2} = 5.2$ years) will also reduce the shielding requirement and frequency of source replenishment which will ease the handling/transportation of radioactive source. In the world about 34.85 kg of ^{137}Cs is produced per day due to the nuclear activity. It is, therefore, required to devise processes for the selective removal of radio-cesium from HLW.

Though separation methods such as precipitation and ion-exchange are used for Cs recovery from wastes, solvent extraction methods have been particularly attractive because of their ease of operation and large throughput (2). Dicarbollides have been reported to be efficient and selective extractants for the preferential removal of ^{137}Cs from nuclear waste solutions (3,4). However, the choice of diluent has been a serious issue for dicarbollide based extractants. On the other hand, solvent extraction methods involving exotic reagents such as the crown ethers, calixarenes, and calix crowns have shown great promise for Cs recovery from the acidic waste solutions (5–7). Among the crown ethers, derivatives of 21-crown-7 have been extensively used for Cs extraction which has a good match between the cavity of the crown ether and the crystal ionic radius of the metal ion (7). Dietz et al., (5) have carried out Cs extraction using crown ether solutions in oxo diluents such as alcohols, ketones, ethers, and carboxylic acids. Kumar et al., (6) have also reported the extraction of ^{137}Cs from nitric acid medium into distilled water medium using several di-benzo-18-crown-6 (DB18C6) derivatives.

Similar to the crown ethers, calix-crown ethers have been employed for better selective extraction of Cs from acidic/alkaline waste solutions (7,8). In general, calix-crown compounds display better extraction/separation efficiencies at much lower ligand concentration (9). Among the calix-crowns, bis-crown-6 of 1,3-alternate calixarene has shown a higher uptake of Cs(I) than the corresponding mono-crown (10,11). Calix-bis-crown compounds usually form 1:1 complex (12). Exceptionally high extraction efficiency for Cs was attributed to pi-interaction with four benzene units of the calixarenes (13,14). On the other hand, the

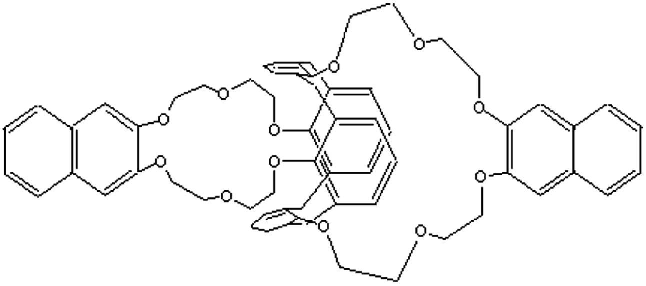

Figure 1. Structural representation of Calix[4]-bis-2,3-napthocrown-6 (CNC).

1,3-conformation led to exceptionally high Cs to Na selectivity which was related to the solvation effect (15,16). A substituted calix-crown compound, calix[4]arene-bis(t-octylbenzo-crown-6), better known as "BOBCalixC6," has been developed at ORNL for effective and selective extraction of Cs from the Savanna River Site (SRS) alkaline waste which contains a large concentration of sodium (17). Application of this reagent

Table 1. Composition of simulated high level waste (SHLW) for pressurized heavy water reactor (PHWR); Acidity: 3 M HNO_3

Constitutent	Concentration ($mg \cdot l^{-1}$)	Constitutent	Concentration ($mg \cdot l^{-1}$)
Sr[a]	186.3	Sb[b]	4.7
Rb[a]	74.5	Se[b]	12.3
Zr[a]	771.3	Dy[c]	2.0
Ag[a]	18.6	Sn[b]	15.6
Ba[a]	308.8	Te[b]	102.8
Cd[a]	16.3	Sm[c]	163.8
Ce[a]	532.5	Tb[c]	5.0
Cs[a]	543.8	Gd[c]	165
Fe[a]	500	Eu[c]	22.6
Cr[a]	100	Pr[c]	243.8
Co[a,f]	127.5	Nd[c]	862.5
Na[a]	3000	La[c,e]	263.8
Ni[a]	100	Pd[d]	267.5
U[a]	18325	Ru[d]	463.8
Mn[g]	181.3	Y[d]	99
Mo[b]	731.3		

[a]Nitrate salt; [b]Metal powder; [c]Oxide and; [d]Chloride salt; [e]Taken in place of Pm; [f]Taken in place of Rh and; [g]Taken in place of Tc.

to recovery of Cs from acidic wastes has its limitations due to the degradation of the reagent (18).

We have evaluated three commercial calix-crown compounds for selective extraction of Cs from nitric acid solutions (19). Out of the three compounds, Calix[4]-bis-2,3-napthocrown-6 (CNC, Fig. 1) was found to be the most efficient when used in nitrobenzene. In view of the lack of literature data on the batch studies on Cs recovery from acidic HLW, which can help in developing a flow sheet, the present investigations were taken up. The second objective was to reduce the nitrobenzene inventory in the solvent system as low as possible. The present study involves the evaluation of CNC in a mixed diluent system (of toluene and nitrobenzene) for selective Cs removal from a PHWR simulated high level waste solution (SHLW, Table 1). Its reusability and long-term chemical stability are also reported.

EXPERIMENTAL

Materials

Calix[4]-bis-2,3-naphtho-crown-6 (CNC, Fig. 1) procured from Acros Organics, Belgium was used as received. AR grade diluents, toluene and nitrobenzene, procured from Fluka Chemie AG, Switzerland, and *n*-dodecane, purchased from Lancaster, UK were used without further purifications. All the other reagents used were of analytical reagent grade. ^{137}Cs tracer was procured from the Board of Radiation and Isotope Technology (BRIT), Mumbai and its radiochemical purity was ascertained by gamma spectrometry employing a high resolution HPGe detector. Simulated high level waste (SHLW) was supplied by the Waste Management Division, BARC, Mumbai. The composition of SHLW (Table 1) was ensured by the ICP-AES as well as the EDXRF technique. Similarly, the acidity of the SHLW was ascertained by acid-base titration in the presence of neutral saturated $K_2C_2O_4$ solution and the overall acidity was adjusted as desired with a suitable concentration of nitric acid.

Distribution Studies

Distribution studies were carried out by equilibrating equal volumes (usually 1 mL) of organic phase containing the desired concentration of CNC and aqueous phase (containing ^{137}Cs tracer) in a rotary thermostated water bath for 60 min at 25.0 ± 0.1°C. The two phases were then centrifuged and assayed by taking suitable aliquots from both the phases. Assay of ^{137}Cs were carried out by gamma counting using a well type NaI(Tl) scintillation detector interphased to a multi-channel analyzer.

The distribution ratio (D_{Cs}) was calculated as the ratio of the concentration of metal ions (expressed in terms of counts per unit time per unit volume) in the organic phase to that in the aqueous phase. All experiments were carried out in duplicate and the data quoted are the average of the two data points. The material balance in all the experiments was within error limits (±5%).

RESULTS AND DISCUSSIONS

Evaluation of Diluents

Calix-crown ligands have shown good solubility as well as high distribution ratio of Cs(I) in nitrobenzene (19–21). However, the use of nitrobenzene on a large scale is not advisable due to its chemical toxicity. Therefore, it is desirable to look for a suitable diluent where Cs(I) selective calix-crowns can be dissolved easily while resulting in a reasonably high distribution ratio for Cs. Earlier studies have indicated poor solubility of CNC in non-polar diluents like toluene and n-dodecane (19). This could be explained on the basis that the presence of twelve oxygen atoms in CNC makes the molecule polar apparently not favoring its solubility in non-polar diluents. The results of the distribution studies with various diluents such as 1-octanol or hexone were not encouraging enough for their use in this work (19).

It was therefore of interest to decrease the chemical toxicity of nitrobenzene by diluting with other non-toxic diluents such as toluene and *n*-dodecane. A mixture of nitrobenzene and *n*-dodecane containing 1×10^{-3} M CNC when equilibrated with an equal volume of 3 M HNO_3 solution, resulted in phase separation (crud formation at the interface) when the *n*-dodecane proportion exceeded 20% (Table 2). This

Table 2. Effect of diluent composition (with nitrobenzene (NB) and either *n*-dodecane or toluene) on distribution ratio of cesium (D_{Cs}); Organic phase: 1×10^{-3} M CNC; Aqueous phase: 3 M HNO_3; Temperature: 25°C

NB (vol %)	n-dodecane (vol %)	D_{Cs}	NB (vol %)	Toluene (vol %)	D_{Cs}
100	–	7.71 ± 0.17	100	–	7.71 ± 0.17
90	10	11.02 ± 0.14	90	10	10.80 ± 0.11
80	20	10.51 ± 0.06	80	20	9.04 ± 0.21
60	40	Phase separation	60	40	8.38 ± 0.18
40	60	Phase separation	40	60	3.01 ± 0.08
20	80	Phase separation	20	80	0.44 ± 0.02

discouraged us to use *n*-dodecane for diluting nitrobenzene. On the other hand, an aromatic diluent like toluene was compatible with nitrobenzene in all proportions (Table 2). In both the cases, a maximum in the D_{Cs} was observed for the 90:10 nitrobenzene : toluene (*n*-dodecane) composition which is attributed to an improvization in diluent solvation property (22). Similar observations have been made in the literature (23).

Extraction of Cs from SHLW

The distribution studies on Cs(I) were carried out from SHLW with 2.5×10^{-3} M CNC employing a mixture of toluene and nitrobenzene in various proportions as the diluent. As shown in Table 3, the D_{Cs} value decreased with an increased proportion of toluene. The extraction of Cs(I) by calix crown ligands has been established as an ion-pair mechanism as given by the following equilibrium reaction (24).

$$Cs^+_{(aq.)} + NO^-_{3(aq.)} + L_{(org.)} \rightleftharpoons (Cs \cdot L)^+ \cdot NO^-_{3(org.)} \tag{1}$$

where the subscripts (aq.) and (org.) represent the aqueous and the organic phases, respectively, L is the ligand in the metal-ligand complexation. The extraction constant (K_{ex}) for the above equilibrium reaction can be represented as follows,

$$K_{ex} = \frac{[(Cs \cdot L)^+ \cdot NO_3^-]_{(org.)}}{[Cs^+]_{(aq.)} \cdot [NO_3^-]_{(aq.)} \cdot [L]_{(org.)}} \tag{2}$$

We understand that neutral complex species, for example, those encountered with beta-diketones as the extractants, will be favored with low dielectric constant diluents such as toluene. On the other hand, ion-pairs

Table 3. Effect of diluent composition on distribution ratio of cesium (D_{Cs}); Organic phase: 2.5×10^{-3} M CNC; Aqueous phase: SHLW at 3 M HNO_3; Temperature: 25°C

Nitrobenzene (% v/v)	Toluene (%, v/v)	DCs
100	–	10.09 ± 0.03
90	10	8.31 ± 0.18
80	20	7.03 ± 0.13
60	40	5.15 ± 0.01
50	50	2.65 ± 0.04
40	60	2.51 ± 0.03
20	80	0.76 ± 0.06

will be preferred in diluents with higher dielectric constants. In a diluent such as nitrobenzene, for which the dielectric constant is relatively high (34.8) ion separated species are extracted. However, a mixture of toluene and nitrobenzene can result in an optimum dielectric constant (18.6 for a mixture of 50% toluene +50% nitrobenzene) for reasonably good extraction. However, decrease in the extraction of Cs(I) with increased proportion of toluene was very obvious from the above discussion. However, 50% (v/v) of the diluents were used in all the subsequent work to optimize the risk of chemical toxicity of nitrobenzene and a reasonably good D_{Cs} value from SHLW.

Extraction of Uranium Using CNC

Though the PUREX process is aimed at recovering U and Pu quantitatively from the spent fuel, the high level waste (HLW) which is a concentrate of the PUREX raffinate contains varying amounts of U depending on the efficiency of the process. As can be seen from Table 1 (a typical composition of a PHWR-SHLW), 18.3 g/L U is present along with other fission products and structural materials. It is presumed that the presence of a significant amount of U may affect Cs recovery using CNC. Therefore, the extraction behavior of Cs from simulated HLW containing varying amount of U (in the concentration range of $2-20\,g/L$) was investigated. The data refers to the extractant concentration of 5×10^{-3} M CNC in pure nitrobenzene and hence result in higher D_{Cs} values compared to the diluent mixture. The results are presented in Fig. 2. A sharp decrease in the D_{Cs} values was observed in the initial stages (from ~30 to ~20 for U concentration $2-8\,g/L$) with increasing U concentration in SHLW and attains a near constant value of 20 for U concentration in the range of $8-20\,g/L$. Though the reason for this behavior is not well understood, it suggests that CNC solutions in the diluent mixture can yield similar results as in the pure nitrobenzene solutions mentioned above and can be used for effective recovery of Cs from high level waste even in the presence of large concentration of U.

Optimization of Strippant

The distribution studies on Cs(I) were performed at 3 M HNO_3 as HLW has acidity in the range of 3–4 M HNO_3. The D_{Cs} value observed at 3 M HNO_3 by 2.5×10^{-3} M CNC in 1:1 nitrobenzene and toluene was 10.09. On the other hand, the D_{Cs} value in distilled water was 10.06, suggesting that the stripping of the metal ion was not possible with distilled water.

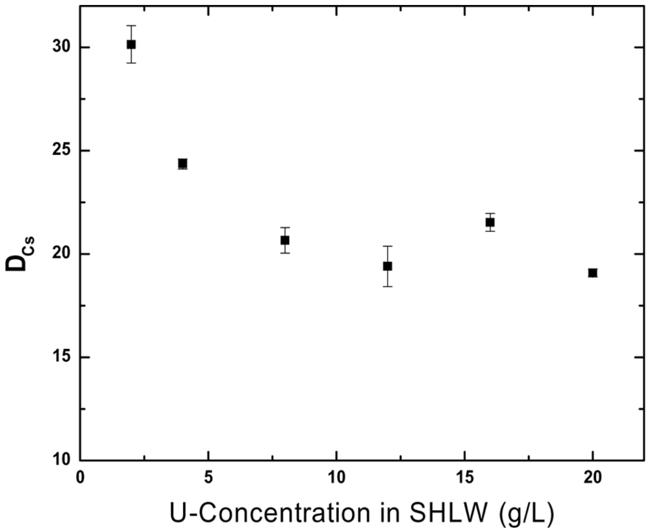

Figure 2. Effect of varying U concentration in SHLW on D_{Cs} values. Aqueous phase: SHLW; Organic phase: 5×10^{-3} M CNC in nitrobenzene.

Stripping of the monovalent alkali metal cation was also not favored by using any conventional complexing agent. Bonnesen et al. reported that the stripping of Cs(I) from the organic phase was facilitated by the addition of tertiary amine in the organic phase (25,26). It is possible to reverse the equilibrium shown in Eq. (1) by increasing the nitrate ion concentration in the organic phase by a common-ion mass-action effect. Bonnesen et al. have suggested the use of extractable alkali metal nitrates such as KNO_3 and $RbNO_3$ or a tertiary amine capable of extracting nitrate for this purpose (24). Harmon et al. synthesized calix crown ligands containing the amino group in the cavity of the molecule (27). They reported that the stripping of Cs(I) was facilitated by the presence of the amino group due to marginal destabilization of the extracted ion-pair. In the present work, Alamine 336 (a tertiary amine) was added in the organic phase in various proportions and the D_{Cs} values obtained are summarized in Table 4. The results indicated efficient stripping of Cs(I) by distilled water in the presence of 0.2–0.4% (v/v) of Alamine 336.

It is apparent from the data reported by Bonnesen et al. (24–26) that as long as the amine remains in the protonated form it would help in the stripping of Cs from the organic phase. As per their proposed mechanism, by contacting the solvent repeatedly with water, the proportion of protonated amine will be smaller and smaller, to finally stop working altogether and this would affect the stripping in the subsequent

Table 4. Effect of Alamine 336 concentration on distribution ratio of cesium (D_{Cs}) from SHLW and distilled water; Organic phase: 2.5×10^{-3} M CNC; Diluent: 1:1 nitrobenzene and toluene; Temperature: 25°C

	D_{Cs}	
Concentration of alamine 336% (v/v)	SHLW	Dist. water
0	2.98 ± 0.02	0.14 ± 0.04
0.2	2.80 ± 0.03	0.06 ± 0.02
0.4	2.57 ± 0.02	0.06 ± 0.01
0.6	2.64 ± 0.02	0.07 ± 0.03
0.8	2.48 ± 0.04	0.09 ± 0.02
1	2.45 ± 0.06	0.07 ± 0.02

contacts. However, multiple contacts have indicated that the D_{Cs} values decreased from 0.07 (first contact) to 0.03 (second contact) to 0.01 (third contact). This underlines the effectiveness of distilled water as the strippant in these studies.

Solvent Extraction Studies Using Modified Extractant

The D_{Cs} values were determined from SHLW at different acidity by the organic phase containing 2.5×10^{-3} M CNC + 0.4% Alamine 336 in 1:1 NB : toluene. As shown in Fig. 3, the D_{Cs} value increased with HNO_3 concentration reaching to a maximum at 3 M HNO_3 and decreased thereafter. The initial increase in the D_{Cs} value was attributed to the increase in the nitrate concentration which facilitates the ion-pair formation as described by equilibrium reaction (1). However, decrease in the D_{Cs} value beyond 4 M HNO_3 could be due to the strong interaction of hydronium ions (H_3O^+) with calixcrown ligand to form CNC-hydronium ion complex (28). In the light of literature and our earlier work with CNC, it appears that at lower acidity, the extracted species was $[CsL]^+ \cdot [NO_3]^-$, while it was $[HL \cdot H_2O]^+ \cdot [NO_3]^-$ at higher acidity. On the other hand, the addition of 0.4% (v/v) Alamine 336 has no significant effect on the distribution of Cs(I) as D_{Cs} value at 3 M HNO_3 were 2.4 and 2.6 with and without Alamine 336, respectively. A higher distribution ratio of Cs(I) at moderate acidity (3–4 M HNO_3) suggested the potential application of the system for the recovery of radio cesium from HLW solutions.

In order to find out the number of contacts required for the complete extraction of Cs(I) from SHLW, repeated contacts were given to the aqueous phase with the fresh organic phase (2.5×10^{-3} M CNC) each

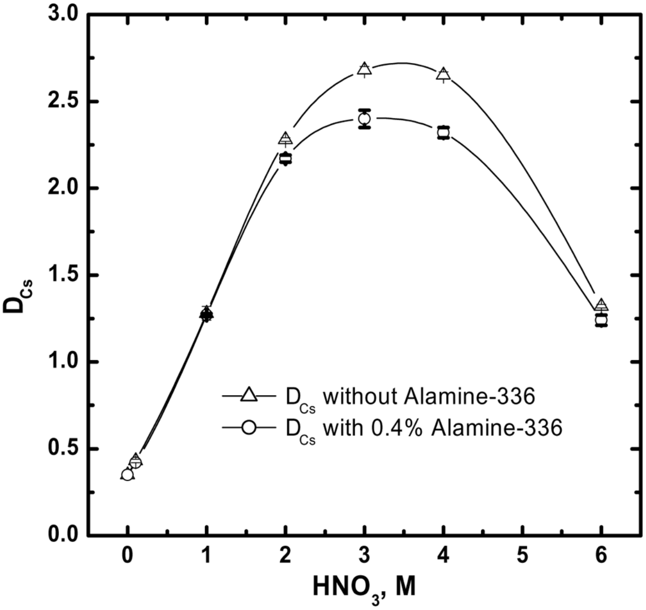

Figure 3. Effect of HNO_3 concentration of SHLW (in the presence as well as absence of Alamine 336) on distribution of Cs(I) from SHLW; Organic phase: 2.5×10^{-3} M CNC; Diluent: 1:1 toluene and nitrobenzene.

time containing 0.4% (v/v) Alamine-336. As shown in Table 5, five stages were required for the quantitative extraction of Cs(I) from SHLW containing 0.32 g/L Cs when O/A ratio was maintained at 0.5. Similarly, the quantitative stripping of Cs(I) could be achieved in two cycles with distilled water at O/A ratio of 2. The results demonstrated excellent potential of the reagent for the recovery of Cs(I) from HLW.

Table 5. Cumulative extraction and stripping of Cs(I) from SHLW; Organic phase: 2.5×10^{-3} M CNC + 0.4% (v/v) Alamine 336; Diluent: 1:1 nitrobenzene and toluene; Strippant: Distilled water, temperature: 25°C

Extraction cycles[a]	% extraction	Stripping cycles[b]	% stripping
1	43.01	1	92.51
2	76.60	2	99.76
3	93.74	3	99.99
4	98.67		
5	99.75		

[a] Phase ratio (O/A) in extraction cycle was 1/2.

[b] Phase ratio (O/A) in stripping cycle was 2.

Cesium Selectivity Studies

Selective extraction of Cs(I) with respect to other fission products was investigated by irradiating a natural uranium target with a thermal neutron flux of $10^{12}\,n \cdot cm^{-2} \cdot s^{-1}$. Subsequently, the irradiated target was dissolved in 3 M HNO_3 and the fission products mixture was spiked with ^{137}Cs tracer. The extraction of various fission products (in addition to Cs) was monitored in the extracted organic phase after equilibrating in a thermostated water bath for 1 hour at 25 ± 0.1°C. Figure 4 represents the gamma spectrum of the fission products present in the organic phase as well as in the aqueous phase recorded using a high resolution HPGe detector inter-phased with a multi-channel analyzer. It was observed that the fission products such as ^{143}Ce, ^{140}La, ^{140}Ba, ^{103}Ru, ^{99}Mo, ^{99m}Tc, ^{97}Zr, ^{91}Sr, etc. were not extracted to any significant extent into the organic phase. The organic phase exhibited only one prominent peak due to ^{137}Cs activity suggesting the selective extraction of the cesium. Similar results have been reported earlier from our laboratory where the selective transport of Cs(I) was obtained by supported liquid membranes containing crown ether and CNC as the carrier extractant (29,30). It is particularly interesting to note that no extraction of Sr(II) and Ba(II) were seen even

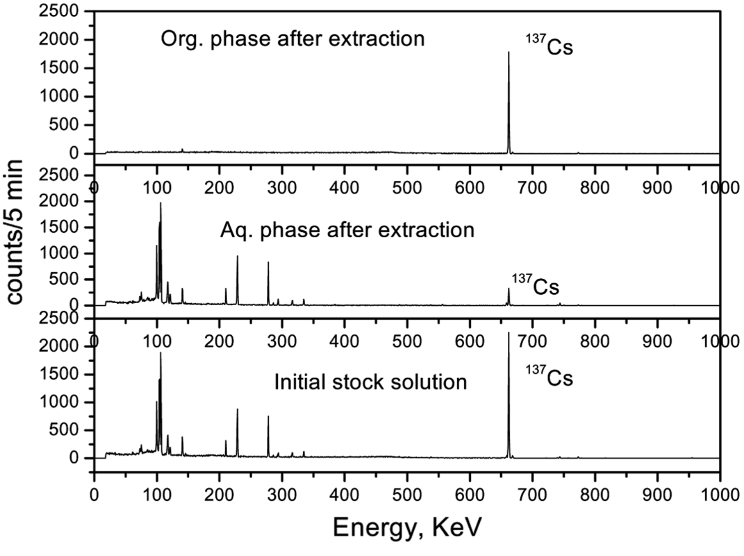

Figure 4. Gamma spectra of fission products in organic and aqueous phases; Aqueous phase: 3 M HNO_3; Organic phase: 2.5×10^{-3} M CNC + 0.4% (v/v) Alamine 336; Diluent: 1:1 toluene and nitrobenzene; Temperature: 25°C; Equilibration time: 1 hour.

though their ionic size has good compatibility with the 18-membered crown ligands (31).

Stability of the Ligand

In order to use the given system for the separation of metal ions from HLW, it was essential to understand the radiation as well as hydrolytic (chemical) stability of the reagent. The chemical stability was evaluated by keeping the organic phase (2.5×10^{-3} M CNC and 0.4% (v/v) Alamine 336 in 1:1 toluene/nitrobenzene) in contact with the aqueous phase (SHLW) for more than 6 months at $24 \pm 2°C$ which is near to the ambient temperature. The extraction and stripping data for Cs(I) determined over a period of time was constant even after 6 months of experiments (D_{Cs} in SHLW $= 2.6 \pm 0.2$). The results demonstrated the excellent chemical stability of the reagent. Though the chemical stability of BOBCalix was reported to be good in alkaline medium, its stability in the acidic medium was poor (25). The radiation stability of the solvent system was also evaluated which is reported elsewhere (32).

Reusability of the Ligand

The reusability of the organic phase was investigated by contacting with SHLW followed by stripping with distilled water in five successive cycles. The stability of the resultant lean organic phase was then evaluated by determining D_{Cs} value from SHLW. It was observed that even after five

Table 6. Distribution data of Cs(I) in five successive cycles of extraction and stripping; Aqueous phase: 3 M HNO_3; Organic phase: 2.5×10^{-3} M CNC + 0.4% (v/v) Alamine 336; Diluent: 1:1 nitrobenzene and toluene; Strippant: Distilled water, temperature: 25°C

Number of cycles	D_{Cs} at 3 M HNO_3
1	2.59
2	2.68
3	2.54
4	2.50
5	2.53
Mean	2.57
S.D.	0.07
R.S.D. (%)	2.72

successive cycles of loading and stripping, the D_{Cs} was almost constant at the original value of 2.6 ± 0.2 (Table 6), suggesting excellent reusability of the reagent.

CONCLUSIONS

A mixture of nitrobenzene and toluene (1:1) was evaluated as a suitable diluent for the extraction of Cs(I) from simulated HLW was studied by using Cs-selective calix[4]-bis-2,3-naphtho-crown-6 ligand. Quantitative extraction of Cs(I) from SHLW was achieved in five stages at $O/A = 1/2$. Addition of 0.4% (v/v) Alamine 336 in the organic phase facilitated the stripping of the monovalent cation. Quantitative stripping of Cs(I) from the loaded organic phase was achieved in two stages with distilled water at $O/A = 2$. Selectivity studies suggested the possible utilization of calix[4]-bis-2,3-naphtho-crown-6 ligand for selective extraction of radio-cesium from high level nuclear waste solution. The results reflected the possible application of the present solvent system for the recovery of radio-cesium from the HLW solution.

ACKNOWLEDGEMENTS

The authors thank Dr. B. A. Moyer, Chemical Sciences Division, ORNL for his useful suggestions.

REFERENCES

1. IAEA Technical Data Series No. 356, International Atomic Energy Agency, Vienna, (1993).
2. Schulz, W.W.; Bray, L.A. (1987) Solvent extraction recovery of byproduct ^{137}Cs and ^{90}Sr from HNO_3 solutions—A technology review and assessment. *Sep. Sci. Technol.*, *22*: 191–214.
3. Rais, J.; Seluky, P.; Kadlecova, L.; Kyrs, M. (1975) Study of extraction isolation of ^{137}Cs and ^{90}Sr from acidic waste solutions, Report UJV 3820-Ch, Nuclear Research Institute, Rez, Czechoslovakia.
4. Miller, R.L.; Pinkerton, A.B.; Hurlburt, P.K.; Abney, K.D. (1995) Extraction of cesium and strontium into hydrocarbon solvents using tetra-C-alkyl cobalt dicarbollide. *Solv. Extr. Ion Exch.*, *13*: 813–827.
5. Dietz, M.L.; Horwitz, E.P.; Jensen, M.P.; Rhoads, S.; Bartsch, R.A.; Palka, A.; Krzykawski, J.; Nam, J. (1996) Substituent effects in the extraction of cesium from acidic nitrate media with macrocyclic polyethers. *Solv. Extr. Ion Exch.*, *14*: 357–384.

6. Kumar, A.; Mohapatra, P.K.; Manchanda, V.K. (1998) Extraction of cesium-137 from nitric acid medium in the presence of macrocyclic polyethers. *J. Radioanal. Nucl. Chem.*, *229*: 169–172.
7. Thuery, P.; Nierlich, M.; Lamare, V.; Dozol, J.F.; Asfari, Z.; Vicens, J. (2000) Bis-(crown ether) and azobenzocrown derivatives of calix[4]arene. A review of structural information from crystallographic and modeling studies. *J. Incl. Phenom. Macrocycl. Chem.*, *36*: 375–408.
8. Ungaro, R.; Casnati, A.; Ugozzoli, F.; Pochini, A.; Dozol, J.-F.; Hill, C.; Rouquette, H. (1994) 1,3-dialkoxycalix[4]arenecrowns-6 in 1,3-alternate conformation: cesium-selective ligands that exploit cation-arene interactions. *Angew. Chem. Int. Ed. Engl.*, *33*: 1506–1509.
9. Dozol, J.F.; Dozol, M.; Macias, R.M. (2000) Extraction of strontium and cesium by dicarbollides, crown ethers and functionalized calixarenes. *J. Incl. Phenom. Macrocycl. Chem.*, *38*: 1–22.
10. Dozol, J.F.; Simon, N.; Lamare, V.; Rouquette, H.; Eymard, S.; Tournois, B.; De Marc, D.; Macias, R.M. (1999) A solution for cesium removal from high salinity acidic or alkaline liquid waste: the crown calix[4]arenas. *Sep. Sci. Technol.*, *34*: 877–909.
11. Casnati, A.; Pochini, A.; Ungaro, R.; Ugozzoli, F.; Arnaud, F.; Fanni, S.; Schwing, M.-J.; Egberink, R.J.M.; de Jung, F.; Reinhoudt, D.N. (1995) Synthesis, complexation and membrane transport studies of 1,3-alternate calix[4]arene-crown-6 conformers, a new class of cesium selective ionophores. *J. Am. Chem. Soc.*, *117*: 2767–2777.
12. Haverlock, T.J.; Sachleben, R.A.; Bonnesen, P.V.; Moyer, B.A. (2000) Analysis of equilibria in the extraction of cesium nitrate by calix[4]arene-bis(*t*-octylbenzo-crown-6) in 1,2-dicholro ethane. *J. Incl. Phenom.*, *36*: 21–37.
13. Ikeda, A.; Shinkai, S. (1992) Unusually high ionophoricity of 1,3-alternate-calix[4]arenes: π-donor participation in the complexation of cations? *Tet. Lett.*, 7385–7388.
14. Ugozzoli, F.; Ori, O.; Casnati, A.; Pochini, A.; Ungaro, R.; Reinhoudt, D.N. (1995) Evidence for cation-π interactions in calixcrown · KPic complexes from X-ray crystal structure analysis and energy calculations. *Supramol. Chem.*, *5*: 179–184.
15. Wipff, G.; Lauterbach, M. (1995) Complexation of alkali cations by calix[4]-crown ionophores: conformation and solvent dependent Na/Cs binding selectivity and extraction: MD simulations in the gas phase, in water and at the chloroform-water interface. *Supramol. Chem.*, *6*: 187–207.
16. Varnek, A.; Wipff, G. (1996) Theoretical calculations of extraction selectivity: alkali cation complexes of calix[4]-bis-crown6 in pure water, chloroform, and at a water/chloroform interface. *J. Computat. Chem.*, *17*: 1520–1531.
17. Leonard, R.A.; Conner, C.; Liberatore, M.W.; Sedlet, J.; Aase, S.B.; Vandegrift, G.F.; Delmau, L.H.; Bonnesen, P.V.; Moyer, B.A. (2001) Devolopment of solvent extraction process for csium removal from SRS tank waste. *Sep. Sci. Technol.*, *36*: 743–766.

18. Bonnesen, P.V.; Haverlock, T.J.; Engle, N.L.; Sachleben, R.A.; Moyer, B.A. (2002) ACS Symposium Series 757, Lumeta, G.J., Rogers, R.D., Gopalan, A.S. eds.; 27–44.
19. Mohapatra, P.K.; Ansari, S.A.; Sarkar, A.; Bhattacharyya, A.; Manchanda, V.K. (2006) Evaluation of calix-crown ionophores for selective removal of cesium from acidic nuclear waste solution. *Anal. Chim. Acta*, *517*: 308–314.
20. Asfari, Z.; Wenger, S.; Vicens, J. (1995) Calixcrowns and related molecules. *Pure and Appl. Chem.*, *67*: 1037–1043.
21. Haverlock, T.J.; Bonnesen, P.V.; Sachleben, R.A.; Moyer, B.A. (1997) Applicability of a calixarenes-crown compound for the removal of cesium from alkaline tank waste. *Radiochim. Acta*, *76*: 103–108.
22. Marcus, Y. (1989) Diluent effects in solvent extraction. *Solv. Extr. Ion Exch.*, *7*: 567–575.
23. Sriram, S.; Manchanda, V.K. (2002) Transport of metal ions across a supported liquid membrane (SLM) using dimethyldibutyl- tetradecyl-1,3-malonamide (DMDBTDMA) as the carrier. *Solv. Extr. Ion Exch.*, *20*: 97–114.
24. Bonnesen, P.V.; Delmau, L.H.; Haverlock, T.J.; Moyer, B.A. (1996) ORNL Report, ORNL/TM-13704.
25. Bonnesen, P.V.; Haverlock, T.J.; Sachleben, E.R.A.; Moyer, B.A. (2000) Development of Process Chemistry for the Removal of Cesium from Acidic Nuclear Waste by calix[4]arene-crown-6 Ethers. In: Lumetta, G.J.; Rogers, R.D.; Gopalan, A.S., eds.; ACS Symposium series 757, American Chemical Society: Washington, DC – 2000.
26. Delmau, L.H.; Bonnesen, P.V.; Moyer, B.A. (2004) A solution to stripping problems caused by organophilic anion impurities in crown-ether-based solvent extraction system: a case study of cesium removal from radioactive waste. *Hydrometallurgy*, *72*: 9–19.
27. Harmon, B.W.; Ensor, D.D.; Delmau, L.H.; Moyer, B.A. (2007) Extraction of cesium by a calix[4]arene-crown-6 ether bearing a pendant amine group. *Solv. Extr. Ion Exch.*, *25*: 373–388.
28. Wang, W.J.; Lin, J.; Wang, A.; Zheng, P.; Wang, M.; Wang, B. (1988) Thermodynamics and coordination characteristics of the hydronium-uranium(VI)-dicyclohexano-24-crown-8 extraction complex. *Inorg. Chim. Acta*, *149*: 151–154.
29. Mohapatra, P.K.; Manchanda, V.K. (2003) Liquid membrane based separations of actinides and fission products. *Ind. J. Chem.*, *42A*: 2925–2938.
30. Raut, D.R.; Mohapatra, P.K.; Ansari, S.A.; Manchanda, V.K. (2008) Evaluation of a calix[4]-bis-crown-6 ionophore for selective Cs-137 transport across liquid membrane from acidic solutions. *J. Membr. Sci.*, *310*: 229–236.
31. Rawat, N.; Mohapatra, P.K.; Lakshmi, D.S.; Bhattacharyya, A.; Manchanda, V.K. (2006) Selective transport of strontium from nitric acid medium using a flat-sheet membrane containing a macrocyclic carrier. *J. Membr. Sci.*, *275*: 82–88.
32. Raut, D.R.; Mohapatra, P.K.; Manchanda, V.K. Evaluation of radiolytic stability of calix[4]-bis-crown-6 ionophore for selective Cs-137 extraction/transport from acidic solutions (communicated).