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Selective separation of Cs(I) extraction from actual high level waste using a solvent containing calix [4]-bis 2,3-naphtho-crown-6

P.K. Mohapatra[a,*], P.S. Dhami[b], S. Panja[b], P. Jagasia[b], S.C. Tripathi[b], P.K. Dey [b], V.K. Manchanda[a]

[a]*Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India*
Fax: +91 22 25505151; email: mpatra@barc.gov.in
[b]*Fuel Reprocessing Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India*

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ABSTRACT

Solvent extraction studies were carried out on the selective separation of radio-cesium from actual high level waste (HLW) using calix [4]-bis-2,3-naphtho-crown-6 (CNC) in nitrobenzene - toluene mixture. The separation studies were carried out in two stages. In the first stage, a 100 times diluted HLW was used and the purity was ascertained by gamma ray spectrometry using a HPGe detector. Quantitative separation of radio-cesium (monitored by Cs-137 gamma peak at 661 keV) was observed with almost no contamination from any of the other fission products present. In the second stage, actual HLW was used for the Cs separation study. Four stages of extraction and two stages of stripping using distilled water gave >99% recovery. About 10 mCi Cs was recovered by this method. Reusability of the solvent was also carried out and though there was no loss in selectivity, slight decrease in the extraction efficiency was observed after the reagent was allowed to be in contact with the HLW for 10 d.

Keywords: Cesium recovery; High level waste; Separation; Solvent extraction; Calix-crown; Radio-cesium; Waste management

1. Introduction

Removal of ^{137}Cs from high level waste (HLW) would not only facilitate the safe disposal of the latter in deep geological repository as vitrified mass, it also solves the MANREM problem to a large extent. Moreover, the recovered radio-cesium can be used as a radiation source in gamma irradiators in the environmental pollution control, food preservation and sterilization of medical accessories, etc. [1]. The use of ^{137}Cs ($t_{1/2}$ = 30.1 y) in place of ^{60}Co ($t_{1/2}$ = 5.2 y) in the irradiators will also reduce the shielding requirement and frequency of source replenishment. In the world about 34.85 kg of ^{137}Cs is produced per day due to the nuclear activity. It is, therefore, required to develop efficient separation methods for the recovery of ^{137}Cs from HLW.

A variety of methods based on precipitation, ion-exchange and solvent extraction are reported in the literature for the recovery of ^{137}Cs from various radioactive waste solutions [2–9]. Ion-exchange based methods such as RFPR resin have been used for recovery from intermediate level wastes where the Cs concentration is much lower [10]. On the other hand, though AMP based inorganic ion exchanger resins have been suggested for the recovery from acidic wastes such as the HLW, stripping has been problematic [11]. Solvent extraction methods based on the use of exotic reagents such as chlorinated cobalt dicarbolide (CCD), crown ethers and calix-crowns have also shown promise [12–16]. Out of these, calix-crown based extractants have been

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*Corresponding author.

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particularly promising due to their high extraction efficiencies and high separation factors with respect to elements present in the wastes, especially, sodium [16]. Calix-crown-6 ligands such as BOBCalixC6 (calix[4]-arene-bis(*tert*-octylbenzo-crown-6) have been employed for the recovery of Cs from alkaline wastes such as those encountered at the Savannah River site while the calix[4]-bis-2,3-naphtho-crown-6 (CNC) has been found promising for Cs recovery from acidic wastes [17,18]. Exceptionally high extraction efficiency for Cs was attributed to pi-interaction with four benzene units of the calixarenes [19,20]. Though there are reports on the use of BOBCalixC6 for Cs recovery from acidic wastes, a detailed investigation has suggested chemical degradation of the reagent on prolonged use [21]. On the other hand, CNC has been found to be stable to chemical degradation in acidic medium even after keeping in contact for 100 d [22].

We have developed a solvent containing CNC in a mixture of nitrobenzene and toluene (1:1 volume ratio) for selective and effective extraction of Cs from simulated HLW [22]. Batch extraction studies have indicated quantitative extraction of Cs from SHLW in five stages while three stages were required for quantitative stripping. Recycling studies under laboratory conditions using the stripped organic phase have shown promise with SHLW feeds. However, it is of interest to understand the extraction behaviour and reusability of this reagent when applied to actual HLW.

The present study was taken up to investigate the separation efficiency and reusability of the developed solvent using actual HLW. The first part of the study includes the use of the CNC based solvent for Cs recovery from a 100 times dilute actual HLW. The second part includes recovery of Cs from actual undiluted HLW.

2. Experimental

2.1. 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 Chemicals were used without further purifications. All the other reagents used were of analytical reagent grade.

2.2. Methods

Solvent extraction experiments were performed by equilibrating equal volumes of organic and the diluted or the actual HLW in stopperred glass tubes inside a hot cell under ambient conditions. Though an equilibration time of 1 h was used in our studies with SHLW [22], equilibration of about 30 min and 10 min were done for studies carried out at glove box (100 times diluted HLW) and hot cell (undiluted HLW), respectively. The radioactivity measurements of the fission products were carried out using HPGe detector coupled to a multi-channel analyzer. The distribution ratio value was defined as the ratio of the activity per unit volume in the organic phase to that in the aqueous phase. Errors in the measurements were due to sampling and counting errors and were limited to ±5%. The recycling studies were carried out by allowing the solvent mixture in contact with the actual HLW for the required number of days followed by separating the organic phase and carrying out subsequent extraction studies using the barren solvent mixture after contacting with de-ionized water (complete stripping of Cs was ensured by successive contacts with de-ionized water).

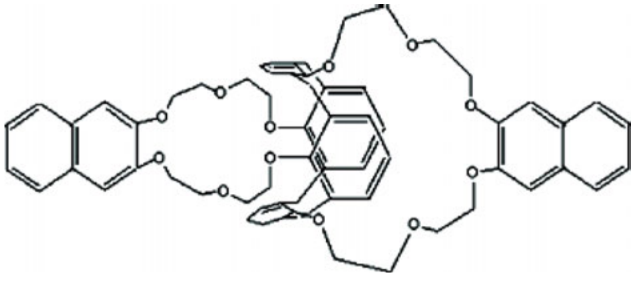

Fig. 1. Structural formula of calix-[4]-bis(2,3-naptho)-18-crown-6 (CNC)

3. Results and discussion

3.1. Studies with diluted HLW

The extraction was found to be driven by the ion pair mechanism as given by the following extraction equilibrium:

$$\mathrm{Cs^+}_{(\mathrm{aq.})} + \mathrm{NO_3^-}_{(\mathrm{aq.})} + n\mathrm{L}_{(\mathrm{org.})} \rightleftharpoons \left(\mathrm{Cs.nL}\right)^+ \cdot \mathrm{NO}^-_{3(\mathrm{org.})} \quad (1)$$

where L represent the calix-crown ligand and the subscripts ‘(aq)’ and ‘(org)’ represent the species in the organic and aqueous phases, respectively [20]. Usually, the value of n is 1 under tracer concentrations [22,23]. It is expected that with higher concentration of Cs, both the crown-6 moieties may be complexed by $\mathrm{Cs^+}$ ion which may result in a lower value of n. The composition of the undiluted HLW is given in Table 1. The concentration of the fission products is given in Ci/L while that of U and Pu is given in g/L. Activity due to radio-cesium is about 6 Ci/L out of which, ^{137}Cs account for about 5.3 Ci/L. In order to optimize the extraction and stripping conditions, experiments were carried out to recover radio-cesium from 100 times diluted actual HLW. The

Table 1
Composition of the high level waste used in the study involving diluted HLW

Constituents	Concentration	Fission products	Concentration (Ci/L)
[HNO$_3$]	3.15 M	^{144}Ce	22.3
[U]	10 g/L	^{125}Sb	0.285
[Pu]	1.97 mg/L	^{106}Ru	6.5
Gross β	125 Ci/L	^{137}Cs	10.02
Gross α	<0.1 Ci/L	^{95}Zr	—
T.S.	19.35 g/L	^{95}Nb	0.018

objective was to see the decontamination from other radioactive fission products present in the HLW.

3.1.1. Extraction studies

The initial feed activity as estimated by using an HPGe counter is given in Table 2. The acidity of the diluted feed solution was adjusted to 2.0 M and the batch extraction studies were carried out in a glove box at organic to aqueous phase ratio of 1:1. The stage wise batch extraction data is also presented in Table 2. In the Table, the cps of the organic and the aqueous phases are given after each contact. It is clear that in 3 contacts near quantitative extraction of Cs is possible with almost no contamination from other fission products. Though some amount of ^{106}Ru activity was detected in the organic phases, the raffinate of 3rd contact indicated almost entire amount of ^{106}Ru as observed in the feed suggesting no contamination from the radionuclide. The extraction data in terms of Ci/L is presented in Table 3 where the dilution factor is taken into account. The extraction data indicated >99.9 % extraction in four stages while the raffinate (A4) indicates that about 0.6% Cs is not recovered.

3.1.2. Stripping studies

Stripping of the organic extract containing both ^{137}Cs and ^{134}Cs was carried out by contacting with equal volumes of distilled water. The organic extracts from the four batch experiments were mixed to make a composite extract and its composition is given in Table 4. Negligible acid uptake in the extraction step ensured near quantitative stripping in only two stages. The stripping data are also presented in Table 4. As shown in the Table, 2.46 Ci/L out of 2.55 Ci/L or about 96.3% stripping was observed in the first contact and a further 3.3% was achieved in the second contact, making a cumulative stripping of 99.6%. The lean organic was counted to yield 0.003 Ci/L or about 0.1% of the activity left over suggesting that two stages were sufficient for the quantitative stripping of radio-cesium from the extract. The results also showed negligible contamination due to ^{106}Ru activity.

Table 2
Feed = 100 times diluted HLW in 2.0 M HNO$_3$, Phase ratio = 1:1, Volume = 2 mL, Contact time: 1 h, Extractant = 2.5×10^{-3} M CNC in 1:1 nitrobenzene and toluene mixture

Radio-nuclides	Counts per sec (cps) as detected by HPGe detector after the number of contacts given in bracket						
	Feed	Org (I)	Aq (I)	Org (II)	Aq (II)	Org (III)	Aq (III)
^{144}Ce	876	UDL	873	UDL	878	UDL	879
^{125}Sb	11.0	UDL	10.2	UDL	10.0	UDL	11.0
^{106}Ru	139	1.11	136	0.543	138	0.245	139
^{144}Pr	19.0	UDL	18.1	UDL	18.5	UDL	18.3
^{137}Cs	935	717	214	163	58.9	44.2	13.1
^{134}Cs	76.3	57.7	17.2	12.8	3.88	2.78	0.897

Note: 50 µl samples were used for analysis by HPGe detector.

Table 3
Extraction data presented in Ci/L after taking into consideration the dilution factor

Radio-nuclides	Feed (Ci/L)	O$_1$ (Ci/L)	A$_1$ (Ci/L)	O$_2$ (Ci/L)	A$_2$ (Ci/L)	O$_3$ (Ci/L)	A$_3$ (Ci/L)	O$_4$ (Ci/L)	Raffinate (A$_4$) (Ci/L)
^{144}Ce	22.3	BDL	22.3	BDL	22.3	BDL	22.3	BDL	22.3
^{125}Sb	0.285	BDL	0.28	BDL	0.27	BDL	0.275	BDL	0.27
^{106}Ru	6.50	0.029	6.46	0.028	6.44	0.031	6.42	0.031	6.36
^{137}Cs	10.02	7.44	2.47	1.94	0.63	0.46	0.18	0.18	0.066
^{95}Zr	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
^{95}Nb	0.018	BDL	0.017	BDL	0.017	BDL	0.016	BDL	0.018

Table 4
Composite organic extract emanating from the four co-current batch extraction experiments was taken for stripping studies. Strippant: Distilled water. Phase ratio: 1:1. Contact time: 30 min

Radio-nuclides	Composite Org. (Ci/L)	O_1 (Ci/L)	A_1 (Ci/L)	O_2 (Ci/L)	A_2 (Ci/L)	Lean Org (Ci/L)
^{137}Cs	2.554	0.073	2.46	0.003	0.084	0.003
^{106}Ru	0.031	0.028	BDL	0.026	BDL	0.026

3.2. Extraction studies with undiluted HLW

As in the solvent extraction studies reported using simulated high level waste (SHLW) and the studies on the recovery of radio-cesium from 100 times diluted HLW (*vide supra*) the subsequent studies using undiluted HLW involved 2.5×10^{-3} M CNC in 50% toluene +50% nitrobenzene as the solvent [20]. This solvent yielded D_{Cs} values of 2.5 and 8.3 for SHLW and 3 M HNO_3, respectively and was considered suitable for the recovery studies using actual HLW [22]. The composition of the HLW used in the present work is given in Table 5.

Table 5
Composition of the actual high level waste used in the present work. Slight variation in the composition as compared to that given in Table 1 is due to difference in the batches

Constituents	Concentration
[HNO_3], M	3.03
[U], g/L	10.70
[Pu], mg/L	1.93
Gross β, Ci/L	122.19
Gross γ, Ci/L	39.44
Fission product nuclides	
^{144}Ce, Ci/L	26.44
^{106}Ru, Ci/L	8.96
^{137}Cs, Ci/L	5.30
^{95}Zr, mCi/L	36
^{95}Nb, mCi/L	56

3.2.1. Extraction studies

The distribution data using the solvent mentioned above and the actual HLW feed are presented in Table 6. As indicated, the selective separation of Cs is very clearly seen and >99% extraction was possible in four contacts. In view of hot cell operations involving high radiation field, contact time was limited to 10 min. However, near quantitative extraction was possible due to favourable kinetics of extraction, and no significant extraction of other radionuclides was observed even after the four extraction steps. This was encouraging as both the extraction and separation efficiencies were satisfactory (Table 6).

3.2.2. Stripping studies

The stripping of the extracted Cs activity was carried out subsequently using distilled water as the strippant in a manner similar to mentioned above (under 100 time diluted HLW) with the exception that the contact time was limited to 10 min. The ^{137}Cs loaded organic phase from all the four contacts were collected together and a composite extract was prepared for the stripping experiment in a manner mentioned above. Analysis of the composite organic phase was carried out for U, Pu and was found to be <5 mg/L and <0.1 mg/L, respectively. ^{106}Ru was not detected in the composite organic phase. The stripping data is presented in Table 7. As indicated in the table, almost entire amount of ^{137}Cs was stripped in two contacts.

Table 6
Extraction data with actual HLW. Phase ratio = 1:1, Volume = 2 mL, Contact time: 10 min. Extractant = 2.5×10^{-3} M CNC in 1:1 nitrobenzene and toluene mixture

Radio-nuclides	O_1 (Ci/L)	O_2 (Ci/L)	O_3 (Ci/L)	O_4 (Ci/L)	Raffinate (Ci/L)
^{144}Ce	BDL	BDL	BDL	BDL	26.54
^{106}Ru	BDL	BDL	BDL	BDL	8.99
^{137}Cs	2.95	1.37	0.74	0.20	0.053l
^{95}Zr	BDL	BDL	BDL	BDL	0.034
^{95}Nb	BDL	BDL	BDL	BDL	0.058

Table 7
Stripping studies using the composite organic extract as indicated in Table 6. Marginally, lower than expected activity level is due to dilution errors. Strippant: Distilled water, Phase ratio: O/A = 1, Contact time: 10 min

Radio-nuclide	Composite Org. (Ci/L)	O_1 (Ci/L)	A_1 (Ci/L)	O_2 (Ci/L)	A_2 (Ci/L)
^{137}Cs	1.25	0.081	1.13	0.006	0.155

3.3. Reusability studies

The reusability of the solvent was carried out in two ways. Firstly, by carrying out the extraction and stripping studies with the regenerated solvent after the first set of extraction experiments (data given in Table 8). Secondly, the solvent was kept in contact with the HLW for 10 d with intermittent mixing. The organic phase was subsequently regenerated and was used for fresh extraction and stripping studies. The extraction data using the regenerated solvent (just after a single cycle of 4 extractions and 2 stripping stages) for a subsequent extraction cycle are presented in Table 8. The D_{Cs} value was 1.25 for the regenerated solvent after one day in contact and one cycle of extraction and stripping as against 1.26 reported for the fresh solvent. As seen from the Tables above, the D_{Cs} values increased in the subsequent stages of extraction. On the other hand, the D_{Cs} value decreased significantly to 0.96 when the solvent was regenerated after keeping in contact with the HLW for 10 d. This is attributed to the radiolytic degradation of the solvent. The stripping data was, however, were satisfactory as quantitative stripping was possible in two cycles in each case. Moreover, as seen in Table 8, the selectivity of extraction was not lost. These results suggest that the solvent system developed for the extraction of radio-cesium from high level waste works efficiently and can be deployed for the recovery of Cs-137.

4. Conclusions

The extraction / separation behaviour of radio-cesium from the actual HLW using the calix-crown ligand CNC appear promising. The extraction and stripping efficiencies were satisfactory as quantitative extraction and stripping were achieved in 4 and 2 stages only. However, the extraction efficiency decreased significantly after keeping in contact with HLW for 10 d. This would increase the number of stages and may require replenishment of the solvent after prolonged use.

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Table 8
Extraction studies using recycled solvent using actual HLW (composition in Table 5). Phase ratio = 1:1, Volume = 2 mL, Contact time: 10 min Extractant = 2.5 × 10^{-3} M CNC in 1:1 nitrobenzene and toluene mixture

Radio-nuclides	Studies with lean organic phase after one set of experiments[a]		Studies with lean organic phase after second set of experiments[b]	
	Organic phase from first contact (Ci/L)	Raffinate from first contact (Ci/L)	Organic phase from first contact (Ci/L)	Raffinate from first contact (Ci/L)
^{144}Ce	BDL	26.50	BDL	24.36
^{106}Ru	BDL	8.92	BDL	9.14
^{137}Cs	2.94	2.36	2.55	2.70
^{95}Zr	BDL	0.038	BDL	0.048
^{95}Nb	BDL	0.055	BDL	0.065

[a] The solvent was exposed to the radiation field in the hot cell for 1 d.

[b] The solvent was exposed to the radiation field in the hot cell for 10 d.

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