



Assessing the feasibility study of highly efficient and selective co-sequestration process for cesium and strontium utilizing calix-crown and crown-ether based combined solvent systems

Kankan Patra¹ · Arijit Sengupta^{2,3} · R. K. Mishra⁴ · V. K. Mittal¹ · T. P. Valsala¹ · C. P. Kaushik^{3,4}

Received: 18 November 2021 / Accepted: 15 January 2022 / Published online: 3 February 2022
© Akadémiai Kiadó, Budapest, Hungary 2022

Abstract

Efficient and selective extraction of ^{137}Cs and ^{90}Sr from high level liquid waste (HLLW) is of utmost importance in the back end nuclear fuel cycle to minimize long term radiological surveillance of HLLW due to the long half-life of ^{137}Cs ($t_{1/2} = 30$ years) and ^{90}Sr ($t_{1/2} = 29$ years). 1,3-di-octyloxycalix[4]arene-crown-6 (CC6) and dicyclohexano-18-crown-6 [DCH18CH] are suggested as potential candidates for individual extraction of ^{137}Cs and ^{90}Sr , respectively. An attempt was made for simultaneous separation of ^{137}Cs and ^{90}Sr with enhanced distribution ratio using combined solvent system having suitable combination of CC6 and DCH18CH in *n*-octanol from simulated HLLW. Using the combined solvent system in 100% *n*-octanol, ^{137}Cs and ^{90}Sr were found to have significantly high extraction efficiency ($D_{\text{Cs}} = 18.8$ and $D_{\text{Sr}} = 3.1$) with 5 min extraction time. No interference from mono and divalent cations (Na^+ and Mg^{2+}) was observed. The extraction processes were found to be spontaneous.

Keywords Crown ether · Co-extraction · Metal–ligand stoichiometry · Interference

Introduction

A considerable amount of the radioactivity in HLLW generated from spent nuclear fuel recycling comes from the fission products ^{137}Cs and ^{90}Sr [1]. Collectively, ^{137}Cs and ^{90}Sr account for over 99% of the relative radioactivity of dissolved nuclear fuel solutions; once the actinides have been separated. Removal of ^{137}Cs ($t_{1/2} = 30$ years) and ^{90}Sr ($t_{1/2} = 29$ years) would increase the safe handling of liquid waste and minimize the storage and disposal costs of these radioactive components [2–10]. Effective separation of ^{137}Cs and ^{90}Sr from spent nuclear fuel is also a vital issue

in nuclear industry due to short-term heat loading in a geological repository. ^{137}Cs has a potential to migrate in soil particles along with surface waters [11]. ^{137}Cs has imposed serious public-health related problem; due to transportability through the atmosphere and high solubility. ^{137}Cs has huge bioavailability, which is very similar to potassium (K^+) ions and ^{137}Cs easily assimilated through aquatic organisms and terrestrial [12]. Consequently, ^{137}Cs can simply enter into human body and stay there for long time, resulting to potential irradiation of human living tissue. Thus, effective removal of ^{137}Cs needs to be investigated with very urgency. ^{90}Sr is one of the most important anthropogenic radionuclides present in marine environment, mainly due to accidents and operation of nuclear facilities [13]. At the same time, ^{90}Sr is difficult to separate using conventional methods from the aqueous medium due to its lower chemical potential i.e. charge to size ratio [14].

It is important to find out a suitable system, having higher selectivity for targeted ions. Cs was selectively recognized by calix[4]arene crown-6 moieties [15–20], and Sr was effectively separated using supramolecular compounds, crown ether derivatives, like 4,4'(5')-di-tert-butyl-dicyclohexano-18-crown 6 (DT) and DCH18C6 [21–25]. Several separation processes like cesium extraction (CSEX) [26],

✉ Arijit Sengupta
arijita@barc.gov.in

¹ Nuclear Recycle Board, Bhabha Atomic Research Centre, Tarapur 401504, India

² Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

³ Homi Bhabha National Institute, Anushaktinagar, Mumbai 400 094, India

⁴ Nuclear Recycle Group, Bhabha Atomic Research Centre, Mumbai 400 085, India

caustic-side solvent extraction process (CSSX) [27], and strontium extraction (SREX) [28] have been reported in literature for individual separation of Cs and Sr. In this regards, Rais et al. reported the effective separation of Cs and Sr using 25,27-bis(1-octyloxy)calix[4]arene-26,28-crown-6 and DCH18C6 ligands respectively [29]. Recently, different solvent extraction based method were studied to remove Sr [28, 30–32] and Cs [26, 33–39]. Though, majority of literature reported the separation of Sr and Cs individually; the separation processes for Cs and Sr can be made easier by combining both the extraction processes together. The first literature report on this approach was using polyethylene glycol and chlorinated cobalt dicarbollide in a phenyltrifluoromethyl sulfone diluent [40]. Cs and Sr were also reported to be separated simultaneously using calix[4]arenebis-(tert-octylbenzo-crown-6) (BOBCalixC6) and 4',4',(5')-di-(*t*-butyldicyclohexano)-18-crown-6 (DtBu18C6) mixed with a phase modifier, 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*s*-butylphenoxy)-2-propanol (Cs-7SB) [41]. DCH18C6 in *n*-octanol medium for separation of Sr and 25,27-bis(isopropoxy) calix[4]-26,28-crown-6 (iPr-C[4]C-6) in *n*-octanol medium for separation of Cs from HLLW were also reported [42, 43].

The aim of present study is to separate ^{137}Cs and ^{90}Sr simultaneously from HLLW. Based on earlier reports, DCH18C6 for ^{90}Sr [21–25] and CC6 for ^{137}Cs [15–20] in *n*-octanol medium were selected for the present investigation. A novel combined solvent system using a mixture of 1,3-dioctyloxy calix [4]arene-crown-6 (CC6) and dicyclohexano-18-crown 6 [DCH18CH] in *n*-octanol was successfully demonstrated for simultaneous extraction of ^{137}Cs and ^{90}Sr from simulated HLLW. The potential and feasibility of the solvent system were evaluated. The results clarified that, the simultaneous ^{137}Cs and ^{90}Sr removal process was rapid and reached saturation almost instantly. The effects of different promising diluents were examined on the extraction behavior of ^{137}Cs and ^{90}Sr . The effect of competitive ions, monovalent cation like sodium (Na^+) and di-valent cation magnesium (Mg^{2+}) were studied. This solvent system revealed to be promising for the simultaneous removal of ^{137}Cs and ^{90}Sr due to its fast kinetics, selectivity, considerable volume reduction capacity and cost benefit as both the radionuclide can be removed in a single step and represent an effective scheme to develop a systematic process flow sheet for removal of ^{137}Cs and ^{90}Sr from simulated HLLW solution.

Experimental

Materials: chemicals, isotopes and solutions

CC6 and DCH18CH (Fig. 1, 2) were purchased from S. D. Fine Company, India. The radiotracer, ^{137}Cs and $^{85/89}\text{Sr}$

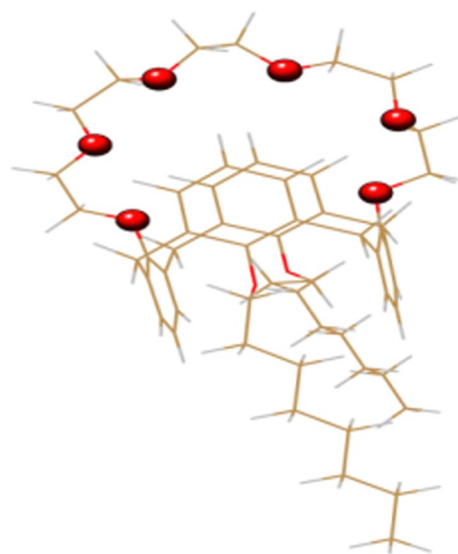


Fig. 1 1, 3-dioctyloxy calix[4]arene-crown-6 (CC6). (Color code: O = Red; H = Light grey C = Tan)

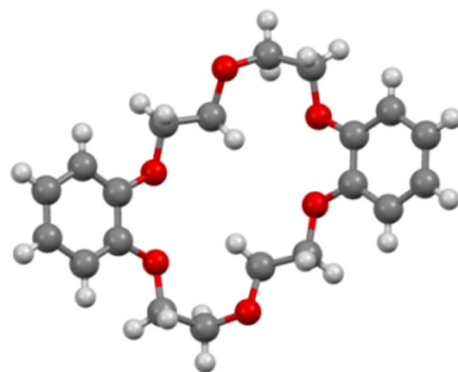


Fig. 2 Dicyclohexano-18-crown-6 (DCH18C6) In the structure, O = Red; C = Tan; H = Light grey)

used in the present study, were purchased from Board of Radiation and Isotope Technology (BRIT), India. The solvent 100% *n*-octanol was procured from S.D. Fine company, India. Double distilled water and Supra-pure HNO_3 were used throughout the investigation. The composition of simulated HLLW given in Table 1 represents the HLLW obtained from 3 years cooled Pressurized Heavy Water Reactor (PHWR) spent fuel reprocessing. All the experiments were conducted with an appropriate quantity of ^{137}Cs and $^{85/89}\text{Sr}$ radiotracer spiked into HNO_3 medium. During the experiment, radiation monitoring instruments and proper personal protective equipment (PPE) were used.

Table 1 Composition of simulated HLLW

Sr. No	Property	Value
1	Molarity	3–3.5 Acidic
2	<i>Specific Activity</i>	
2.1	Gross α	17.05 Ci/lit
2.2	Gross β	75.40 mCi/lit
3	<i>Principal Isotopes Identified</i>	
3.1	Cs ¹³⁷	7.082 Ci/lit
3.2	Sr ⁹⁰	4.587 Ci/lit
3.3	Cs ¹³⁴	56.00 mCi/lit
3.4	Zr ⁹⁵	27.60 mCi/lit
3.5	Eu ¹⁵⁴	17.89 mCi/lit
3.6	Sb ¹²⁵	16.70 mCi/lit
3.7	Ru ¹⁰⁶	9.00 mCi/lit
3.8	Am ²⁴¹	71.00 mCi/lit
3.9	Pu ²³⁹	3.80 mCi/lit
4.0	<i>Elemental Analysis (gm/litre)</i>	
	U 5.2	La 0.12
	Na 4.5	Ce 0.04
	Fe 1.65	Pr 0.06
	Cr 0.17	Nd 0.08
	Ni 0.20	Y 0.04
	Mn 0.48	Al 0.17
	K 0.20	Cs 0.244
	Sr 0.04	Sm 0.057
	Mo 0.13	Zr 0.004
	Ru 0.04	Se 0.051
	Pd 0.03	Te 0.024
	Ba 0.25	

Distribution ratio and radiometry

To determine the distribution ratio (D_M) of metal ions, 5 mL of organic phase constituting CC6 and DCH18CH in *n*-octanol and 5 mL of aqueous phase having ¹³⁷Cs and ^{85/89}Sr radio tracer was equilibrated for 20 min. After equilibration the complete phase separation was achieved by centrifuging the above biphasic system for 5 min. For understanding the dependency of distribution ratio of cesium and strontium ion on varying solvent composition having different diluent polarity; the diluent compositions were varied with respect to relative composition of *n*-dodecane and *iso*-deacyl alcohol, while other parameters were kept constant. D_M of the respective metal ions were determined in terms of the ratio of the analytical concentration of metal ions in organic phase to aqueous phase. All extraction experiments were conducted at 25 ± 1 °C in a thermostatic water bath procured from Lab India, Mumbai, India. ¹³⁷Cs (604.7 keV) and ^{85/89}Sr (514 keV) activity were counted using gamma counting system having intrinsic HPGe detector associated with 4 K MCA.

Concentration of nitric acid in aqueous and organic phases were estimated by potentiometric titration (0.1 M NaOH), using a Metrohm 905 Titrando device. It was confirmed that, the mass balance has error with in $\pm 5\%$ for all the techniques.

The dependency of distribution ratio of cesium and strontium ion on varying solvent composition as the diluents phase was carried out using the experimental parameters mentioned below. Organic phase: 0.03 M CC6 and 0.1 M DCH18C6 in variable solvent compositions; aqueous phase: spiked with ¹³⁷Cs and ^{85/89}Sr radio tracer in 5 M HNO₃. 5 mL of organic and aqueous phase were taken for the experiment. Contact time: 30 min. Triplicate experiments were carried out and the error is within the limit of $\pm 5\%$. The temperature of the extraction was kept 30 °C.

Determination of D_{Cs} and D_{Sr} values as a function of contact time was performed using the experimental parameters as stated below. Organic Phase: 0.03 M CC6 and 0.1 M DCH18C6 in 100% *n*-octanol; aqueous phase: spiked with ¹³⁷Cs and ^{85/89}Sr metal in 5 M HNO₃. Equal volume (5 mL) of organic phase and aqueous phase was taken for the study. The temperature of the experiment was kept 30 °C. Triplicate experiments were carried out and error is within the limit of $\pm 5\%$. Others parameters remained constants unless otherwise mentioned.

Determination of D_{Cs} values as a function of variable concentration of CC6 was carried out using the parameters mentioned herewith. Organic Phase: (0.003–0.03) M CC6 in *n*-octanol; aqueous phase: spiked with ¹³⁷Cs metal ions in 5 M HNO₃. Experiment was carried out at room temp. Triplicate experiments were carried out and error limit is within $\pm 5\%$.

Determination of D_{Sr} values as a function of varying concentration of DCH18C6 were done using the experimental parameters described below. Organic Phase (0.01–0.3) M DCH18C6 in *n*-octanol; aqueous phase: spiked with ^{85/89}Sr metal ions in 5 M HNO₃. Extraction study was conducted at 25 ± 1 °C. Triplicate experiments were carried out and error limit is within $\pm 5\%$.

Extraction dependency of cesium and strontium on the varying acid concentration (HNO₃, HCl, HClO₄) were performed as follows: Organic phase: 0.015 M CC6 and 0.1 M DCH18C6 in *n*-octanol; Aqueous phase: varying concentration of acid (HNO₃, HCl, HClO₄) spiked with ¹³⁷Cs and ^{85/89}Sr metal ions. Experiment was carried out at 25 ± 1 °C. Triplicate experiments were carried out and the error limit is $\pm 5\%$.

Extraction dependency of D_{Cs} and D_{Sr} on the interfering metal (Na⁺, Mg²⁺) ion concentrations have been investigated using the following procedure. Organic phase: 0.015 M CC6 and 0.1 M DCH18C6 in 100% *n*-octanol; Aqueous phase: varying concentration (0.1–3.0) M of metal ions (Na⁺ and Mg²⁺) spiked with ¹³⁷Cs and ^{85/89}Sr metal ions in 5 M HNO₃.

Experiment temp was kept at 25 ± 1 °C. Triplicate experiments were carried out and the error limit is $\pm 5\%$.

Results and discussion

Effect of diluents phase composition on D_{Cs} and D_{Sr}

Along with metal binding nature of the ligands/extractant, polarity of the solvent phase also has an important role in the distribution ratio of the radionuclides from an aqueous phase standpoint. In view of this, different solvent systems with varying polarity were studied to determine the polarity effect on extraction efficiency of D_{Cs} and D_{Sr} . Appropriate choice of solvent system was carried out for maximum extraction efficiency based on previous report [45]. D_{Cs} and D_{Sr} values were determined in 1:1 mixture of *iso*-decyl alcohol and *n*-dodecane with 0.03 M CC6 and 0.1 M DCH18C6, individually. The distribution value obtained for cesium ($D_{Cs} = 7.4$) was found to be similar compared to the results reported by Sharma et al. (2014) [46]. By increasing solvent polarity (i.e. increasing the concentration *iso*-decyl alcohol), extraction efficiency for Cs (D_{Cs}) and Sr (D_{Sr}) were found to increase (Fig. 3). This experimental result motivated us to employ highly polar *n*-octanol medium as the diluent in the present investigation. The choice of diluents can also be justified considering its environmental friendly nature. Very good D_{Cs} (~ 21.8) value along with moderate D_{Sr} (~ 2.8) (Fig. 3) values were achieved by using 0.03 M CC6 and 0.1 M

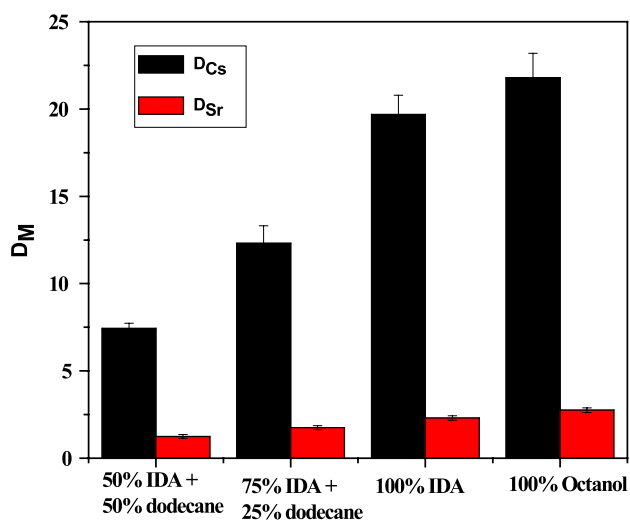


Fig. 3 Dependency of distribution ratio of cesium and strontium ion on varying solvent composition as the diluents phase. Organic phase: 0.03 M CC6 and 0.1 M DCH18C6 in variable solvent compositions; aqueous phase: spiked with ^{137}Cs and $^{85/89}\text{Sr}$ radio tracer in 5 M HNO_3 . Contact time: 30 min. (Triplicate experiments were carried out and the error is within the limit of $\pm 5\%$)

DCH18C6 in 100% *n*-octanol. Hence, further extraction experiments were carried out using 100% *n*-octanol.

Effect of contact time on D_{Cs} and D_{Sr} extraction

Extraction kinetics is one of the most vital properties of the solvent systems for presenting an efficient metal ion extraction process. In majority cases, the evaluation of extraction rate is based on determining equilibrium time for the metal ions separation. However, several ligands (calix- crown/ crown-ether) showed their own equilibrium times; due to the different inherent physical and chemical characteristics, which consists of solvent polarity and binding nature based on the metal ligand complexation. Therefore, the optimum equilibration time required for the maximum extraction of Cs^+ and Sr^{2+} from the acidic aqueous phase with 0.03 M CC6 and 0.1 M DCH18C6 in *n*-octanol was studied, individually. The extraction profiles for Cs^+ and Sr^{2+} were established by varying equilibration time in the range of 2 to 30 min (Fig. 4). The extraction efficiency of Cs^+ and Sr^{2+} increased with equilibration time from 2 to 5 min. With further increase in equilibration time, there was no change in D_{Cs} and D_{Sr} values. Therefore, a contact time of 5 min was chosen for further extraction procedures.

Understanding the speciation and thermodynamics

To determine the optimum concentration of CC6 and DCH18C6 for maximum extraction of Cs and Sr;

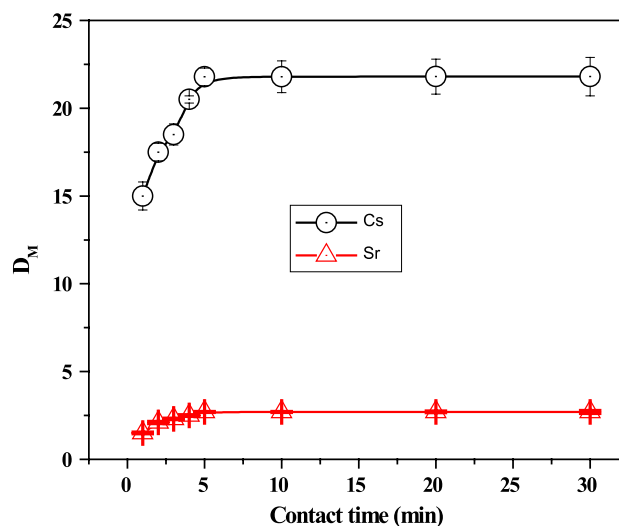
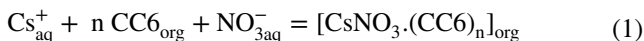


Fig. 4 Determination of D_{Cs} and D_{Sr} values as a function of contact time, Organic Phase 0.03 M CC6 and 0.1 M DCH18C6 in 100% *n*-octanol; aqueous phase: spiked with ^{137}Cs and $^{85/89}\text{Sr}$ metal in 5 M HNO_3 . (Triplicate experiments were carried out and error is within the limit of $\pm 5\%$)

experiments were carried out using CC6 and DCH18C6 in *n*-octanol.

The complexation between Cs^+ and CC6 can be expressed in presence of nitrate ions using the following equation as described below. To understand the nature of complexation; the metal–ligand stoichiometry was determined.



The equilibrium constants or the extraction constant of equation 0.1 can be expressed as

$$k_{\text{ex}} = \frac{[[\text{CsNO}_3 \cdot (\text{CC6})_n]_{\text{org}}]}{[\text{Cs}_{\text{aq}}^+]} \frac{1}{[\text{CC6}_{\text{org}}]^n} \frac{1}{[\text{NO}_{3\text{aq}}^-]} \quad (2)$$

At constant HNO_3 concentration and temperature, concentration of nitrate ion is constant in aqueous phase and the first term is nothing but the analytical concentration of Cs^+ ion in organic phase divided by that in aqueous phase, i.e. D_{Cs} . Then Eq. (2) can be simplified as

$$k'_{\text{ex}} = \frac{D_{\text{Cs}}}{[\text{CC6}_{\text{org}}]^n} \quad (3)$$

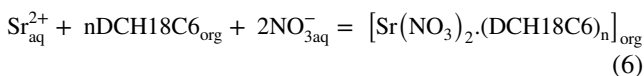
where; k'_{ex} is known as conditional extraction constant. The 'n' is the number of ligand molecules attached to Cs^+ ion. Now applying logarithm on both sides of the equation,

$$\log D_{\text{Cs}} = \log k'_{\text{ex}} + n \log [\text{CC6}_{\text{org}}] \quad (4)$$

The change in Gibb's free energy due to the complexation and subsequent mass transfer can also be calculated from the equilibrium constant using the following equation

$$\Delta G = -2.303 RT \log k'_{\text{ex}} \quad (5)$$

A plot of $\log D_{\text{Cs}}$ versus $\log [\text{CC6}_{\text{org}}]$ (Fig. 5) was found to be a straight line having a slope of 0.998 ± 0.014 conforming the formation of 1:1 metal–ligand complex. The change in Gibb's free energy was calculated as -16.42 kJ/mole. Cs^+ ion was also reported to form 1:1 stoichiometric complex with similar type of ligands [11, 14]. The negative ΔG value for the extraction revealed that, the process is thermodynamically favourable i.e. spontaneous in nature. Similar attempt was also made to understand the mechanism of the complexation of Sr extraction using DCH18C6 in *n*-octanol medium. The equilibrium constants can be expressed as



From Eq. 6 can be expressed as

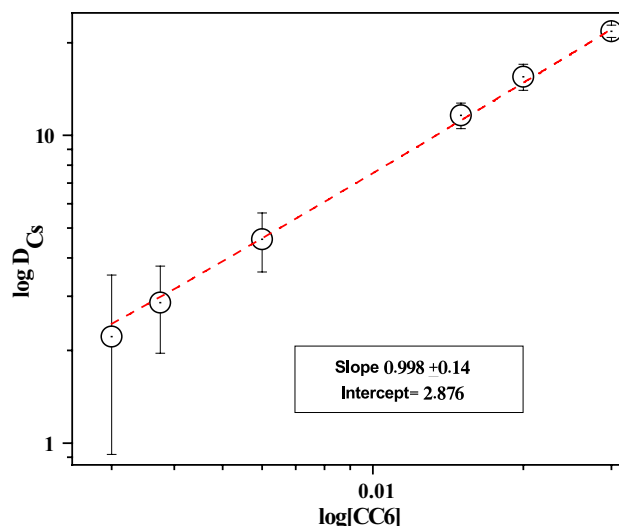
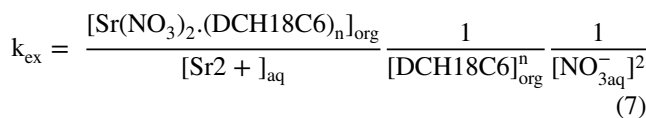


Fig. 5 Determination of D_{Cs} values as a function of variable concentration of CC6, Organic Phase (0.003–0.03) M CC6 in *n*-octanol; aqueous phase: spiked with ^{137}Cs metal ions in 5 M HNO_3 . (TriPLICATE experiments were carried out and error limit is within $\pm 5\%$)



At a particular nitric acid concentration, aqueous phase nitrate ion concentration is constant and the above equation can be simplified as follows

$$k'_{\text{ex}} = \frac{D_{\text{Sr}}}{[\text{DCH18C6}_{\text{org}}]^n} \quad (8)$$

where, k'_{ex} is known as conditional extraction constant. Now using logarithm in both side of Eq. 8, we can be get the Eq. 9

$$\log D_{\text{Sr}} = \log k'_{\text{ex}} + n \log [\text{DCH18C6}_{\text{org}}] \quad (9)$$

$$\Delta G = -2.303 RT \log k'_{\text{ex}} \quad (10)$$

A plot of $\log D_{\text{Sr}}$ versus $\log [\text{DCH18C6}_{\text{org}}]$ (Fig. 6) obtained a straight line having a slope of 0.99 ± 0.002 , revealing the formation of 1:1 metal–ligand complex. Beyond a certain concentration of ligand, the distribution ratio became almost unchanged with increase in ligand concentration as shown in Fig. 6. The change in Gibb's free energy (ΔG) was evaluated as -7.70 kJ/mole. The negative ΔG value revealed the extraction process was spontaneous in nature.

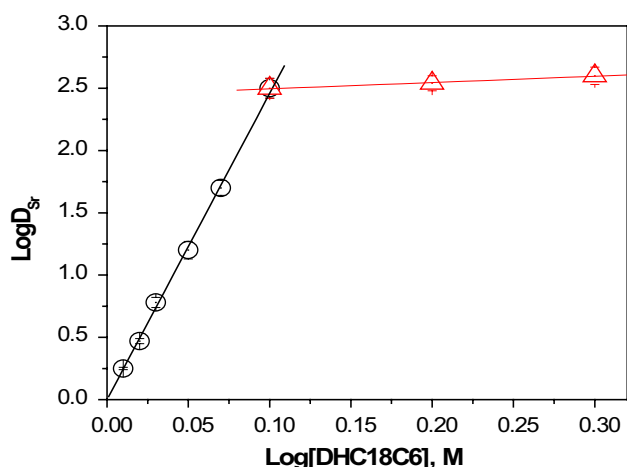


Fig. 6 Determination of D_{Sr} values as a function of varying concentration of DCH18C6, Organic Phase (0.01–0.3) M DCH18C6 in *n*-octanol; aqueous phase: spiked with $^{85/89}Sr$ metal ions in 5 M HNO_3 . (Triplicate experiments were carried out and error limit is within $\pm 5\%$)

Formulation of combined solvent system and simultaneously extraction of Cs^+ and Sr^{2+}

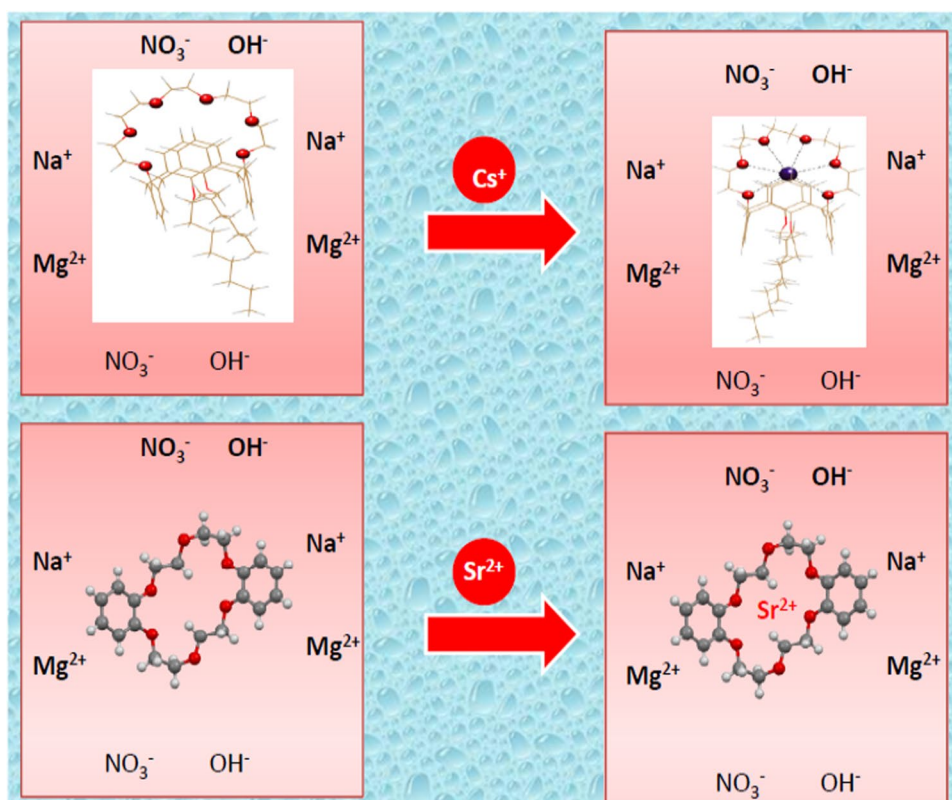
For simultaneous separation of Cs^+ and Sr^{2+} from simulated HLLW, mixed organic solvents (0.015 M CC6 + 0.1 M DCH18C6) were used in 5 M HNO_3 medium. For this

purpose, simulated HLLW was prepared, where $^{85/89}Sr$ and ^{137}Cs radiotracers were spiked. Then mixed organic solvents i.e. 0.015 M CC6 + 0.1 M DCH18C6 were prepared in 100% *n*-octanol medium. To achieve the maximum extraction efficiency, equivalent amount of organic phase (i.e. 0.015 M CC6 + 0.1 M DCH18C6 in 100% *n*-octanol) and aqueous phase (spiked with $^{85/89}Sr$ and ^{137}Cs radiotracers) were equilibrated. After separating the two phases by centrifuging the activity of Cs & Sr was analysed using gamma spectrometry and D_M values for the metal ions were calculated. Significantly high D value of Cs^+ ($D_{Cs} = 18.8$) and Sr^{2+} ($D_{Sr} = 3.1$) were observed. Figure 7 represents the extraction of Cs^+ and Sr^{2+} using 0.015 M CC6 + 0.1 M DCH18C6 in *n*-octanol.

Extraction of D_{Cs} and D_{Sr} in different acids (HNO_3 , HCl , $HClO_4$)

The extraction profiles for Cs^+ and Sr^{2+} were established as a function of different acid concentrations (HNO_3 , HCl , $HClO_4$) using 0.015 M CC6 and 0.1 M DCH18C6 in *n*-octanol [Fig. 8]. The experimental results revealed that, the D_{Cs} and D_{Sr} followed the order $HNO_3 > HClO_4 > HCl$ in the range of 1–6 M acidity, advocating the ‘ion-pair’ mechanism. In case of HCl , the extraction efficiency for Cs^+ and Sr^{2+} were observed to be lower value. This might be attributed to the lower proficiency of $[Cs^+ - Cl^-]$ and $[Sr^{2+} - Cl^-]$ ion-pair formation. This can be explained in terms of comparatively higher hydration energy

Fig. 7 Representation of Cs^+ and Sr^{2+} complexation with combined ligand consisting of CC6 and DCH18C6 for selective extraction of Cs and Sr in the presence of high concentration of Na^+ , Mg^{2+} , OH^- and NO_3^- ions



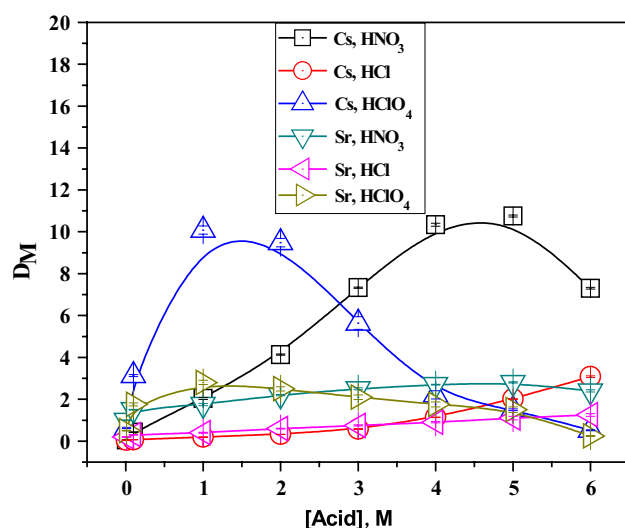


Fig. 8 Extraction dependency of cesium and strontium on the varying acid concentration (HNO₃, HCl, HClO₄). Organic phase: 0.015 M CC6 and 0.1 M DCH18C6 in *n*-octanol; Aqueous phase: varying concentration of acid (HNO₃, HCl, HClO₄) spiked with ¹³⁷Cs and ^{85/89}Sr metal ions (Triplicate experiments were carried out and the error limit is $\pm 5\%$)

of Cl⁻ ion. For HNO₃, with an increase in acid concentration, the D_{Cs} and D_{Sr} values were found to increase gradually, reaching maximum at 5 M HNO₃ with a subsequent marginal reduction. The initial rise might be attributed to the requirement of NO₃⁻ ions in formation of Cs⁺-NO₃⁻ / Sr²⁺-NO₃⁻ ion-pairs. However, beyond 5 M HNO₃, the competition between Cs⁺/Sr²⁺ and H⁺ for ion-pair formation with NO₃⁻ ions played influential role in determining the trend in D values.

Interference study of Na⁺ and Mg²⁺ on distribution ratio of metal ions Cs⁺ and Sr²⁺

Selectivity is a crucial parameter for extraction of particular metal ion as the distribution ratio can be influenced in presence of similar type of metal ions (like mono-valent Na⁺ ions and di-valent Mg²⁺ ions). Thus, it is essential to understand the effect of these ions on the extraction property of Cs⁺ and Sr²⁺. Figure 9 clearly represented the interference of Na⁺ and Mg²⁺ on the extraction of Cs⁺ and Sr²⁺. Experimental data showed that, there was no imperative effect of Na⁺ and Mg²⁺ on the extraction behaviour of Cs⁺ and Sr²⁺. This can be attributed to the size selective complexation of these ligands with metal ions.

Conclusions

A novel combined solvent system comprising of CC6 (0.015 M) and DCH18C6 (0.1 M) dissolved in 100% *n*-octanol was successfully demonstrated as effective materials for efficient separation of Cs and Sr in a single

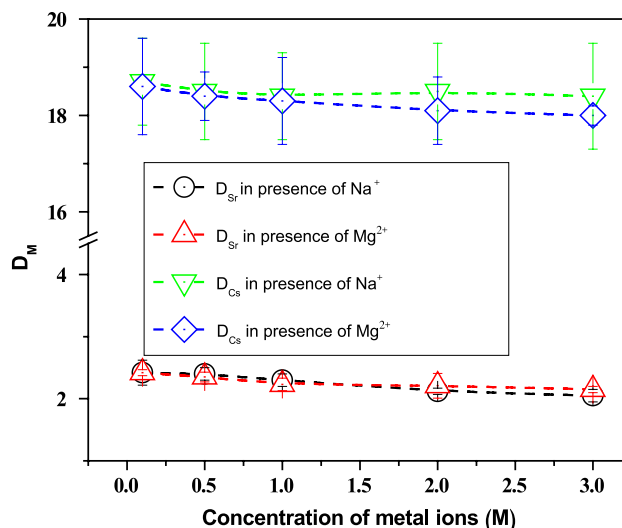


Fig. 9 Extraction dependency of D_{Cs} and D_{Sr} on the interfering metal (Na⁺, Mg²⁺) ion concentrations. Organic phase: 0.015 M CC6 and 0.1 M DCH18C6 in 100% *n*-octanol; Aqueous phase: varying concentration (0.1–3.0) M of metal ions (Na⁺ and Mg²⁺) spiked with ¹³⁷Cs and ^{85/89}Sr metal ions in 5 M HNO₃. (Triplicate experiments were carried out and the error limit is $\pm 5\%$)

step from simulated HLLW with high selectivity and fast kinetics. The highly polar *n*-octanol can effectively be used to boost the distribution ratio of metal ions (D_{Cs} and D_{Sr}) significantly with respect to iso-decyl alcohol and *n*-dodecane. Highly polar *n*-octanol tends to satisfy easily the primary coordination sphere of metal ion (Cs⁺ and Sr²⁺) and thus enhancing efficient mass transfer from aqueous phase to the organic phase. Effect of interfering cations like Na⁺ and Mg²⁺ were studied and no such effect on the extraction of Cs⁺ and Sr²⁺ were observed. The formation of ion-pair complex involving nitrate as counter anion with 1:1 metal–ligand stoichiometry has been confirmed for both the metal ions. High distribution ratio were achieved for Cs and Sr (D_{Cs} = 18.8 and D_{Sr} = 3.1) by using the combined solvent system. This has a potential for Cs and Sr removal in a single step process from radioactive waste management facility. The extraction processes were found to be spontaneous in nature.

Acknowledgements We acknowledge U.Dani, G.M, R & WM, BARC (T), Dr. P.K.Pujari, Director, RC & I Group and Head, RCD, BARC; Dr. R.Acharya, Head, Actinide Spectroscopy Section, RCD, BARC.

References

1. U.S. Patent, 10/808,039, 2004
2. Chao X, Wang J, Chen J (2012) Solvent extraction of strontium and cesium: a review of recent progress. *Solvent Extr Ion Exch* 2012(30):623–650. <https://doi.org/10.1080/07366299.2012.700579>

- Gupta NK, Sengupta A (2017) Understanding the sorption behavior of trivalent lanthanides on amide functionalized multi walled carbon nanotubes. *Hydrometallurgy* 171:8–15
- Kumar P, Sengupta A, Singha Deb AK, Musharraf Ali SK (2017) Poly(amidoamine) dendrimer functionalized carbon nanotube for efficient sorption of trivalent f-elements: a comparison between 1st and 2nd generation. *Chem Selects* 2:975–985
- Gupta NK, Sengupta A (2017) Substituted sulphoxide ligands in piperidinium based ionic liquid: novel solvent systems for the extraction of Pu^{4+} and PuO_2^{2+} . *J Radioanal Nucl Chem* 311(3):1729–1739
- Boda A, Deb AKS, Sengupta A, Sk M, Ali KTS (2017) Elucidation of complexation of tetra and hexavalent actinides towards amide ligand in polar and non-polar diluents: combined experimental and theoretical approach. *Polyhedron* 123:234–242
- Kishor P, Adya VC, Sengupta A, Salvi NA (2017) Understanding the sorption behavior of tetra and hexavalent plutonium on fungus *Rhizopus arrhizus* dead biomass. *J Radioanal Nucl Chem* 311(1):903–912
- Gupta NK, Sengupta A, Boda A, Adya VC, Ali M (2016) Oxidation state selective sorption behavior of plutonium using N, N-dialkylamide functionalized carbon nanotubes: experimental study and DFT calculation. *RSC Adv* 6:78692–78701
- Priya S, Sengupta A, Jayabun SK, Adya VC (2016) Piperidinium based ionic liquid in combination with sulphoxides: highly efficient solvent systems for the extraction of thorium. *Hydrometallurgy* 164:111–117
- Schulz WW, Bray LA (1987) Solvent extraction recovery of byproduct ^{137}Cs and ^{90}Sr from HNO_3 solutions—a technology review and assessment. *Sep Sci Technol* 1987(22):191–214. <https://doi.org/10.1080/01496398708068948>
- Masamichi CHINO, Hiromasa NAKAYAMA, Haruyasu NAGAI, Hiroaki TERADA, Genki KATATA, Hiromi YAMAZAWA (2011) Preliminary estimation of release amounts of ^{131}I and ^{137}Cs accidentally discharged from the Fukushima Daiichi nuclear power plant into the atmosphere. *J Nucl Sci Technol* 2011(48):1129–1134. <https://doi.org/10.1080/18811248.2011.9711799>
- Staunton S, Dumat C, Zsolnay A (2002) Possible role of organic matter in radiocaesium adsorption in soils. *J Environ Radioact* 58:163–173. [https://doi.org/10.1016/S0265-931X\(01\)00064-9](https://doi.org/10.1016/S0265-931X(01)00064-9)
- Právělie R (2014) Nuclear weapons tests and environmental consequences: a global perspective. *Ambio* 43:729–744. <https://doi.org/10.1007/s13280-014-0491-1>
- Noshkin VE, Mott NS (1967) Separation of strontium from large amounts of calcium, with application to radiostromium analysis. *Talanta* 14:45–51. [https://doi.org/10.1016/0039-9140\(67\)80045-6](https://doi.org/10.1016/0039-9140(67)80045-6)
- Wintergerst MP, Levitskaia TG, Moyer BA, Sessler JL, Delmau LH (2008) Calix[4]pyrrole: a new ion-pair receptor as demonstrated by liquid–liquid extraction. *J Am Chem Soc* 2008(130):4129–4139. <https://doi.org/10.1021/ja7102179>
- Sachleben RA, Bonnesen PV, Descazeaud T, Haverlock TJ, Urvoas A, Moyer BA (1999) Surveying the extraction of cesium nitrate by 1,3-alternatecalix[4]arene crown-6 ethers in 1,2-dichloroethane. *Solvent Extr Ion Exch* 17:1445–1459. <https://doi.org/10.1080/07366299908934657>
- Ramakrishna V, Suresh E, Boricha VP, Bhatt AK, Paul P (2005) Synthesis, crystal structures and competitive binding property of a family of calix[4]arene-biscrown-5/6 and their application in extraction of alkali metal ions from sea bitters. *Polyhedron* 2015(101):65–77. <https://doi.org/10.1016/j.poly.2015.07.001>
- Sengupta A, Mohapatra PK (2012) Extraction of radiostromium from nuclear waste solution using crown ethers in room temperature ionic liquids. *Supramol Chem* 24(11):771–778
- Patra K, Sadhu B, Sengupta A, Patil CB, Mishra RK, Kaushik CP (2021) Achieving highly efficient and selective cesium extraction using 1,3-Di-octyloxy-calix[4]arene-crown-6 in n-Octanol based solvent system: experimental and DFT investigation. *RSC Adv* 11:21323–21331
- Pathak S, Jayabun SK, Boda A, Ali SKM, Sengupta A (2020) Experimental and theoretical insight into the extraction mechanism, kinetics, thermodynamics, complexation and radiolytic stability of novel calix crown ether in ionic liquid with Sr^{2+} . *J Mol Liq.* <https://doi.org/10.1016/j.molliq.2020.113864>
- Sengupta A, Rajeswari B, Kadam RM (2019) Diluents induced tuning of the extraction characteristics of radio Cs from acidic nuclear waste solution by crown ether. *J Environ Chem Eng.* <https://doi.org/10.1016/j.jece.2019.103216>
- Wu Y, Kim SY, Tozawa D, Ito T, Tada T, Hitomi K, Kuraoka E, Yamazaki H, Ishii K (2012) Equilibrium and kinetic studies of selective adsorption and separation for strontium using DtBu-CH18C6 loaded resin. *J Nucl Sci Technol* 49:320–327. <https://doi.org/10.1080/00223131.2012.660022>
- Rounaghi GH, Mofazzeli F (2005) Study of complex formation between dicyclohexano-18-Crown-6 (DCH18C6) with Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} cations in methanol-water binary mixtures using conductometric method. *Mol Recognit Chem* 51:205–210. <https://doi.org/10.1007/s10847-004-5691-z>
- Chen Z, Wu Y, Wei YZ (2014) Adsorption characteristics and radiation stability of a silica-based DtBuCH18C6 adsorbent for Sr(II) separation in HNO_3 medium. *J Radioanal Nucl Chem* 299:485–491. <https://doi.org/10.1007/s10967-013-2750-1>
- Hawkins CA, Momen MA, Garvey SL, Kestell J, Kaminski MD, Dietz ML (2015) Evaluation of solid-supported room-temperature ionic liquids containing crown ethers as media for metal ion separation and preconcentration. *Talanta* 135:115–123. <https://doi.org/10.1016/j.talanta.2014.12.019>
- Bezhin NA, Dovhyi II, Lyapunov AY (2015) Sorption of strontium by the endoreceptor dibenzo-18-crown-6 immobilized in a polymer matrix. *J Radioanal Nucl Chem* 303:1927–1931. <https://doi.org/10.1007/s10967-014-3770-1>
- Bonnesen PV, Delmau LH, Moyer BA, Leonard RA (2000) A robust alkaline-side CSEX solvent suitable for removing cesium from savannah river high level waste. *Solvent Extr Ion Exch* 18:1079–1107. <https://doi.org/10.1080/07366290008934723>
- Leonard RA, Conner C, Liberatore MW, Sedlet J, Aase SB, Vandegrift GF, Delmau LH, Bonnesen PV, Moyer BA (2007) Development of a solvent extraction process for cesium removal from SRS tank waste. *Sep Sci Technol* 36:743–766. <https://doi.org/10.1081/SS-100103618>
- Horwitz EP, Dietz ML, Fisher DE (1991) (1991) SREX: a new process for the extraction and recovery of strontium from acidic nuclear waste streams. *Solvent Extr Ion Exch* 9:1–25. <https://doi.org/10.1080/07366299108918039>
- Rais J, Tachimori S, Yoo E, Alexová J, Bubeníková M (2015) Extraction of radioactive Cs and Sr from nitric acid solutions with 25,27-Bis(1-octyloxy)calix[4]-26,28-Crown-6 and Dicyclohexyl-18-Crown-6: effect of nature of the organic solvent. *Sep Sci Technol* 50:1202–1212. <https://doi.org/10.1080/01496395.2014.978464>
- Horwitz EP, Dietz ML, Fisher DE (1990) Extraction of stontium from nitric acid solutions using dicyclohexano-18-crown-5 and its derivatives. *Solvent Extr Ion Exch* 8:557–572. <https://doi.org/10.1080/07366299008918017>
- Law JD, Wood DJ, Herbst RS (1997) *Sep Sci Technol* 32:223–240
- Wood DJ, Law JD (1997) Evaluation of the SREX solvent extraction process for the removal of ^{90}Sr and hazardous metals from acidic nuclear waste solutions containing high concentrations of interfering alkali metal ions. *Sep Sci Technol* 32(1–4):241–253. <https://doi.org/10.1080/01496399708003197>
- Leonard RA, Conner C, Liberatore MW, Sedlet J, Aase SB, Vandegrift GF, Delmau LH, Bonnesen PV, Moyer BA (2001) Development of a solvent extraction process for cesium removal from

- srs tank waste. *Sep Sci Technol* 36(5–6):743–766. <https://doi.org/10.1081/SS-100103618>
35. Bonnesen PV, Delmau LH, Moyer BA, Lumetta GJ (2003) Development of effective solvent modifiers for the solvent extraction of cesium from alkaline high-level tank waste. *Solvent Extr Ion Exch* 21(2):141–170. <https://doi.org/10.1081/SEI-120018944>
 36. Leonard RA, Aase SB, Arafat HA, Conner C, Chamberlain DB, Falkenberg JR, Regalbutto MC, Vandegrift GF (2003) Experimental verification of caustic-side solvent extraction for removal of cesium from tank waste. *Solvent Extr Ion Exch* 21(4):505–526. <https://doi.org/10.1081/SEI-120022518>
 37. Delmau LH, Lefranc TJ, Bonnesen PV, Bryan JC, Presley DJ, Moyer BA (2005) Fundamental studies regarding synergism between Calix[4]arene-bis(tert-octylbenzo-crown-6) and alcohol modifiers in the solvent extraction of cesium nitrate. *Solvent Extr Ion Exch* 23(1):23–57. <https://doi.org/10.1081/SEI-200044379>
 38. Walker DD, Norato MA, Campbell SG, Crowder ML, Fink SD, Fondeur FF, Geeting MW, Kessinger GF, Pierce RA (2005) Cesium removal from savannah river site radioactive waste using the caustic-side solvent extraction (CSSX) process. *Sep Sci Technol* 40(1–3):297–309. <https://doi.org/10.1081/SS-200042239>
 39. Delmau LH, Haverlock TJ, Bazelaire E, Bonnesen PV, Ditto ME, Moyer BA (2009) Alternatives to nitric acid stripping in the caustic-side solvent extraction (CSSX) process for cesium removal from alkaline high-level waste. *Solvent Extr Ion Exch* 27(2):172–198. <https://doi.org/10.1080/07366290802672394>
 40. Delmau LH, Birdwell JF Jr, McFarlane J, Moyer BA (2010) Robustness of the CSSX process to feed variation: efficient cesium removal from the high potassium wastes at Hanford. *Solvent Extr Ion Exch* 28(1):19–48. <https://doi.org/10.1080/07366290903408433>
 41. Law JD, Herbst RS, Peterman DR, Tillotson RD, Todd TA (2004) Development of a cobalt dicarbollide/polyethylene glycol solvent extraction process for separation of cesium and strontium to support advanced aqueous reprocessing. *Nucl Technol* 147(2):284–290. <https://doi.org/10.13182/NT04-A3532>
 42. Riddle CL, Baker JD, Law JD, McGrath CA, Meikrantz DH, Mincher BJ, Peterman DR, Todd TA (2005) Fission product extraction (FPEX): development of a novel solvent for the simultaneous separation of strontium and cesium from acidic solutions. *Solvent Extr Ion Exch* 23(3):449–461. <https://doi.org/10.1081/SEI-200058035>
 43. Ye WJ, Wang JC, He QG (2009) Coextraction of strontium and cesium by dicyclohexano-18Crown-6/25, 27-Bis (2-propyloxy) Calix [4] -26, 28-Crown-6-n-Octanol *J Nuclear Radiochem* 31(3): 167–172. ISSN 0253–9950; TRN: CN1103380093577
 44. Wang JC (2015) (2015) Co-extraction of strontium and cesium from simulated high-level liquid waste (HLLW) by calixcrown and crown ether. *J Nucl Sci Technol* 52(2):171–177. <https://doi.org/10.1080/00223131.2014.938136>
 45. Raut DR, Mohapatra PK, Ansari SA, Sarkar A, Manchanda VK (2008) Selective transport of radio-cesium by supported liquid membranes containing calix[4]crown-6 ligands as the mobile carrier. *Desalination* 232:262–271. <https://doi.org/10.1016/j.desal.2007.10.039>
 46. Sharma JN, Kumar A, Kumar V, Pathan S, Janardahan C, Tessi V, Watal PK (2014) Process development for separation of cesium from acidic nuclear waste solution using 1,3-dioctylxycalix[4] arene-crown-6 + isodecyl alcohol/*n*-dodecane solvent. *Sep Sci Technol* 135:176–182. <https://doi.org/10.1016/j.seppur.2014.08.016>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.