Studies on the Separation of Cesium from High Level Liquid Waste

By

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DECLARATION

I, hereby declare that the investigations presented in this Thesis has been carried out by me. The work is original and has not been submitted earlier in whole or part for a degree / diploma to this or any other Institution / University.

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List of Publications arising from the thesis

Journal

1. "Hollow fiber supported liquid membrane studies using a process compatible solvent containing calix [4]arene-mono-crown-6 for the recovery of radio-cesium from nuclear waste", **Poonam Jagasia**, Seraj A. Ansari, Dhaval R. Raut, Prem S. Dhami, Pritam M Gandhi, Amar Kumar and Prasanta K. Mohapatra,

   Sep. and Purif. Technol. 170 (2016) 208–216

2. "Pertraction of radio-cesium from acidic feeds across supported liquid membranescontaining calix-crown-6 ligands in a fluorinated diluent", **P. Jagasia**, P. K. Mohapatra, D. R.Raut, P.S. Dhami, V. C. Adya, A. Sengupta, P. M. Gandhi and P. K. Wattal, *J. of Membr. Sci. 487(2015)127–134*

3. "Studies on the radiolytic stability of newly developed solvent systems containing four calix-crown-6 ligands for radio-cesium recovery", **P. Jagasia**, P. K. Mohapatra, P. S. Dhami, A. B. Patil, V. C. Adya, A. Sengupta, P. M. Gandhi and P. K. Wattal

   J Radioanal Nucl Chem (2014) 302:1087-1093

4. "Evaluation of Novel Solvent Systems Containing Calix-crown-6 Ligands in A Fluorinated Solvent for Cesium Extraction from Nitric Acidic Feeds", **Poonam Jagasia**, P. K. Mohapatra, P. S. Dhami, P. M. Gandhi & P. K. Wattal

   Sep. Sci. Technol., (2014) 49: 2151–2157, 2014

5. "Recovery of radio-cesium from actual high level liquid waste using solvents containing calix[4]arene-crown-6 ligands" **P. Jagasia**, P.S. Dhami, P.K. Mohapatra, S.A. Ansari, S.Y. Jadhav, G.K. Kalyankar, P.M. Gandhi, U.K. Kharul

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Conference / Symposium:

1. "Cesium extraction from high level waste using irradiated calix-crown-6 ligands in FS-13", **Poonam Jagasia**, V. C.Adya, A. Sengupta, P. S. Dhami and P. K. Mohapatra, *DAE-BRNS 5th Symposium on Nuclear Analytical Chemistry (NAC-V), BARC, Mumbai, pp 300, Jan, 20-24, 2014.*
2. "Evaluation of Novel Calix-crown-6 based solvent systems for the recovery of Radio-cesium from Actual High Level Waste", **Poonam Jagasia**, P. K. Mohapatra and P. S. Dhami, *Proceeding of DAE-BRNS Biennial Symposium on Emerging Trends in Separation Science and Technology, SESTEC-2014, pp. 101, Feb.25-28, 2014.*
3. "Comparative Extraction and Transport Studies of Cs(I) Employing Four Different Calixcrowns Dissolved in the Phenyl Trifluoro Methyl Suphone (FS-13) as the Diluent", **Poonam Jagasia**, D. R. Raut, P.S. Dhami and P.K. Mohapatra *12th National Symposium on Nuclear and Radiochemistry (NUCAR-2015), pp. 274, Feb. 9-13, 2015.*
4. "Cs(I) Transport Studies Employing Calix-crown-6 Ligands Dissolved in Phenyl Trifluoro Methyl Sulphone", **Poonam Jagasia**, P.S. Dhami, P.M. Gandhi,P.K. Wattal and P.K. Mohapatra *12th National Symposium on Nuclear and Radiochemistry (NUCAR-2015), pp. 274, Feb. 9-13, 2015.*
5. "Transport of Cs(I) Across a Supported Liquid Membrane Containing a Calix- crown-6 Ligand Dissolved in n-dodecane + Iso-decanol", **P. Jagasia**, D.R. Raut, P.S. Dhami, P.M. Gandhi, P.K. Wattal, P.K. Mohapatra *International Conference on Membrane based Separations (MEMSEP-2015).*

March 21-23, pp.127, 2015.

6. “Cesium extraction from simulated high level waste using calix-crown ligands:Radiolytic stability, decontamination and stripping studies”,**P. Jagasia,** V.C. Adya, Sengupta, P.S. Dhami and P. K. Mohapatra

   11th Biennial DAE-BRNS Nuclear and Radiochemistry Symposium NUCAR-2013,

   pp. 339, Feb., 19-23, 2013.

7. “Evaluation of Novel Calix-crown-6 Based Solvent Systems for Cesium Extraction from High Level Waste studies”, **Poonam Jagasia**, P. K. Mohapatra and P.S. Dhami

   11th Biennial DAE-BRNS Nuclear and Radiochemistry Symposium NUCAR-

   pp. 340, Feb., 19-23,2013.

8. “Calixarene based hollow fiber liquid membrane for recovery of cesium from acidic waste solution”, **Poonam Jagasia**, S. A. Ansari, P.S. Dhami, P.M. Gandhi, A. Kumar and P.K. Mohapatra,

   Proceedings of DAE-BRNS Biennial Symposium on Emerging Trends in Separation

   Science and Technology, (SESTEC-2016), pp. 173, May 17-20, 2016.

(Poonam P. Jagasia)

"The art of progress is to preserve order amid change

and to preserve change amid order".

Alfred North Whitehead

Dedicated to my Parents and Family

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April, 2017 **Poonam P. Jagasia**

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Synopsis

Synopsis

Nuclear science and technology is an advanced field of study in which nuclear energy is used in diverse areas such as in medicine, industry, hydrology, agriculture, pollution control etc. Nuclear energy is released in controlled conditions in devices known as nuclear reactors where fissile nuclides such as ^{235}U (or ^{239}Pu) undergo fission with neutrons to release large amounts of energy. In some ways the device is similar to a coal-burning furnace where the principal output heat is converted to electricity, a more convenient form of energy. Production of nuclear energy involves number of operations in a cycle usually referred to as the nuclear fuel cycle. It starts with uranium mining and milling, followed by various steps like uranium extraction and purification, fuel fabrication, reactor operation, reprocessing of spent reactor fuel for recovery and reuse of uranium and plutonium, and finally ends with management and disposal of radioactive wastes.

For sustainable operation of reactors in a continuous manner, the refueling is done periodically. The fuel that is discharged from the reactor is termed as spent fuel which is cooled for certain period for the decay of short-lived fission products. It is then processed for the recovery of unused fertile (such as ^{238}U) and freshly formed fissile material (such as ^{239}Pu) employing the well-known PUREX (Plutonium Uranium Reduction EXtraction) process. During the reprocessing of the spent fuel, different types of wastes get generated [1]. Each type of waste, invariably highly radioactive, requires different treatment technique depending on the level of radioactivity and their physical state and chemical nature. High Level Liquid Waste (HLLW) is a stream that contains more than 95% of the radioactivity generated in the entire fuel cycle [2]. It is also a source of many useful radionuclides such as ^{137}Cs, ^{90}Sr, ^{90}Y, ^{103}Ru, ^{106}Ru, ^{99}Tc, ^{99}Mo, ^{95}Zr, ^{95}Nb etc. These waste streams also contain a wide range of isotopes of actinide elements like U, Np, Pu, Am, Cm, etc.

The fission product nuclide, ^{137}Cs ($t_{1/2}$ ~30 y) which is a major constituent of HLLW, has large heat output (~0.42 W/g) and its removal from HLLW is important from waste management point of view as it may create deformations in the vitrified waste product resulting in the release of the vitrified radionuclides into the environment [3]. Secondly, the separation of the radiotoxic nuclides including ^{137}Cs will reduce the waste volume significantly. Long half-life and high energy gamma ray (661 keV) emitted from ^{137}Cs make this radionuclide a viable alternative source for gamma irradiators to replace the commonly used ^{60}Co ($t_{1/2}$=5.2 y, γ=1173 keV and 1332 keV) for the sterilization of medical accessories, food preservation, sewage sludge treatment, etc. [4]. In view of these, it is required to separate the radio-cesium from the HLLW for its subsequent use. Several techniques using a variety of compounds have been used for the separation of radio-cesium from acidic as well as basic aqueous waste solutions [5]. Precipitation techniques [6] have been reported using phosphortungustic acid, tetra phenyl borate anion and metal ferro cyanide/ferricyanide. Ion-exchange methods have also been reported for the recovery of Cs [7]. Inorganic ion-exchangers like zirconium phosphate, ammonium molybdophosphate (AMP) [8] etc., have also been employed for the removal of cesium from solutions but adoptability at higher acidity, non-selectivity and non-availability of these materials limit their use at larger scale. Recently, a new class of ion-exchangers composed of combination of $[(CH_3)_2NH_2]^+$ and $[Ga_2Sb_2S_7]^{2-}$ ions have been found to be highly selective for cesium [9]. Zeolites and crystalline silicotitanate (CST) have also been reported to be highly selective for cesium (I) in the presence of large concentration of sodium and other alkali metals [10]. Simultaneous recovery of Cs and Sr has been carried out by adding poly ethylene glycol (PEG-400) with chlorinated cobalt dicarbollide (CCD) in diluents like nitrobenzene / Phenyltrifluoromethyl sulphone (PTMS) [11]. Recently, crown ethers such as dibenzo-18-crown-6 and calyx[4]crown-6 ligands have drawn attention due to their selectivity for Cs(I) ion [12-14]. These compounds are soluble in polar diluents like nitrobenzene, 1-octanol etc. However, these diluents are unsuitable for large scale applications.

Solvent extraction techniques are best suited for plant scale adoption using a separation scheme. Among the various extractant calix crown-6- ligands are best choice for separation of Cs(I) from HLLW solutions. Extraction chromatography and liquid membrane techniques are considered eco-friendly due to low solvent inventory involved and are finding more and more attention in recent years when separation is to be achieved from aqueous feed solutions having lower metal concentrations. Out of these, liquid membrane based techniques are important in view of the possibility of simultaneous extraction and stripping. Hence, expensive and exotic chemicals can be used in liquid membrane based separation methods.

In view of above, the main objective of the present study was to evaluate several calix[4]crown-6 ligands *viz.*calix[4]arene-bis-crown-6 (CC), calix[4]arene-bis-benzocrown-6 (CBC), calix[4]arene-bis-naphtho-crown-6 (CNC) and bis(octyloxy)calix[4]arene-mono-crown-6 (CMC) in PTMS(phenyl trifluromethyl sulphone) in batch mode for Cs extraction and stripping under different experimental conditions from nitric acid medium. Various extraction parameters such as contact time, concentrations of the ligand, nitric acid and metal ions in feed etc., which influence the extraction of Cs(I) are studied in greater detail. Metal-ligand complexes are established using slope analysis method. Extraction studies are also carried out using irradiated solvents up to 1000 kGy using ^{60}Co gamma source. Possible degradation products are evaluated using GC-MS data. The most suitable calix[4] crown-6 ligand is subsequently employed for Cs recovery from simulated PHWR-HLLW feed solution spiked with ^{137}Cs radiotracer. The study is then extended to the recovery of radio-cesium from real HLLW solution generated from the spent fuel reprocessing of research reactor origin at BARC, Trombay. About 10 mCi ^{137}Cs was recovered using CBC in PTMS based solvent system. This is the first report on the extraction of Cs(I) using calix-crown-6 ligands in a fluorinated solvent such as PTMS. Though similar studies with these extractants are reported in diluents *viz.* nitrobenzene, toluene and 2-nitrophenyloctyl ether, the results obtained with the present solvent systems are different and are highly encouraging as compared to those reported previously.

As the solvent extraction data are basic input for the liquid membrane based separation methods the study is extended for the transport of metal ions under different experimental conditions. The most suitable calix[4] crown-6 ligand (which is different from the one used for the solvent extraction study) is then employed in supported liquid membrane based separation in two different configurations *viz.* flat sheet supported liquid membrane(FSSLM) and hollow fiber supported liquid membrane (HFSLM). After optimizing the transport parameters in flat sheet membrane mode under different experimental conditions the recovery of Cs is demonstrated from simulated PHWR-HLLW feed solution using hollow fiber supported liquid membrane mode. Finally, the recovery of radio-cesium is demonstrated from diluted real HLLW solution of research reactor origin.

Thus, the present thesis deals with the separation of ^{137}Cs from PUREX-HLLW using solvent extraction and membrane based techniques. The Thesis is divided into the following six Chapters.

CHAPTER 1: INTRODUCTION

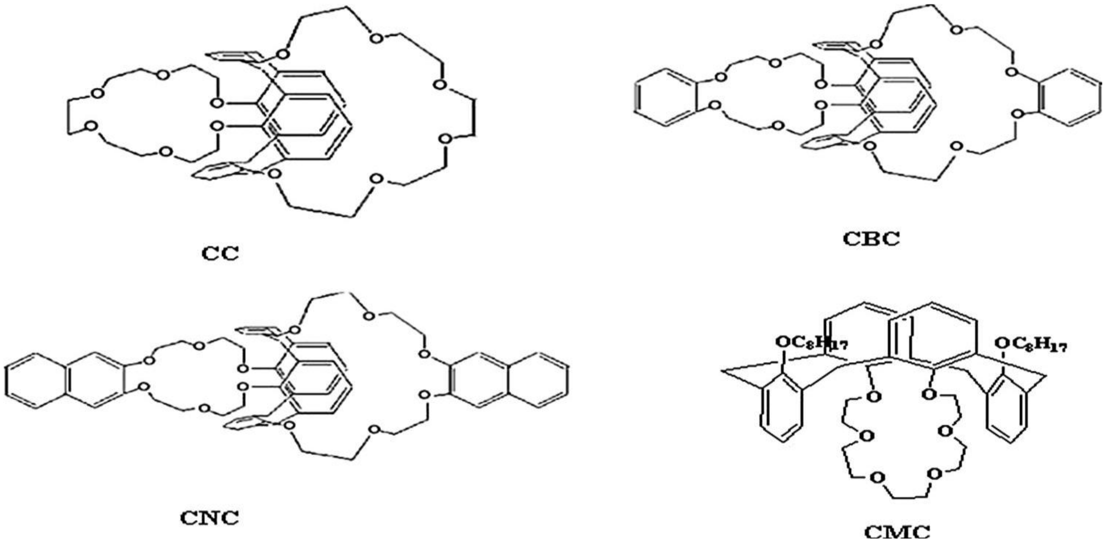
This Chapter gives a brief description on nuclear energy, nuclear fuel cycle with relevant details on spent fuel reprocessing by PUREX process, types of radioactive wastes, etc. During reprocessing of the spent fuel various categories of liquid wastes are generated. Among these HLLW is a rich source of many useful radionuclides hence its composition is described. The Chapter also describes various methods of separation *viz.* precipitation, solvent extraction, ion-exchange, and relatively newer methods namely extraction chromatography and membrane based techniques. As the study is on the separation of radio-cesium, a detailed literature survey on the recovery of Cs(I) from HLLW or analogous feeds is described. Advantages of separation methods involving solvent extraction and membrane utilizing solvents as carrier are discussed in detail. A brief introduction to the liquid membrane separations, types of liquid membranes and diffusion co-efficient and mass transfer co-efficient calculation are also included. This Chapter also covers the aims and objectives of the Thesis.

CHAPTER 2: EXPERIMENTAL

In this Chapter, methodologies involving solvent extraction using various calix crown-6 ligands *viz.* calix [4] arene-bis-crown-6 (CC), calix [4] arene-bis-benzocrown-6(CBC),calix[4] arene-bisnaphtho-crown-6 (CNC) and bisoctyloxy)calix [4] arene-mono-crown-6 (CMC) (Fig. 1) is described in the batch mode. Distribution data are obtained by equilibrating known volumes of organic and aqueous phases in leak tight stopperred glass tubes at constant temperature in a thermostated bath. Sources of the chemicals, radiotracers, solvents along with their purities, purification methods (if any) are also described. This Chapter also includes radiometric assay of the radionuclides with brief description of various radiation counters employed during the studies. Equipments used during this study are also discussed. Finally details of the experimental procedure are included in this Chapter.

CHAPTER 3: SOLVENT EXTRACTION STUDIES USING CALIX CROWN LIGAND

This Chapter describes the evaluation of novel solvent systems containing calix [4] crown-6 ligands (Fig. 1) in a fluorinated solvent and also in a mixture of n-dodecane and iso-decanol for cesium extraction from nitric acidic medium. Results of solvent extraction studies carried out in batch mode using all the four calix [4] crown-6 ligands under different extraction conditions. Feed acidity of ~ 3-4 M HNO_3 is found to be most optimal using 1×10^{-3}M ligands in PTMS as the diluent. The extraction efficiency of the calix-crown-6 ligands is found out to be: CBC > CNC > CMC ~CC, which was attributed to trends of their partition coefficients.



CC CBC

CNC CMC

Fig. 1: Structural formulae of the calix [4] crown-6 ligands used in the present study

CNC is considered to be the most suitable extractant in view of its better organo-philicity. The results of effects of concentrations of nitric acid and Cs carrier in feed are also discussed.

Extracted species of the type [CsL^+] [NO_3^-] is established using slope analysis method. Stripping of Cs from the loaded organic phase is found to be more effective when the organic phase contained Alamine 336 (0.5% v/v percent). Co-current extraction and stripping results are also described in this chapter.

A separate solvent extraction study is taken up using a mixture of n-dodecane and iso-decanol (3: 2 volume ratio)as the diluents. In view of thepoor solubility of the ligands such as CC, CNC, and CBC in this diluent mixture, only studies involved solutions of CMC. The results are encouraging for the application of this solvent system to a supported liquid membrane study (Chapter 5) for which PTMS based solvent system showed poor stability over a period of several days.

CHAPTER 4: RADIOLYTIC STABILITY STUDIES

Any solvent system can be successfully employed for radio-cesium recovery from HLLW provided the radiolytic stability of the solvent is satisfactory. Keeping this in mind the calix [4] crown-6 ligands were irradiated in a ^{60}Co gamma ray irradiator and the stability of the ligands were tested in two ways, i) changes in the solvent extraction behaviour and ii) analysis of the degradation products.

Results from the irradiation studies clearly indicate that the distribution ratio values of Cs(I) (D_{Cs}) remain almost same when the ligands are irradiated up to 100 kGy level. Above this the D_{Cs} decreased with increasing absorbed dose upto the maximum dose of 1000 kGy. The solvent containing CBC has shown higher resistance to degradation possibly due to the aromatic substituent though analogous behaviour was not seen with CNC. Possible degradation path ways for all the four calix crown ligands are described in this Chapter. The degradation mechanism for calix[4]crown-6 extractants has been found similar to that reported earlier that is the radical degradation mechanism of similar class of compounds [15].

CHAPTER 5: SUPPORTED LIQUID MEMBRANE STUDIES

Supported liquid membrane (SML) transport results using the four calix [4] crown-6 ligands in the fluorinated diluent, PTMS are described in the first part of this Chapter. The transport data suggest that CBC is the most suitable calix-crown-6 ligands among the various ligands evaluated. Overall, the transport rates are faster than those reported previously using calix-crown-6 ligands in other diluents *viz.* nitrobenzene or the n-dodecane and NPOE mixture. The acid co-transport rates are reasonably acceptable up to 5h, beyond which a sharp increase is observed suggesting long term use of the membranes may be marred by the presence of nitric acid in the receiver compartment. Studies with SHLW appeared encouraging due to relatively higher mass transfer rates (as compared to those reported previously) and also very good selectivity to make the transport system highly promising for application for nuclear waste remediation. The Cs(I) transport rates from SHLW (simulated high level waste) can be improved even further by increasing the calix crown-6 concentration in the SLM. However, studies with SLM stability has shown mixed results as the liquid membranes can be used for a couple of days only with marginal loss in transport rates beyond which a sharp fall in Cs(I) transport rates was noticed.

As an alternative, SLM studies are carried out with a solvent system containing 0.01M CMC in 40% iso-decanol + 60% n-dodecane (Chapter 3).The transport data are quite encouraging and the transport rates are found to increase with increasing HNO_3 concentrations. Reasonably high Cs (I) transport is observed with 3 M HNO_3 as the feed which is the acidity of HLLW. Stability of the membrane was found to be excellent when monitored for 12 days of continuous operation. The permeability coefficient, mass transfer coefficient and various diffusional parameters of the diffusing metal/ligand species were calculated to understand the permeation behaviour of cesium. At moderate acidity of ~3 M HNO_3, which is the acid concentration of the high level waste, near quantitative (>99%) transport of cesium was possible within 2 h of operation at 300 mL scale. Transport is suppressed under simulated high level waste condition due to presence of large concentrations of cesium (0.32 g/L), but > 90% transport was observed in 6 h. The present work explored the possible use of CMC in hollow fiber contactor for radioactive waste treatment where the ligand inventory is very low.

CHAPTER 6: SEPARATION STUDIES FROM REAL HLLW

In this Chapter, extraction of Cs was attempted from [simulated] PHWR-HLLW using both the solvent extraction as well as the SLM techniques. Presence of uranium in the waste does not show any significant effect in the extraction of Cs. Selective extraction of radio-cesium from three different sets of experiments involving simulated HLLW, diluted HLLW and real undiluted HLLW is observed by using 1×10^{-3}M CBC in PTMS. Quantitative extraction of Cs is observed from real HLLW in four contacts leaving behind all the other radionuclides present in the waste. Extracted Cs from the organic phase is stripped quantitatively in only two contacts using 0.01 M HNO_3 as the strippant. Stripping is found to be more effective when 0.5 volume percent Alamine 336 is introduced in the organic solvent. The hollow fiber contactor based SLM studies carried out using 0.01 M CMC in 40% iso-decanol + 60% n-dodecane are found to be highly promising as ca. 90% radio-cesium recovery is reported which matched very well in repeat experiments. Furthermore, the hollow fibers are found to be quite stable even after keeping in contact with the radioactive feed for about 50 days as indicated by almost reproducible transport results. Results from these studies clearly indicate that the hollow fibre SLM method can be scaled up for the large scale processing of HLLW for radio-cesium recovery.

Chapter 7: SUMMARY AND CONCLUSIONS

Important findings and conclusions drawn from the earlier Chapters along with the scope of the work is described in this Chapter. The two separation methods studied in the Thesis clearly demonstrated the recovery of radio-cesium from high level liquid waste using calix [4] arene-crown-6 based solvent systems. While the solvent extraction method involved calix [4] arene-bis-benzo-crwon-6 (CBC) in PTMS, the hollow fiber supported liquid membrane method used a polysulphone fiber contactor and bis-octyl-benzo-calix [4] arene-mono-crown-6 (CMC) in 40% iso-decanol + 60% n-dodecane. Separated radio-cesium did not show any other fission product contamination in it as assayed by gamma ray spectrometry. It is proposed to employ the separation results to actual waste processing in the near future.

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LIST OF ABBREVIATIONS

AMP	Ammonium molybdophosphates
BLM	Bulk Liquid Membrane
CBC	calix[4]arene-bis-benzocrown-6
CC	calix[4]arene-bis-crown-6
CCD	Chlorinated cobalt dicarbollide
Ci	Curie
CMC	bis(octyloxy)calix[4]arene-mono-crown-6
CNC	calix[4]arene-bis-napthocrown-6
CPK	Corey-Pauling-Koltun
CST	Crystalline silicotitanates
D	Distribution ratio
DIAMEX	DIAMide EXtraction
ELM	Emulsion Liquid Membrane
eV	Electron volt
FBR	Fast Breeder Reactor
FSSLM	Flat Sheet Supported Liquid Membrane
GC-MS	Gas Chromatography-Mass Spectrometry
HAW	High Active Waste
HFSLM	Hollow Fiber Liquid Membrane
HLLW	High Level Liquid Waste
HPGe	High purity germanium
ICP-AES	Inductively Coupled Plasma - Atomic Emission Spectrometry
IDA	Iso-decanol

LIST OF ABBREVIATIONS

INEEL	Idaho National Engineering and Environmental Laboratory
kGy	kilogray
LM	Liquid membrane
mCi	millicurie
MeV	mega electron volt
MF	microfiltration
MWd/te	Megawatt day per tone
NPOE	o-nitrophenyloctyl ether
ORNL	Oak Ridge National Laboratory
PAN	Poly-acrylo nitrile
PEG	Polyethylene glycol
PHWR	Pressurised Heavy Water Reactor
PP	Polypropylene
PS	Polysulphone
PTFE	polytetrafluoroethylene
PTMS	Phenyltrifluoromethylsulphone
PUREX	Plutonium Uranium Reduction EXtraction
RFPR	Resorcinol formaldehyde polycondensate resin
SHLLW	Simulated High Level Liquid Waste
SLM	Supported Liquid Membrane
TALSPEAK	Trivalent Actinide Lanthanide Separation by Phosphorous reagent Extraction from Aqueous Komplexes
TBP	tri-n-butyl phosphate

LIST OF ABBREVIATIONS

TRUEX	TRans Uranic EXtraction
UF	ultrafilteration
UNEX	UNiversal solvent EXtraction

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Chapter 1

INTRODUCTION

Chapter 1

1.1 Nuclear Energy

The economic growth of a country is highly dependent on the production and utilisation of energy. To meet the energy requirements, generally conventional energy sources like hydel power, fossil fuels such as coal, natural gas, oil, etc. are being used globally. As these sources are depleting rapidly, alternative resources are being explored. Modern science has enabled production of electricity through a number of sources like wind, bio-gas, tidal power and solar energy. Among others, nuclear energy is a clean, green and renewable source of energy which will play important role in future. Presently, it contributes ~17% of the total power production in the world.

Apart from power production, nuclear technology has seen tremendous growth in production and application of radiations and radioisotopes in the field of medicine, industry, food preservation, agriculture, etc. Artificially produced radioisotopes are widely utilized as sources of radiation for radiography, gauging, and as tracers for a number of measurements that are not easily made by other methods. There are two ways by which these radioisotopes are produced; by neutron activation method and also by charged particle bombardment. Radioisotopes, formed by nuclear reactions on targets in reactors or accelerators, require further processing in almost all cases to obtain them in a form suitable for use. Specifications for final products and testing procedures for ensuring quality are also an essential part of a radioisotope production. At present, there are above 200 radioisotopes used on a regular basis, most of it produced artificially.

The nuclear energy programme of our country envisages three stages (1-2) of which the first stage involves natural uranium fuelled Pressurized Heavy Water Reactors

(PHWRs). In the second stage, plutonium that would be produced in the PHWRs as a by-product would be used in Fast Breeder Reactors (FBRs) to enlarge the nuclear power base and at the same time produce more plutonium thereby enabling continuous growth of installed nuclear power generation capacity. This second stage would also be utilized for producing significant quantities of fissile ^{233}U from fertile thorium (^{232}Th) used in the blankets. Once sufficient inventory of ^{233}U is accumulated, the third and the final stage *viz*. thorium fuel cycle which would release energy potential from thorium resources will be realized (3).

1.2 Nuclear Fuel Cycle

Production of nuclear energy involves a complete cycle of operations usually referred to as nuclear fuel cycle (4). Schematic presentation of fuel cycle is given in **Figure 1.1.**

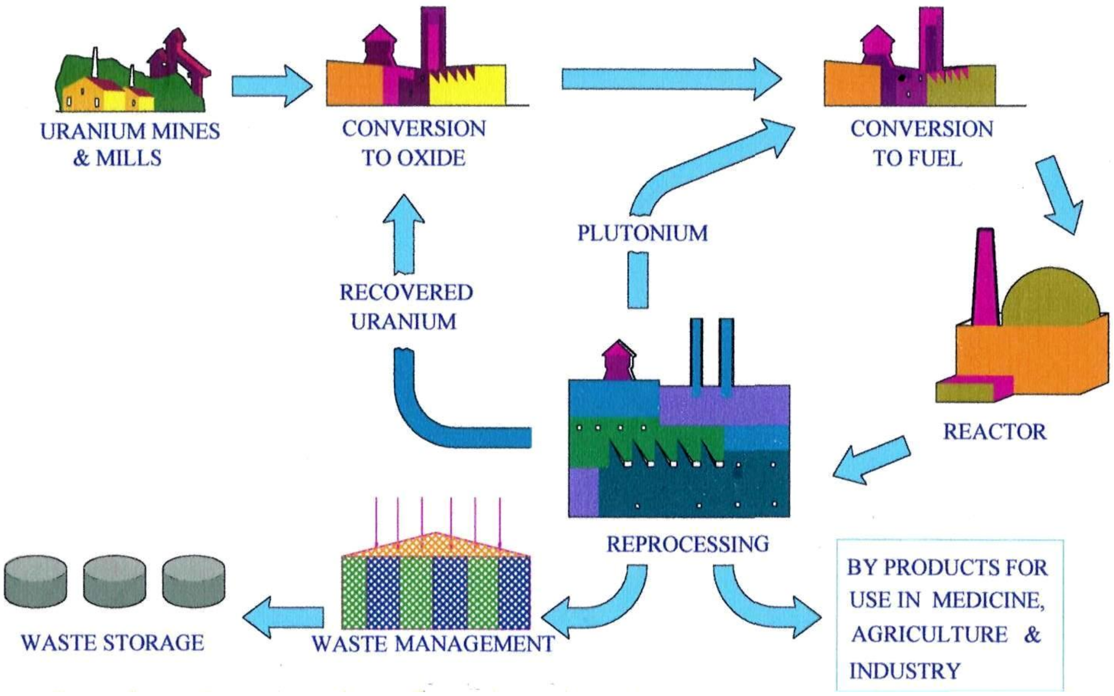


Figure 1.1: Nuclear fuel cycle operations

It starts with uranium mining and milling, uranium extraction and purification, fuel fabrication, reactor operation, reprocessing of spent reactor fuel for recovery of uranium and plutonium, and finally, the management of radioactive wastes. In nuclear reactors, energy is produced through controlled chain reaction due to the fragmentation of a fissile nuclide like ^{235}U which undergoes fission on capturing a neutron. Each fission reaction releases about 200 MeV of energy. This process is also accompanied by the emission of 2-3 neutrons. The exact identity of the fission products and the number of neutrons vary from one fission event to another. A typical fission reaction can be represented as follows-

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{236}_{92}\mathrm{U}^{*} \rightarrow {}^{137}_{56}\mathrm{Ba} + {}^{97}_{36}\mathrm{Kr} + 2\,{}^{1}_{0}\mathrm{n} + 200\ \mathrm{MeV} \qquad (1.1)$$

The fission product yield distribution charts for ^{235}U and ^{239}Pu are shown in **Figure 1.2** $^{(5)}$**.**

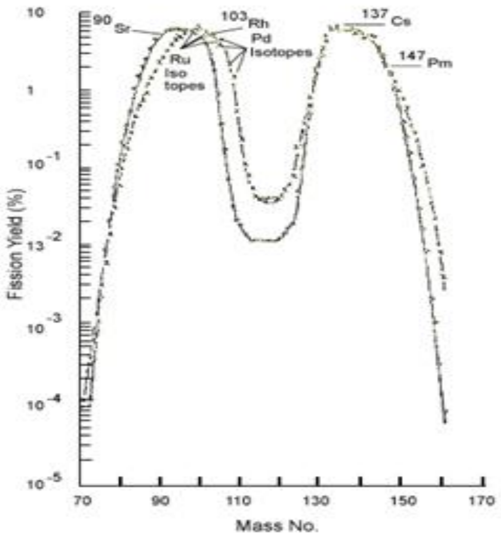


Figure 1.2: Fission yields curves for thermal neutron induced fission of ^{235}U and ^{239}Pu

From this it can be clearly seen that the mass numbers of all the fission products lies between 70 and 160. Most probable mass numbers which occur in about 6.5% of fission are about 97 and 135 mass units. The fission products are neutron rich, highly unstable and undergo β decay. The fission process thus leads to the formation of highly radioactive products.

The probability of a nuclear reaction, called the reaction cross section (σ) is measured in the unit of barns (b) which is equal to 10^{-24} cm^2. The probability depends on the energy of neutron and nature of the heavy nuclei (6). With neutrons having energies greater than 1.6 MeV both ^{235}U and ^{238}U undergo fission with similar probability (σ = 1-3 b). However, when neutron energy is decreased to the thermal energy region (0.025 eV), the probability of fission for ^{235}U goes up several times (σ = 535 b), whereas it becomes very close to zero for ^{238}U. Fission cross section of ^{239}Pu, with thermal neutrons is 742 b which is more than that for ^{235}U. Those nuclides which can readily sustain a fission chain reaction are called fissile nuclides. ^{235}U is the only naturally occurring fissile nuclide. ^{238}U is always present along with ^{235}U and undergoes neutron absorption resulting in the formation of ^{239}U which decays to ^{239}Pu as follows.

$$\begin{array}{ccccccc} & (n,\gamma) & & -\beta & & -\beta & \\ {}^{238}U & \rightarrow & {}^{239}U & \rightarrow & {}^{239}Np & \rightarrow & {}^{239}Pu \\ (4.5\times10^{9}\ y) & & (23.5\ min.) & & (2.33\ d) & & (2.43\times10^{4}\ y) \end{array}$$

During power production uranium and plutonium undergo many other nuclear reactions with neutrons which lead to the production of isotopes of Pu. Prominent among them are ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu which are radioactive. Some of these reactions are depicted below:

$$\begin{tikzcd}
{}^{239}\mathrm{Pu} \arrow[r, "{(n,\gamma)}"] & {}^{240}\mathrm{Pu} \arrow[r, "{(n,\gamma)}"] & {}^{241}\mathrm{Pu} \arrow[r, "{(n,\gamma)}"] \arrow[d, "-\beta"] & {}^{242}\mathrm{Pu} & \\
 & & {}^{241}\mathrm{Am} \arrow[r, "{(n,\gamma)}"] & {}^{242}\mathrm{Am} \arrow[r, "-\beta"] \arrow[d, "-\alpha"] & {}^{242}\mathrm{Cm} \\
 & & & {}^{238}\mathrm{Pu} &
\end{tikzcd}$$

$$^{237}\mathrm{Np} \xrightarrow{(n,\gamma)} {}^{238}\mathrm{Np} \xrightarrow{-\beta} {}^{238}\mathrm{Pu}$$

^{237}Np ($t_{1/2} = 2.1\times10^{6}$ y) is formed as per the following reactions.

$$^{238}\mathrm{U} \xrightarrow{(n,2n)} {}^{237}\mathrm{U} \xrightarrow{-\beta} {}^{237}\mathrm{Np} \qquad \text{(\~70\% production)}$$

$$^{235}\mathrm{U} \xrightarrow{(n,\gamma)} {}^{236}\mathrm{U} \xrightarrow{(n,\gamma)} {}^{237}\mathrm{U} \xrightarrow{-\beta} {}^{237}\mathrm{Np} \qquad \text{(\~30\% production)}$$

$$^{241}\mathrm{Am} \xrightarrow{-\alpha} {}^{237}\mathrm{Np}$$

Except for ^{241}Pu all other radionuclides, mentioned above, decay by α emission. ^{241}Pu decays by β emission to yield ^{241}Am. Out of the isotope mentioned, only ^{239}Pu and ^{241}Pu are fissile with thermal neutrons and the other isotopes act as absorber materials. However, in a fast reactor, even the other isotopes undergo fission and contribute to production of energy. In the nuclear reactor, the energy produced during fission is removed with a suitable coolant which is used to generate steam. The steam drives a turbine and electricity is produced. Reactors used for power production are prominently thermal reactors in which the fission is caused by thermal neutrons. These reactors employ uranium oxide as fuel. Natural uranium contains ~0.742% ^{235}U and small amounts of ^{234}U (0.005%), the rest being ^{238}U. PHWRs use natural uranium as fuel and heavy water as moderator for slowing down the neutrons. Light water reactors (LWRs) use either low enriched uranium with ~3% of ^{235}U or natural uranium mixed with equivalent quantity of ^{239}Pu as fuel and the light water as moderator. Plutonium is produced as a byproduct in these reactors and partly compensates for the loss of fissile material during the reactor operation. In PHWRs, the burn-up of the fuel is about 6000 - 10,000 MWd/te of fuel. The burn-up is a measure of the amount of fissile material consumed before the fuel is removed from the reactor and is expressed in terms of heat energy produced. The burn-up is as high as 30,000 MWd/te of fuel in LWRs due to higher fissile material content.

Fast breeder reactors (FBRs) do not use any moderators. In contrast to the thermal reactors, the fissile material content in the fuel of these reactors is 15 - 20% and the burn-up can be as high as 80,000 - 100,000 MWd/te of fuel. In these reactors, the quantity of plutonium generated through neutron capture of ^{238}U is more than the fissile material that is consumed. Research reactors constructed for the production of useful radioisotopes through neutron irradiation and for carrying out the related studies use uranium metal as fuel and have a low burn-up of the order of ~1000-2000 MWd/te of fuel.

The fuel after being used in reactor is termed as spent fuel and it contains the unused uranium (^{235} U from fission reaction and ^{238} U from activation reaction) and the actinides formed i.e. neptunium, plutonium, americium, curium, etc. along with various fission product elements *viz*. strontium, yttrium, zirconium, niobium, molybdenum, tellurium, ruthenium, rhodium, palladium, cesium, lanthanides, etc. After the fuel is discharged from the reactor it is cooled for certain period for the decay of short-lived fission products. It is then processed for the recovery of the unused fertile material and freshly formed fissile material. A brief discussion on reprocessing is described below.

1.3 Spent Fuel Reprocessing

Separating the fissile and fertile materials from fission products in the spent fuel after allowing the decay of short-lived fission products is termed as spent fuel reprocessing. After certain period of irradiation, the uranium fuel is discharged from the reactor and is replaced with fresh fuel because the fuel is depleted in its fissile material during irradiation and the accumulated fission products of heavy elements acts as neutron poisons. After the fuel is discharged from the reactor, it is cooled for a certain period of time for the decay of short lived fission products. Since the irradiated fuel contains valuable nuclear materials, it is then reprocessed for the recovery of unused uranium and freshly formed plutonium. Plutonium Uranium Reduction EXtraction (PUREX) process is the most common process in use for the reprocessing of spent fuel (7-9). It is essentially a solvent extraction process, which utilizes tri-n-butyl phosphate (TBP) solvent diluted with an inert hydrocarbon such as n-dodecane or *n*-paraffin. The main steps of the process are as follows-

- Decladding
- Dissolution
- Feed conditioning

- Co-decontamination and partitioning cycle
- Final purification of uranium and plutonium and reconversion to their oxides

The first three steps together are also referred as head-end treatment. Cladding material and decladding technique vary depending upon the reactor type. Generally, aluminium is used as cladding material in research reactors where natural uranium metal is used as the fuel. Chemical decladding using alkali is employed to remove the aluminium jacket preferentially leaving the fuel rod undissolved which is dissolved in concentrated nitric acid. In power reactor fuel assemblies, zircaloy is used as the cladding material. The decladding method followed is mechanical where the zircaloy is chopped and remains undissolved while uranium is leached using concentrated nitric acid. Similar method is followed in FBRs where stainless steel is used as the cladding material.

After the decladding step, the dissolver solution is conditioned before it is ready for solvent extraction. Feed clarification, adjustment of feed acidity, adjustment of oxidation state of Pu and concentration of uranium are main steps followed at the head end. Feed clarification is done to avoid choking, plugging and emulsification during extraction. The free acidity is kept as ca. 2-3 M which is optimum to obtain the extraction of the required component to get the maximum decontamination from fission product nuclides. Since Pu^{4+} exhibits highest extraction by TBP as compared to the other oxidation states of Pu, it is required to adjust accordingly using sodium nitrite or nitrogen dioxide gas. These reagents oxidise Pu(III) to Pu(IV) and reduce Pu(VI) to Pu(IV). Uranium exists in its most stable and extractable hexavalent state (UO_2^{2+}) in the dissolver solution. The concentration of uranium is kept ~350 g/L so as to get maximum decontamination factor with respect to fission products. Uranium and plutonium are co-extracted into 30%TBP in n-dodecane in the co-decontamination step according to the following equilibrium reaction.

$$UO_2(NO_3)_{2(a)} + 2TBP_{(o)} \leftrightarrow UO_2(NO_3)_2.2TBP_{(o)} \qquad (1.2)$$

$$Pu(NO_3)_{4\,(a)} + 2TBP_{(o)} \leftrightarrow Pu(NO_3)_4.2TBP_{(o)} \qquad (1.3)$$

The loaded organic phase is scrubbed with nitric acid (2-3 M) for the removal of the fission products from valuable nuclear materials. Subsequently, mutual separation of uranium and plutonium is achieved by a partitioning step in which plutonium is reduced to its inextractable trivalent state by contacting the loaded TBP phase with an aqueous solution of a suitable reducing agent such as uranous nitrate in nitric acid medium of moderate concentration. This back extracts the plutonium from the loaded organic phase leaving behind uranium in the organic phase. After complete partitioning, uranium is back extracted with 0.01 M nitric acid. The uranium and plutonium product streams are again purified by solvent extraction/ion exchange processes. Finally, plutonium is precipitated as oxalate and calcined to its oxide whereas uranium is precipitated as ammonium diuranate before its conversion to its oxide. More than 99.9% of uranium and plutonium can be recovered in a properly designed process.

PUREX process generates two major high active waste, namely, the undissolved metal fuel cladding usually zircalloy or stainless steel and the acidic solutions containing an important source of useful and stable radio nuclides such as neptunium, americium, curium and the small amounts of unrecovered uranium and plutonium along with highly radioactive fission products such as ^{137}Cs, ^{90}Sr, ^{144}Ce, ^{106}Ru, ^{95}Zr, ^{147}Pm, $^{152\text{-}154}$Eu etc. This acidic waste is referred to as the high active waste (HAW). This radioactive waste solution containing various fission products is concentrated about 10 times by evaporation for volume reduction and its acidity is adjusted between 3-4 using formaldehyde. The concentrated waste solution is known as the high level liquid waste (HLLW) solution.

1.4 Nuclear Waste

Different types of wastes, namely gaseous, liquid and solid are generated in the various steps of nuclear fuel cycle, and they need treatment depending on the levels of radioactivity, physical state and chemical nature. The main sources of radioactive liquid waste are the reactors and the reprocessing plants. These wastes contain a wide spectrum of fission products in varying concentrations, most of which are beta- gamma emitters while the actinides are mostly alpha emitters. In addition, inert materials like corrosion products are also present. The radioactive liquid wastes, are broadly classified into five categories (10) based on their activity (**Table 1.1)**. These wastes are also conventionally classified as potentially active (PAW-Cat.1), Low level (LLW-Cat.2), intermediate level (ILW-Cat.3) and high level (HLW-Cat.4 and Cat.5) wastes. Effluents containing significant quantities of alpha active isotopes (actinides) in addition to beta gamma activity are termed as alpha waste. Reprocessing plants generate all types of wastes, whereas effluents received from reactors, are generally of low and intermediate levels.

Table 1.1: Classification of radioactive wastes

Category	Solid	Liquid	Gases
	Surface dose (mGy/h)	Activity level (Bq/m^3)	Activity level (Bq/m^3)
I	< 2	$< 3.7 \times 10^4$	-
II	2 to 20	3.7×10^4 to 3.7×10^7	3.7 to 3.7×10^4
III	> 20	3.7×10^7 to 3.7×10^9	$> 3.7 \text{ x } 10^4$
IV	Alpha bearing	3.7×10^9 to 3.7×10^{14}	-
V	-	$> 3.7 \text{ x } 10^{14}$	-

1.5 High Level Liquid Waste

The main liquid waste generated after aqueous reprocessing of the spent fuel is HLLW which contain >99.5% of fission products, small concentrations of uranium, plutonium and minor actinides along with corrosion products. The composition of HLLW depends on several factors like type of the reactor, nature of the fuel, burn-up, cooling period, reagents added during reprocessing, efficiency of the reprocessing plant, etc. One tonne of the spent fuel from PHWR generate ~800 L of HLLW (11) and that in FBR is about 3,300 L (12). Gross activity level in the PHWR-HLLW and FBR-HLLW is about 200 Ci/L and 300Ci/L, respectively. Small fractions of the unrecovered uranium and plutonium remain in the HLLW during reprocessing. Pentavalent neptunium and trivalent transplutonium elements like americium and curium, being practically inextractable in TBP, also remain in the raffinate along with the fission products. The concentration of uranium and plutonium in PHWR-HLLW is in the range of 5-15 g/L and 15-30 mg/L, respectively (11). Concentrations of neptunium and americium are also in the same range as that of plutonium while curium is present in rather small quantities (0.05-

0.1 mg/L). On the other hand, the concentrations of americium and curium in FBR-HLLW can be as high as 300 and 5 mg/L (11), respectively. **Table 1.2** gives the inventory of the prominent fission products in typical HLLW solutions generated during the reprocessing of spent fuels from PHWR and FBR, cooled for 3 years computed using the ORIGIN code (11- 12).

Table 1.2: Fission product inventory in PHWR-HLLW and FBR-HLLW

Nuclide	$t_{1/2}$	PHWR-HLLW(11)	FBR-HLLW(12)
		Activity (Ci/L)	
^{90}Sr	28.5 y	15.10	12.12
$^{90}Y^{*}$	64.1 h	15.10	12.12
^{106}Ru	368 d	22.24	51.61
$^{106}Rh^{**}$	30 s	22.24	51.61
^{134}Cs	2.06 y	5.97	3.24
^{137}Cs	30.17 y	21.67	30.60
^{144}Ce	284.8 d	32.02	28.41
$^{144}Pr^{***}$	17.3 m	32.02	28.41
^{147}Pm	2.62 y	26.20	49.20
^{155}Eu	4.96 y	< 1.00	7.80

*In equilibrium with ^{90}Sr, ** In equilibrium with ^{106}Ru, *** In equilibrium with ^{144}Ce.

As mentioned above, HLLW generated from spent fuel reprocessing is highly hazardous and contains bulk of the radioactivity due to fission products generated during the reactor operations (9). The minor actinides (Np, Am and Cm) present in it are a potential hazard for a million years. Apart from the minor actinides the other important heat generating nuclides present in HLLW are ^{137}Cs ($t_{1/2}$ ~30.1 y) and ^{90}Sr ($t_{1/2}$= 28.5 y). The recovery of these radionuclides has a two-fold objective; firstly, their removal from HLLW facilitates the safe disposal of the latter in deep geological repository as vitrified mass (13) and secondly, the recovered radionuclide may find several societal applications (14-15). During fission, several isotopes of the fission product elements are generated. The present thesis being on Cs recovery, its isotopes produced during fission are discussed below.

1.6 Isotopes of Cesium

^{133}Cs is naturally occurring isotope of cesium which is stable while all the other isotopes of cesium, formed in the nuclear reactor, are radioactive. Various isotopes of cesium produced in the reactor are given in **Table 1.3** along with their $t_{1/2}$ (half-life) values. It can be seen that ^{133}Cs, ^{134}Cs,^{135}Cs and ^{137}Cs are major isotopes of Cs produced in the reactor, with ^{137}Cs accounting for almost 43% of the total cesium.

1.7 Decay Scheme and Applications of ^{137}Cs

In nuclear reactors, ^{137}Cs is produced as a fission product with a fission yield of ~6.4%. It is converted to its metastable state ^{137m}Ba by β^- decay (E_{max} = 0.514 MeV) with ~94.6% abundance while a fraction of it also decays directly to ^{137}Ba by emitting a 1.175 MeV β^- particle with only ~5.4% probability. The ^{137m}Ba has a finite half-life of ~2.55 minutes. After decaying to ^{137m}Ba, the excess energy is dissipated in the form of γ radiation (E_γ = 661 keV). Its decay scheme is given in **Figure 1.3.**

Table 1.3: Various isotopes of Cesium

Isotopes	Half-life ($t_{1/2}$)
^{129}Cs	1.33 d
^{130}Cs	29.2 m
^{131}Cs	9.7 d
^{132}Cs	6.5 d
^{133}Cs	Stable
^{134}Cs	2.1 y
^{135}Cs	2.3×10^{6} y
^{136}Cs	13.2 d
^{137}Cs	30.1 y

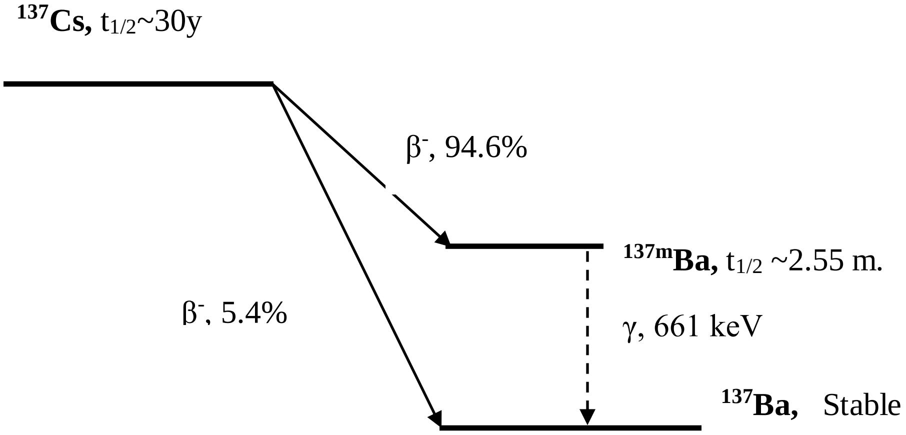


Figure 1.3: Decay scheme of ^{137}Cs

Due to its reasonably long half-life and emission of high energy gamma rays ^{137}Cs has many potential application as a radiation source $^{(13, 14)}$. It has potential to replace

^{60}Co ($t_{1/2}$ = 5.2 y, 1.173 MeV, and 1.332 MeV) as gamma irradiators. It will reduce shielding requirements and frequency of source replenishment. ^{137}Cs based gamma ray irradiator can also be used in various other applications. Some of them are listed below:

- Self-shielded ^{137}Cs sources have been used in blood irradiators.
- Irradiation of food samples kills the harmful microorganisms and bacteria resulting in increased shelf life of the food items.
- Different medical products and accessories can be sterilized by the use of gamma ray irradiation.
- Disinfection of sewage sludge by gamma radiation is done in order to render it suitable as a fertilizer or soil conditioner in the urban environment.
- It is also used in brachytherapy for treatment of certain types of cancer.
- It is widely used in construction industry for level, flow, moisture and thickness gauging applications.
- ^{137}Cs radiotracer is also commonly used in oil well drilling.
- A gamma camera, also called a scintillation camera, is a device used to image gamma ray emitting radioisotopes, a technique, known as scintigraphy.

Separation of these useful radionuclides such as ^{137} Cs is important not only for the metal values but also from the point of view of safe disposal of these wastes. Several methods are reported in the literature for the separation of radionuclides from HLLW. A brief description of some of the commonly employed separation techniques is given below.

1.8 Separation Methods

1.8.1 Precipitation

Precipitation is one of the simplest and oldest methods of separation in which a constituent from solution is separated in the form of precipitate by adding a suitable precipitating agent. The principle of precipitation method is based on ionic and solubility products. Precipitation takes place when the ionic product exceeds the solubility product. Parameters such as the solubility of the precipitate, settling time, time required for filtration, washing etc. are very important steps in precipitation technique. A slight excess of the reagent is generally required to ensure the complete precipitation. Oxalate, phosphate, hydroxide, fluoride, etc. are some of the precipitation routes that are followed in analytical separations. Although precipitation has been used in cases, it poses several limitations like handling of precipitates, poor recovery due to co-precipitation of other radionuclides, difficulties in the filtration etc. Precipitation is generally used for macro quantities of the substance whereas for lower concentrations, co-precipitation is carried out and further separation is required after co-precipitation.

1.8.2 Ion exchange

Ion-exchange resins find many applications in nuclear industry for the purpose of purification as well as separation of radionuclides (16). Anion-exchangers are regularly used for the purification of uranium in its mining and for the purification of plutonium in PUREX process. Cation exchange resins play important role in the separation of actinides, lanthanides and several fission products. Organic ion-exchangers find limited scope in separations involving HLLW solutions due to high radiation field. They undergo degradation leading to partial decomposition of the ion-exchange material and delinking of functional groups with the generation of gaseous products. Inorganic ion-exchangers like sodium titanate, sodium niobate, sodium zirconate, zirconium phosphate, etc. (17,18) seem to be superior to organic ion exchangers as they have higher radiation stability.

1.8.3 Solvent extraction

Solvent extraction is a popular separation technique because of its elegance, simplicity, speed and applicability to both trace and macro amounts of metal ions. It is based on the distribution of a solute in two completely immiscible liquids. Normally, one of the liquid phases is an aqueous solution and the other an organic solvent. The ratio of the concentration of the solute in the two phases at equilibrium is known as distribution ratio (D), and is expressed as:

$$D = \frac{\text{Total concentration of the solute in the organic phase}}{\text{Total concentration of the solute in the aqueous phase}} \qquad (1.4)$$

It can be calculated that if V_a mL of aqueous solution containing x_0 g of a solute be extracted n times with V_o mL of a given solvent, then the weight of solute remaining (x_n) in the aqueous layer is given by the expression

$$x_n = x_0 \left(D\,V_a / (D\,V_a + V_o)\right)^n \qquad (1.5)$$

Where, D is the distribution ratio between aqueous and the organic solvent. Using distribution ratio, percentage extraction of metal is calculated as

$$E\,(\%) = \frac{100 \times D}{D + (V_a / V_o)} \qquad (1.6)$$

Extraction may be accomplished in either batch operation or a continuous operation. Removal of the extracted solute from the organic phase is called as ‘stripping’ or ‘back extraction’.

1.8.4 Extraction chromatography

Extraction chromatography is an emerging field with wide application in the separation and purification of metal ions in relatively smaller scale involving lean feeds. It combines the advantages of ion-exchange with those of solvent extraction. This technique uses an organic solvent, impregnated on co-polymeric or inorganic inert supports like chromosorb-102, XAD-4, XAD-7, silica gel, alumina etc. When operated in a column mode, it is possible to separate the metal ions by adjusting parameters such as the column length, particle size, flow rate, etc.

1.8.5 Liquid membrane based separations

Liquid membrane (LM) based separation methods (19) which function on the principle of solvent extraction offers certain distinct advantages over the solvent extraction based methods. The advantages may be summed i) as simultaneous extraction and stripping, ii) lesser space requirements, iii) low energy consumption, iv) low solvent inventory and hence, v) lower capital/operating costs. Furthermore, it provides opportunities for use of even expensive reagents. Liquid membranes usually consist of a water immiscible (organic) layer separating a source and a receiving aqueous phase. The organic phase may be a dispersion of water containing oil droplets in water known as Emulsion Liquid Membrane, (ELM) or a stirred membrane phase with a higher density than the aqueous phases positioned on top of it known as Bulk Liquid Membrane (BLM). Supported liquid membrane (SLM) based separation technique is discovered about five decades ago and is fast emerging as potential separation and concentration media for extremely low metal values in the field of radioactive waste management. The advantages of SLM over the above conventional techniques are:

(1) Simultaneous extraction and stripping,
(2) Possibility of achieving high separation factors,
(3) Economic use of expensive extractants,
(4) Possibility of concentrating the recovered metal ion species during separation itself,
(5) Lower capital and operating costs,
(6) Lesser space requirements and
(7) Low energy consumption.

In case of SLM the organic phase is immobilized in the pores of a polymeric support. Commonly, two types of configurations are used in SLM systems such as flat sheet and hollow fiber. At the source / organic (or membrane) phase inter phase aqueous solutes are complexed, the carrier solute-complex diffuses in the direction of the organic / receiver phase inter phase and decomplexation takes place in the receiver phase. However, in practice, during the transport process, several chemical equilibria as well as diffusive and kinetic resistances may be involved. By variation of materials and experimental conditions, the kinetics and mechanism of carrier mediated transport can be elucidated. Preliminary data required for the development of SLM based separation scheme are gathered from conventional solvent extraction studies which optimizes the transport conditions for metal ions employing organic solvents as carriers after supporting them in suitable polymer supports such as polytetrafluoroethylene (PTFE). A schematic diagram of the concentration profiles of the transport cell under steady-state conditions is shown in **Figure 1.4.**

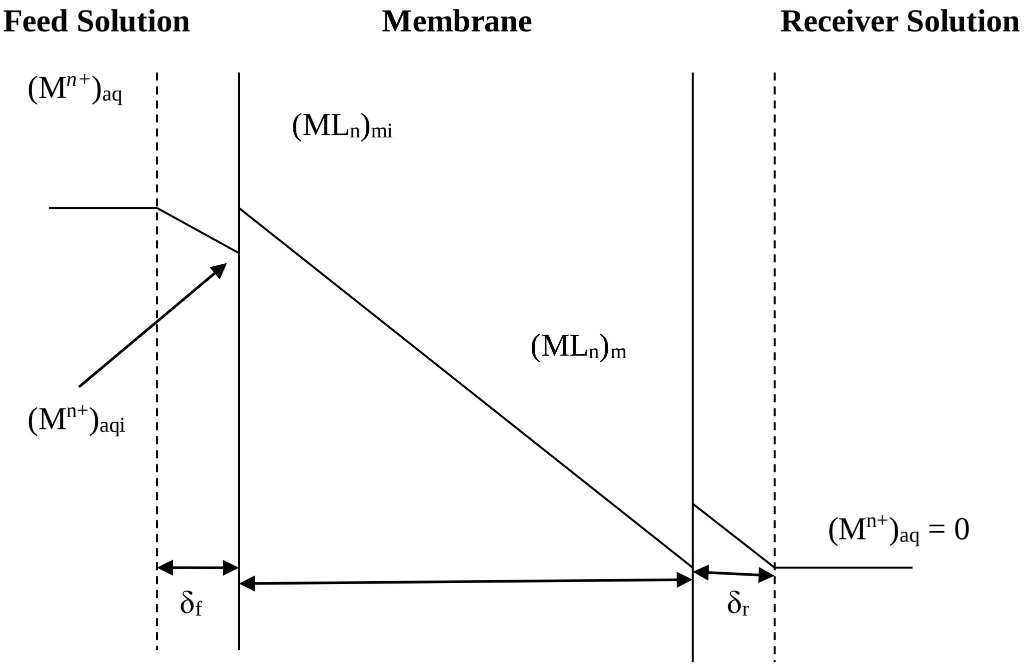


Figure 1.4: Schematic presentation of metal ion transport through membrane

In the feed and receiver solution, there are no concentration gradients due to efficient stirring, whereas at the interface there is a stagnant aqueous film (Nernst layer) whose thickness depends on stirring and cell geometry. The first work in this field was reported by Block et al (20) on carrier-mediated transport of uranium through plasticized membranes coated with neutral organophosphorus esters.

Prime requirement for a successful liquid membrane system is the choice for a selective and efficient carrier for the species to be separated. Liquid membranes may be divided into two categories, *viz*. non-supported liquid membranes (non SLM) and supported liquid membranes (SLM).

In the case of non-SLMs, the most common types are bulk liquid membranes (BLM) and emulsion liquid membranes (ELM). SLM's again can be categorized into two types as mentioned above, *viz.*, flat sheet supported liquid membrane (FSSLM) and hollow fiber liquid membrane (HFSLM). A short description of these liquid membrane techniques is discussed below.

1.8.5.1 Non-supported liquid membrane

1.8.5.1.1 Bulk liquid membranes (BLM)

BLM, consisting of a bulk organic phase separating two aqueous phases (feed and receiver), is an extremely simple system, less expensive and uses small amounts of mobile carrier. Here, the mass transfer from the feed to receiver takes place through a carrier. As the transport through the bulk liquid membrane phase takes place by convection, the unstirred boundary layer often gives the largest transport resistance. BLMs are excellent systems for screening all kinds of ionophores, which need not be highly lipophilic. They have found frequent applications to investigate novel carriers / carrier systems or transport mechanisms. It`s main function is to optimize the data for both SLM and ELM systems. Schematic of a bulk liquid membrane system is given in **Figure 1.5**.

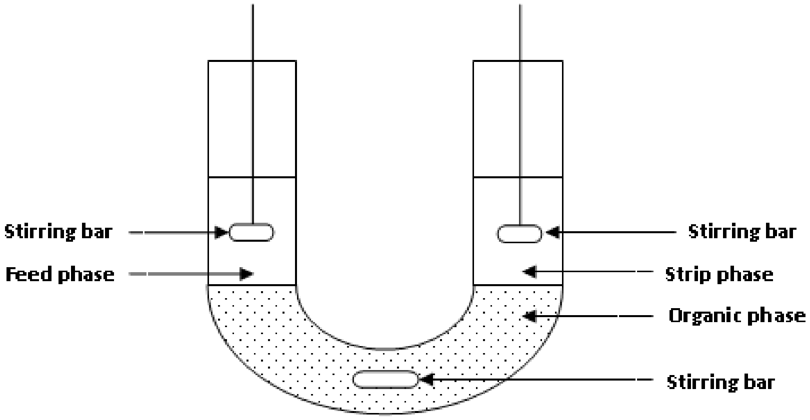


Figure 1.5: Schematic of bulk liquid membrane

1.8.5.1.2 Emulsion liquid membranes (ELM)

ELM is essentially a double-emulsion system (**Figure 1.6**) which can be either water-oil-water or oil-water-oil type. This can be made by stirring a water-oil-water (w/o/w) emulsion into a water source phase. The w/o/w emulsion is stabilized by a surfactant, such as SPAN-80. This emulsion is then dispersed in a continuous phase.

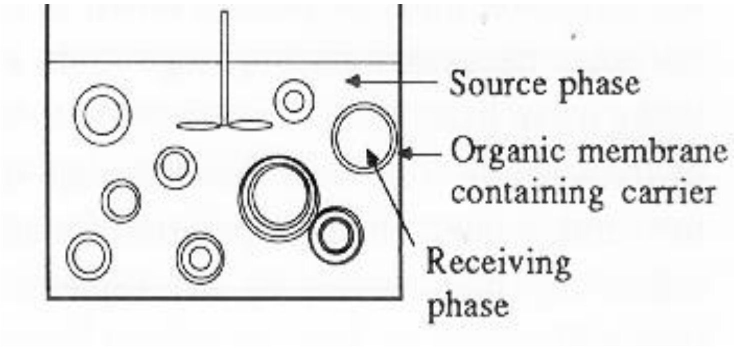


Figure 1.6: Schematic of emulsion liquid membrane

Mass transfer takes place between the continuous phase and the inner phase through the immiscible (membrane) phase. In both purification and recovery applications, the ELM must be demulsified into two immiscible phases after the extraction step. This is done commonly by heating, centrifugation, application of electric fields, spiking an organic solvent, etc. The liquid membrane phase containing the surfactant and carrier will be recycled to the emulsion preparation step while the internal major advantages over BLM and SLM. Firstly, the transported species can be enriched several fold since the receiving phase volume is quite less compared to that of the feed phase. Secondly, the rate of permeation is extremely rapid. Carriers can increase the solubility and selectivity of the metal ion of interest, which also enhances the mass transfer rate and separation efficiency. Since the selection of carriers plays a very important role in carrier-facilitated transport, various kinds of carriers have been exploited for this purpose. In most studies, however, commercial surfactants such as SPAN-80 and polyamine have been used. Recently, a host of novel surfactants having long alkyl chains have been developed by Goto et al (19-20). In comparison with SLM, the transport mechanism of ELM is very complicated. Although ELM excels the BLM and SLM in terms of simplicity and rapidity, owing to the large specific area and thinness of the membrane, the process has limitations that the de-emulsification is necessary for recovery of the concentrated drops, and also the poor stability and swelling of the emulsions.

1.8.5.2 Supported liquid membranes (SLM)

In the SLM system, the feed phase and the receiver phase are separated by a polymeric filter containing the membrane phase containing carrier ligand supported on a polymeric support material. There are two types of supported liquid membranes

i) Flat sheet supported liquid membrane (FSSLM) and
ii) Hollow fiber supported liquid membrane (HFSLM).

1.8.5.2.1 Flat sheet supported liquid membranes (FSSLM)

In case of flat sheet supported liquid membrane (FSSLM), the feed and receiver phases are separated using the organic extractant solution supported on the flat sheet polymeric support material. A schematic presentation of the FSSLM system is given in **Figure 1.7**. The feed and the receiver phases are constantly stirred using magnetic stirrers in order to minimize the aqueous diffusion layer. FSSLM systems are usually associated with slow transport rates.

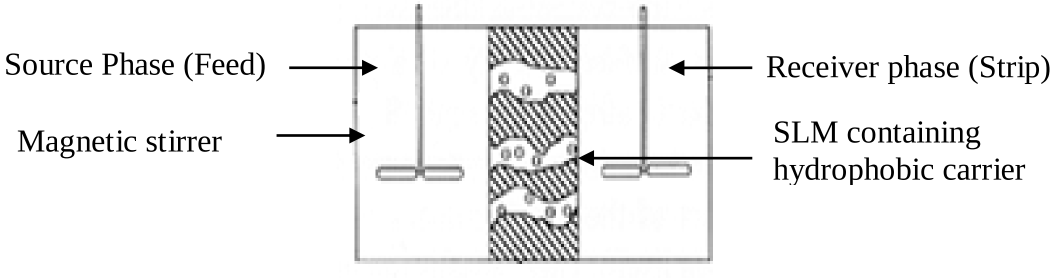


Figure 1.7: Schematic of the flat sheet supported liquid membrane system

1.8.5.2.2 Hollow fiber supported liquid membranes (HFSLM)

Higher mass transfer can be achieved by increasing the membrane surface area many fold using the hollow fiber polymeric support material in place of the flat sheets. The outer shell consists of nonporous material. Inside that shell, there are many thin fibers running along the length of the shell, all in neat rows. The liquid membrane is created by pumping the carrier solution inside the module at low pressure, followed by washing with plenty of water. The feed and the receiver phases are circulated around these fibers through the lumen side and the shell side, respectively in a counter-current direction without allowing mixing of the phases. If the feed and the receiver phases are moving along the same direction, then it is termed as co-current mode while an opposite flow mode is termed as counter-current mode. Non-dispersive extraction takes place when the organic ligand solution is circulated in place of the receiver phase in a counter-current direction. Schematic presentation of the hollow fiber assembly is shown in **Figure 1.8**.

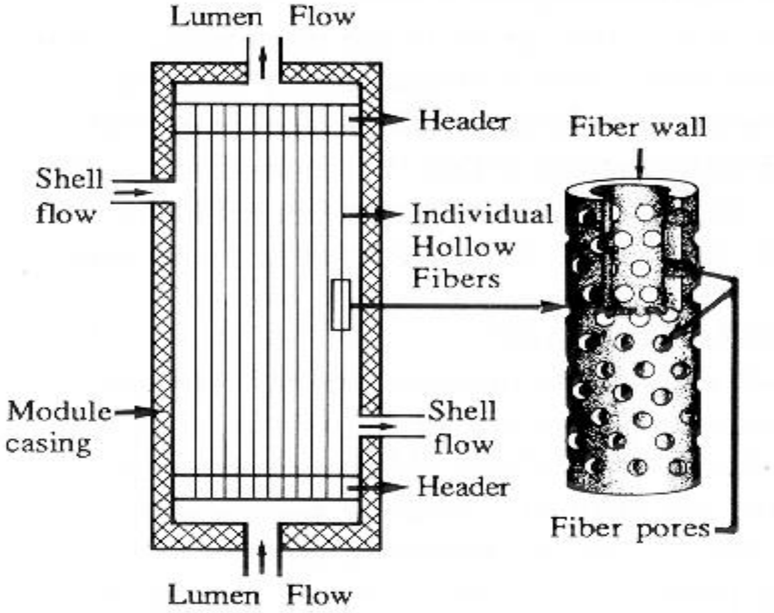


Figure 1.8: Schematic diagram of the hollow fiber supported liquid membrane system and cross section of a hollow fiber

Support materials are generally made from polymers such as polytetrafluoroethylene (PTFE), polypropylene (PP), polysulfone (PS), or other suitable hydrophobic materials that have pore sizes ranging from 0.02 to 1.0 µm. In SLM, where the acidity is different in the two aqueous phases, transfer can take place against the concentration gradient of the permeant, the carrier is forming a complex at one side of the membrane (in feed phase) which then breaks down to liberate the species in the receiving phase. This carrier-mediated transport of solute is controlled by diffusion and the reaction kinetics of the extraction and stripping steps. The advantages of SLM over other conventional techniques are (i) possibility of achieving high separation factors, (ii) economic use of expensive extractants, (iii) possibility of concentrating the recovered metal ion species during the separation itself, (iv) lower capital and operating costs, (v) low energy consumption, etc.

1.8.5.3 Criteria for the selection of membrane support

Both the chemical composition and the structural characteristics of the polymeric support play an important role in cation permeability. In SLMs, numerous support materials are available; mostly made from polypropylene, e.g., Celgard, Accurel etc. Some Teflon membranes (PTFE) are also in use and readily available from various manufacturers. The diffusion-limited flux through a SLM is mainly influenced by the porosity and tortuosity (ratio of length of the pore to the membrane thickness) factors of the support material. The pore size is very important in the evaluation and characterization of porous membrane, in particular for the pressure driven separation processes such as the ultrafilteration (UF) and microfiltration (MF) membranes. Pore size plays an important role in the transport of a desired metal ion as well as in the stability of the SLMs. For achieving better flux, a membrane support should have higher porosity, lower thickness and small pore size. The microporous polymeric support should meet the following intrinsic requirements: i) high porosity, ii) small pore diameter, iii) small thickness, iv) hydrophobic, v) resistance to toxic environments and vi) low cost.

The degradation of SLM mainly depends on the physico-chemical changes taking place in all the species involved in the transport system. The membranes may be unstable because of the loss of single components from the membrane, their chemical instability or the complete loss of the membrane phase. For checking the stability of the membrane system, the membrane is tested by a continuous operation i.e., by replacing the aqueous phase periodically and simultaneously monitoring the transport rate.

The rate and mechanism of facilitated transport of metal ions through FSSLM was described by Danesi et. al (21-22). The physiochemical model used to describe the permeation rate is given by the following generic equation:

$$\mathrm{Ln}[A_t]/[A_0] = -\ (A.\varepsilon\ /V)\ P.t \qquad (1.7)$$

where $[A_0]$ is the concentration of metal ion in feed at t = 0, $[A_t]$ the concentration of metal ion in feed at time t and P is the permeability coefficient. In the above equation, P is time independent and hence flux is linearly decreasing with time. A plot of $\ln[A_t]/[A_0]$ *vs* time allows one to evaluate the permeability coefficient during transport.

1.9 Separation of Radiocesium

Extensive work has been carried out on the separation and recovery of ^{137}Cs from alkaline/acidic feed solutions employing various separation techniques as described below.

1.9.1 Precipitation method

Sodium phosphotungstic acid, $Na_3[P(W_3O_{10})].4H_2O$ has been used for Cs(I) recovery from acidic wastes. Phosphotungstate anion, reacts with Cs(I) ion in aqueous medium containing 0.5 to 2.0 M HNO_3 medium to form an insoluble precipitate. The precipitate can be dissolved in sodium hydroxide solution to recover Cs. The method was used for the recovery of radio-cesium from the PUREX waste at Hanford site, USA (23). Barton et al., (24) noted that cesium alum precipitates are bulky and non-selective. Alum co-precipitation method was used at the Oak Ridge National Laboratory (ORNL) to separate cesium for commercial use (25). Since the goal was commercial use, purity rather than yield was of primary importance.

1.9.2 Ion-exchange methods

Ion-exchange methods have also been employed for the recovery of radiocesium from aqueous feed solutions. Both inorganic as well as organic ion-exchangers are found effective for radio-cesium removal from waste solutions. The various inorganic ion-exchangers used for this purpose include phosphates, titanates, ferrocyanides, oxides, etc. Copper ferrocyanides [$CuFe(CN)_6].nH_2O$], some heteropolyacids (ammonium molybdophosphates, AMP), ammonium tungustophosphates and Zeolites (e.g., clinotilotite and modernite) have been shown to be effective ion-exchanger for cesium recovery (26). Inorganic ion-exchangers are known for high radiation stability, good selectivity, reproducible stoichiometry and compatibility with glass or ceramic waste materials. But the high costs of these inorganic ion-exchangers have been the limiting factor in the application of these methods in plant scale operations.

1.9.2.1 Ferrocyanides and phosphates

Metal ferrocyanides (27) *viz.* copper ferrocyanide [$CuFe(CN)_6].nH_2O$] and potassium titanium ferrocyanide $KTiFe(CN)_6$ have been found to be excellent with respect to the kinetics of uptake, ion-exchange capacity and selectivity for cesium ion but the chemical instability of these ion-exchanger in the acidity range of 0.5-1.0 M is one of the major disadvantages of these materials. Molybdenum ferrocyanide is found to be much more unstable under acidic conditions. The poor selectivity of these ferrocyanides is another serious issue (27). Zirconium hydrogen phosphate has been found to be an excellent sorbent for cesium in the pH range of 2-10 (28).

1.9.2.2 Titanates

Studies on various titanates and silicotitanates were carried out during 1975-78, by the researchers at the Sandia National Laboratory (29) and the use of sodium titanate material was done at Hanford during the same time period (30). It was possible to impregnate sodium titanate onto a resin. Although the capacity for cesium was not high enough, loading of higher concentration of sodium titanate onto the resin could improve the Cs uptake capacity. Crystalline silicotitanates (CST) has been applied for radiocesium recovery from the high-level tank wastes at Hanford. Zeolite materials (31) were also tested for the recovery of Cs from actual tank wastes. Although silicotitanates worked well they could not be accepted due to less characterized data available at that time but the Zeolite materials were not accepted due to poor loading capacity for cesium (~ 1 g/kg of Zeolite) compared to other materials like AMP. Recovery of cesium from the ion-exchanger was not efficient and hence loaded exchanger is treated as final waste form. Commercially, the CST exchangers are available as trade name IONSIV® IE-911 and have been explored by research groups at the Idaho National Engineering and Environmental Laboratory (INEEL) (32,33). The issues regarding the stability of these exchangers and elution properties are yet to be investigated in detail.

1.9.2.3 AMP

Ammonium molybdophosphate (AMP) is a crystalline dark yellow compound having the chemical formula $(NH_4)_3PMo_{12}O_{40}.3H_2O$. The polyhedra consist of porous sphere of 12 MoO_3 octahedra with phosphate group at the centre (34). It is well known that ammonium molybdophosphate (AMP) is an ion-exchanger of very high selectivity for cesium from salt loaded acidic solutions (35- 36). The cesium exchange mechanism has been explained as exchange of cesium with the ammonium ion in the crystal lattice (37). The selectivity for cesium over other alkali metal ions has been reported by Smit et al. (38) The main disadvantage of ammonium molybdophosphate is its microcrystalline structure which makes the column operation difficult. In view of this, AMP is immobilized on some solid support (called ‘binder’) while using column mode. The exchanger, ammonium molybdophosphate-alumina (AMP-A1203) in which alumina acts as a binder, showed better characteristics like better flow rates, radiation stability, performance of adsorption desorption cycles etc.(39). Poly-acrylo nitrile (PAN) has also been used as binder for AMP by various research groups (40-41). The support material has been found not to affect the cesium uptake behaviour by AMP. At INEEL, recovery of cesium from synthetic high level nuclear waste (acidity ~ 3 M) was studied (42). Once the column is loaded, AMP is separated and dissolved in NaOH solution, thus yielding a much smaller volume of HLLW. Various groups have investigated the radiation stability of AMP and found it to be quite good upto 1 MGy dose. The cesium uptake behaviour has been found to be unaffected while radiation dose affects the binding ability of AMP with the solid support. At higher radiation doses leaching of AMP from the support is reported which results in the degradation of the resin. The advantages of AMP are given below.

- Sufficiently high distribution coefficient in moderately high acidic medium
- High Cs-loading capacity compared to other ion-exchangers
- High selectivity for Cs(I) ion
- Faster Cs-uptake
- Easily soluble in alkaline solution

However, certain disadvantages, as listed below, are also known.

- Difficulty in the elution of the absorbed Cs
- Microcrystalline nature of AMP makes column operation difficult
- The high loading in the AMP results in high radiation doses in and hot spots in the column.

1.9.2.4 Flexible sulphide framework for cesium recovery

A new class of inorganic ion-exchanger consisting of combination of $[(CH_3)_2NH_2]^+$ and $[Ga_2Sb_2S_7]^{2-}$ ions has been reported for cesium recovery (43). The framework composed of $[(CH_3)_2NH_2]^+$ and $[Ga_2Sb_2S_7]^{2+}$ layers perforated with holes. Shape selectivity couples with framework flexibility, allowing the compound to respond to the ion-exchange process. The size, shape and flexibility of the holes allow Cs^+ ions in an aqueous solution to selectively pass through and enter the material via an ion-exchange process. Following capture, the structure dynamically closes its holes in a manner reminiscent of a Venus flytrap (44), which prevents the Cs ions from leaching out. The back extraction of cesium from the loaded exchanger is a difficult task in this case also, which is the major drawback of this material. This study improves our understanding of selective ion capture and points to new insights on how to design compounds for practical applications such as the removal of radioactive ^{137}Cs from nuclear waste.

1.9.3 Solvent extraction

Solvent extraction methods have been widely used for cesium recovery using various reagents. As mentioned above, high throughputs, ease of operation, high selectivity are some of the advantages of solvent extraction methods which make them more attractive for separation scientists and technologists. Cesium ion being monovalent in nature is very difficult to extract from the solution using common extractants. Since the size of cesium ion is large (ionic radius: 1.69 A^{o}) compared to other alkali metal ions, it is the least hydrated ion in the solution. This property is made use of in the extraction of cesium by hydrophobic anions like chlorinated cobalt dicarbollide (CCD). On the other hand, crown ethers have been found to be size-selective extractants which bind selectively with a particular alkali / alkaline earth metal ion having size compatibility with the cavity size of a suitable crown ether.

1.9.3.1 Crown ethers

The discovery of crown ethers by Pederson (45) was a pioneering effort in the field of supramolecular chemistry. Crown ethers are cyclic polyethers forming a cavity having crown like shape; hence, the name crown ether is given to this class of molecules. Various crown ethers have been synthesized and are named according to the number of total atoms and number of oxygen atoms in the cyclic ring e.g. 15-crown-5 stands for a crown ether having 15 atoms (carbon and oxygen) and 5 oxygen atom in the cyclic ring of crown ether **Fig.1.9** shows structures of various crown ether molecules.

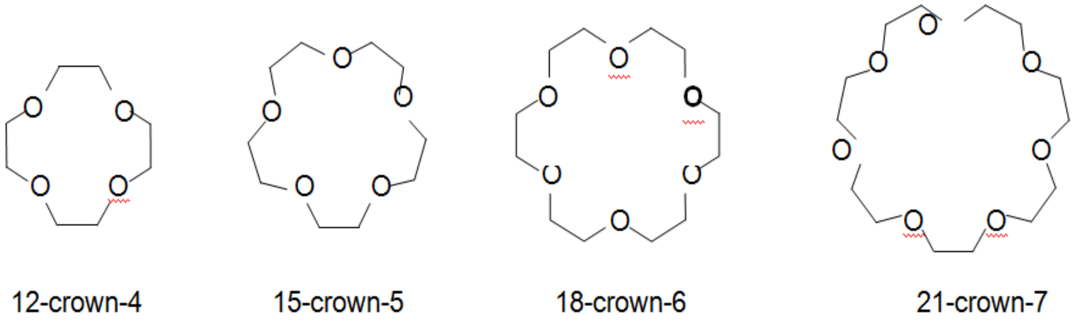

12-crown-4 15-crown-5 18-crown-6 21-crown-7

Fig. 1.9: Structural formulae of various crown ethers

The major factors governing the binding of metal ion with the crown ether are:

1) Cavity size of the crown ether,

2) The hydration of metal ion in the solution and

3) Substituents on the crown ether ring.

Cavity size of the crown ether plays an important role in the binding of the metal ion. It has been observed that metal ions having good size compatibility with the cavity of crown ether, bind more strongly with the particular crown ether. Cation-dipole interactions are responsible for the metal ion complexation with crown ethers (**Fig. 1.10**).

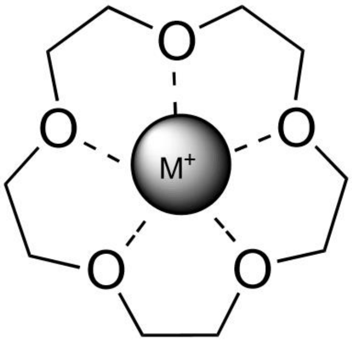


Fig. 1.10: Cation-dipole interactions between metal ion and crown ether

The cavity sizes of different crown ethers had been calculated by various groups using the Corey-Pauling-Koltun (CPK) model. The cavity size of different crown ethers and ionic size of various ions are given in **Table 1.4**.

Table 1.4: Ionic size of various alkali / alkaline earth metal ions and cavity size of different crown ethers

Metal ion	Ionic size (Å)	Crown ether	Cavity radius (Å)
Na^+	0.95	12-crown-4	0.67±0.07
K^+	1.33	15-crown-5	0.97±0.12
Rb^+	1.48	18-crown-6	1.45±0.15
Cs^+	1.69	21-crwon-7	1.92±0.23
Sr^{2+}	1.13	24-crown-8	2.25±0.28
Ba^{2+}	1.43	-	-

Crown ethers are stereo specific extractants as they have a cavity structure that can be highly selective for the alkali and alkaline earth metal ions such as Cs^+ or Sr^{2+}. The substituents on the crown ether ring have been found to have crucial effects on the extraction chemistry of metal ions.

Early work on crown ethers as extractants for cesium and strontium was performed by Gerow et al. (46) at the University of South Carolina and also by Kinard et al.(47) at the Oak Ridge national Laboratory. Researchers at the Argonne National Laboratory developed dibenzo-18-crown-6 ether for the selective recovery of cesium. The substituent groups make the geometry of the crown ether molecule rigid and thereby making it more selective for a particular metal ion. The interaction between the pi-electron cloud of benzo group and the cesium ion is considered to be one of the reasons for the higher selectivity (due to cation-pi interaction) of dibenzo-18-crown-6 for cesium ion over other alkali metal ion. Since the size of Cs^+ ion is bigger than the cavity size of this crown ether, it is observed that the cesium ion sits above the cavity of molecule and coordinate with two crown rings in a sandwich type structure. McDowell et al. (1992) suggested di-tert-butyl-dibenzo-21-crown-7 to be a better extractant for cesium as compared to its unsubstituted homologues. Their studies using 0.5 M of this reagent with di-*n*-dodecyl naphthalene sulphonic acid (HDDNS) in toluene, indicated the possibility of cesium extraction from 0.1 M acidity (48). The nature of the diluent also affects the extraction ability of crown ether significantly. Crown ethers are the least soluble in non-polar diluents and hence, polar diluents are used to prepare their solutions. The polarity may be introduced in the molecule due to the presence of large number of oxygen atoms in the molecule. In addition to this, the polar diluents also stabilize the ion-pair formed and increase the extraction ability of the crown ether.

Blasius et al. (49-50) tested various crown ethers and reported that cesium can be extracted from acidic solutions using dibenzo-21-crown-7 in polar diluents like nitrobenzene, nitro-methane, etc. Under the PUREX process conditions, a solvent comprising of 0.05 M of bis-(4,4'(5')-[1-hydroxy-2ethylhexyl]-benzo)-18-crown-6 (**Figure 1.11**) in 5% nonyl-naphthalene sulphonic (NNS) acid with 27% tri-butyl phosphate (TBP) – 68% kerosene was used by Shuler et al. (51) for cesium recovery (D_{Cs} = 1.6) but the contamination of Zr was observed and attributed to the well known affinity of TBP for Zr.

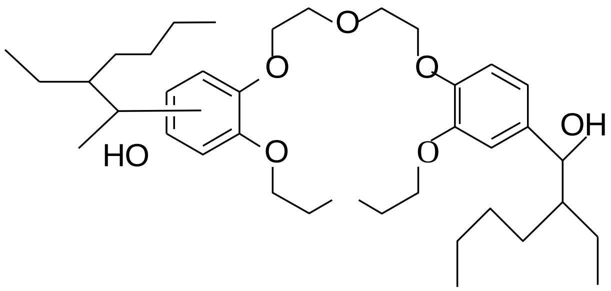
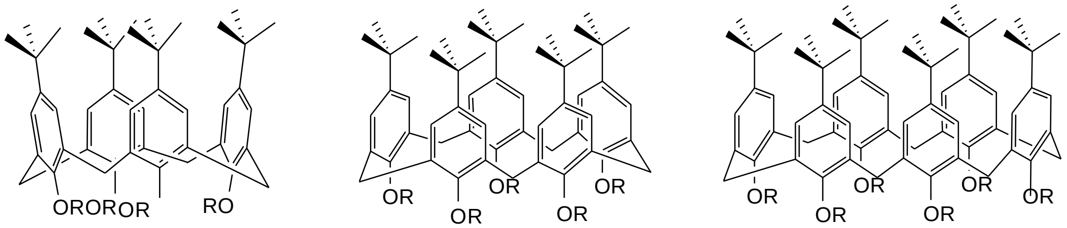


Figure 1.11: Structural formula of bis-(4,4'(5')-[1-hydroxy-2-ethylhexyl]-benzo)-18-crown-6

The primary disadvantages of the crown ethers have been chemical and radiolytic instability, possibility of third phase formation and their high cost. At present, there is no feasible process for the recovery of Cs which can be applied on plant scale based solely on crown ethers.

1.9.3.2 Calixarenes and calix-crown-6 ethers

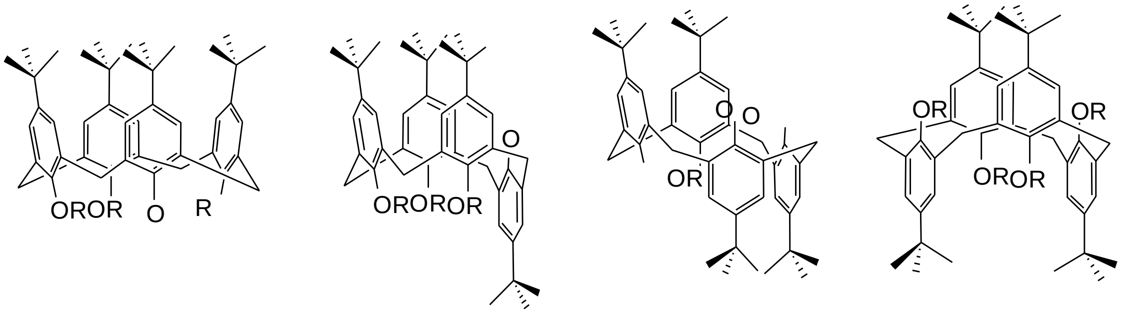
Calixarenes are another class of macrocyclic compounds that have been used for the selective metal ion extraction. Calixarenes are formed by coupling of benzene moieties via methylene (>CH_2) linkers. Some typical calixarene structures are shown in **Fig. 1.12**.



Calix[4]-arene Calix[5]-arene Calix[6]-arene

Fig. 1.12: Structural representation of different calixarenes

Calixarenes are found in various conformations *viz.*, cone, partial cone, 1, 2-alternate, 1, 3 alternate conformations as shown in **Figure 1.13**.



Cone Partialcone 1,2-alternate 1,3-alternate

Figure 1.13: Different conformations of calix [4] arenes

Earlier studies of Zinke et al (52), suggested that the calix[4]arenes are capable of extracting alkali or alkaline earth metal ions. The substituents on calix[4]arene framework are responsible for the extraction of different metal ions. Introduction of *p-tert*-butyl group on the molecule increases the cesium extraction by the calix[4]arene. The substitution by ketone /ester group on calix[4]arene makes it susceptible for alkali metal ion extraction. Izatt et al. were the first to report the recovery of cesium and other alkali metal ions by *p-tert* butyl substituted calixaranes using bulk liquid membranes (53). These calixarenes offer certain advantages *viz.*, lower water solubility, radiation stability, selective nature etc. Calixarenes are soluble in polar organic diluents like nitrobenzene, dichloromethane etc. and have been used for cesium recovery. The efficiency of metal ion extraction decreases with increase in the size of calixarene in the following order: calix[6]arene < calix[5] arene < calix[4]arene. This may be due to the higher flexibility of the larger size molecule making the complexation weaker. In the subsequent modifications, calix[4]arenes have been coupled with the crown ether molecules which are named as calix-crowns. Various calix-crowns have been synthesized and tested for metal ion extraction (54-55). Calix[4]-arene in 1,3-alternate conformation coupled with two crown-6 rings (**Figure 1.14**) has been found to be highly selective for cesium ion (56). This is attributed to the favorable cavity size of crown ring and the cation-pi interaction between cesium ion and benzene rings (57).

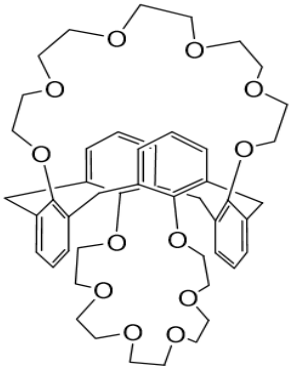


Figure 1.14: Structural formula of calix[4]arene-biscrown-6

Substitution on crown ether ring affects the extraction ability of the calix-crown ligands to a greater extent. Substitution on crown ring by benzene group enhances the cesium extraction many folds. The benzene ring can be assumed to be increasing the organophilicity of the cesium complex thereby facilitating the extraction of cesium. Haverlock et al. (58), have examined calix[4]-arene-bis(2,3-naphtho)-crown-6 (to be abbreviated henceforth as CNC, (**Figure 1.15**) for cesium recovery from acidic waste solutions and found that even at a very low concentration of this ligand, cesium can be selectively recovered from the solution with decontamination factor values > 10^2 for sodium and other metal ions. In case of calix-crowns, the ease of extraction and stripping are the major advantages. The studies revealed the possible application of calix-crown ethers for the recovery of radio-cesium from the nuclear waste of PUREX origin (59).

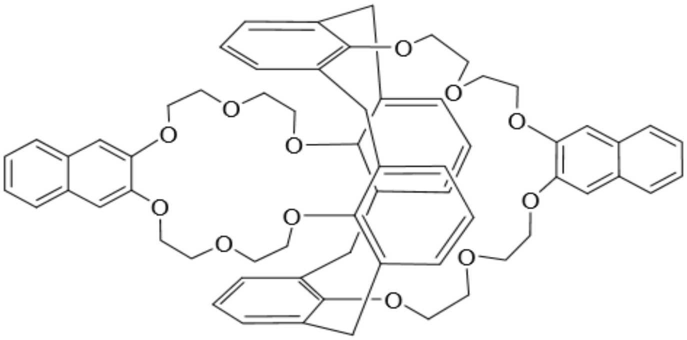


Figure 1.15: Structural formula of calix[4]arene bis(2,3-naphtho)-18-crown-6

1.9.3.3 Chlorinated cobalt dicarbollides (CCD)

CCD is a hydrophobic anion formed by coupling of two chlorine substituted-dicarbollide anions with Co(III) (60-61). The protonated form of this anion is found to be highly selective for cesium ion from low acidic solutions. The structure of CCD is shown in **Fig. 1.16**.

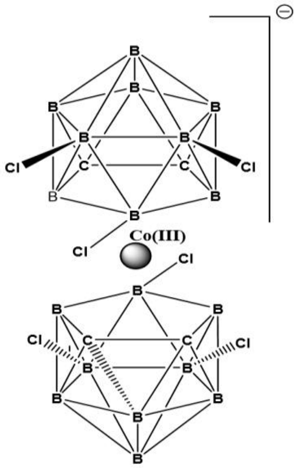


Figure 1.16: Structural formula of chlorinated cobalt dicarbollide (CCD)

It is soluble in polar organic diluents like nitrobenzene or fluorinated diluents (like phenyl trifluoro methyl sulphone or FS-13). The hazardous and corrosive nature of these diluents has always been the major drawback of using the CCD for cesium recovery on large scale though there are reports of mega-curie (MCi) level of Cs recovery in the erstwhile USSR. CCD is found to be a highly selective extractant for cesium from acidic medium. The Czech researchers reported that strontium could also be extracted along with cesium by adding polyethylene glycol (PEG) to the CCD dissolved in nitrobenzene (62). Cesium ion is the least hydrated ion in aqueous solutions compared to other metal ions and combines to the poorly hydrated CCD anion and gets transferred to the organic phase. Addition of PEG is considered to dehydrate the strontium ion and thereby facilitating the extraction of Sr along with Cs. In the UNiversal solvent EXtraction (UNEX) process, cesium and strontium are extracted along-with all lanthanides and actinides by using a mixture of 0.08 M CCD + 0.4 % (v/v) PEG400 + 0.02 M CMPO in FS-13. CCD has main advantage of being highly radiation resistant which makes it a viable candidate for its use in the treatment of nuclear waste (63). The major limitation of the UNEX process is the use of toxic / corrosive diluents. Hence, there is a need for alternative diluent to be explored for CCD and PEG mixture for Cs and Sr co-recovery from radioactive wastes in large scale.

1.10 Scope of the Thesis

The work carried out in this Thesis is mainly on the extraction of radio-cesium from acidic feeds using solutions of calix[4]arenes-crown-6 ligands. Calix-crown-6 ligands commercially obtained were used in this study as we have changed the diluents to obtain novel solvent systems which were not used previously. The calix[4]arene-crown-6 ligands were made soluble in a fluorinated solvent and also in a mixture of *n*-dodecane and iso-decanol for cesium extraction from nitric acidic medium. Results of solvent extraction studies carried out in batch mode using all the four calix [4] crown-6 ligands *viz.* calix[4]arene-bis-crown-6 (CC), calix[4]arene-bis-benzocrown-6 (CBC), calix[4]arene-bis-napthocrown-6 (CNC) and bis(octyloxy)calyx[4]arene-mono-crown-6 (CMC) under different extraction conditions. CNC is considered to be the most suitable extractant in view of its better organo-philicity. The results of effects of concentrations of nitric acid and Cs carrier in feed are also investigated and the nature of the extracted species is established using slope analysis method. Stripping of Cs from the loaded organic phase is found to be more effective when the organic phase contained Alamine 336 (0.5% v/v). A separate solvent extraction study, taken up using a mixture of *n*-dodecane and iso-decanol (3: 2 volume ratio) as the diluent suggested poor solubility of the ligands such as CC, CNC, and CBC and CMC was used for extraction in view of appreciable solubility of the extractant. The results are encouraging for the application of this solvent system to a supported liquid membrane study for which PTMS based solvent system showed poor stability over a period of several days.

Radiolytic stability studies carried out for all the four calix-crown-6 ligands by exposing to gamma rays in a ^{60}Co gamma irradiator. The stability of the ligands were tested in two ways, i) changes in the solvent extraction behaviour and ii) analysis of the degradation products. The results of irradiation of ligands up to 1000 kGy dose rates are studied. Based on the distribution ratios of irradiated and unirradited ligands, relative stability for all the ligands is evaluated on the basis of instability index. Possible degradation path ways are described based on gas chromatographic studies.

Supported liquid membrane (SLM) studies are carried out using the four calix [4] crown-6 ligands in the fluorinated diluent, PTMS (or FS-13) and the transport data for all the ligands are evaluated under different conditions. Permeability coefficients as well as diffusion coefficients are calculated from the Cs mass transfer data. CBC is found to be the most efficient ligand in these studies. On the other hand, 0.01 M CMC in 40% iso-decanol + 60% *n*-dodecane resulted in reasonably good transport with significantly better SLM stability. Based on the encouraging results, studies are extended to hollow fiber supported liquid membrane using the CMC based solvent containing the diluents mixture. At moderate acidity of ~3 M HNO_3, which is the acid concentration of the high level waste, near quantitative (>99%) transport of cesium is possible within 2 h of operation at 300 mL scale. Transport rates are found to be suppressed under simulated high level waste condition due to presence of large concentrations of cesium (0.32 g/L), though > 90% transport was observed in 6 h. The study explored the possible use of CMC in hollow fiber contactor for radioactive waste treatment where the ligand inventory is very low.

In view of the encouraging results, radio-cesium recovery was attempted from actual HLLW feeds. Selective extraction of radio-cesium from three different sets of experiments involving simulated HLLW, diluted HLLW and real undiluted HLLW is observed by using 1×10^{-3}M CBC in PTMS.Quantitative extraction of Cs is observed from real HLLW in four contacts leaving behind all the other radionuclides present in the waste. The extracted Cs from the organic phase is stripped quantitatively in only two contacts using 0.01 M HNO_3 as the strippant. Stripping is found to be more effective when 0.5 volume percent Alamine 336 is introduced in the organic solvent. The hollow fiber contactor based SLM studies carried out using 0.01 M CMC in 40% iso-decanol + 60% *n*-dodecane are found to be highly promising as ca. 90% radio-cesium recovery is reported which matched very well in repeat experiments. Furthermore, the hollow fibers are found to be quite stable even after keeping in contact with the radioactive feed for about 50 days as indicated by almost reproducible transport results. Results from these studies clearly indicate that the hollow fibre supported liquid membrane method can be scaled up for the large scale processing of HLLW for radio-cesium recovery.

EXPERIMENTAL

2.1 Introduction

The experimental details of the solvent extraction and supported liquid membrane transport studies are given in this Chapter. These include details of the chemicals, instrumentation, experimental procedure, data analysis, etc. Detailed description of the solvent extraction experiments under different experimental conditions are described to arrive at the optimum conditions for Cs recovery from PUREX-HLLW. In a similar manner, flat sheet supported liquid membrane (FSSLM) as well as hollow fiber supported liquid membrane (HFSLM) techniques are utilized for studying the transport behaviour of Cs using selected calix-crown-6 ligands.

2.2 Reagents, Chemicals and Materials

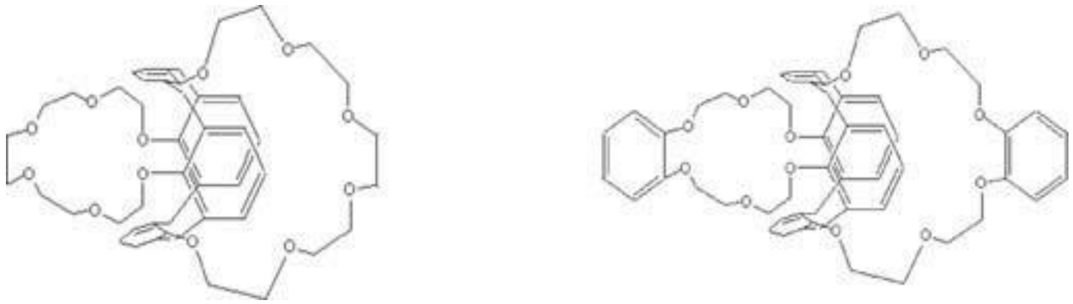
2.2.1 Solvents

2.2.1.1 Calix[4]arene-crown-6 ligands

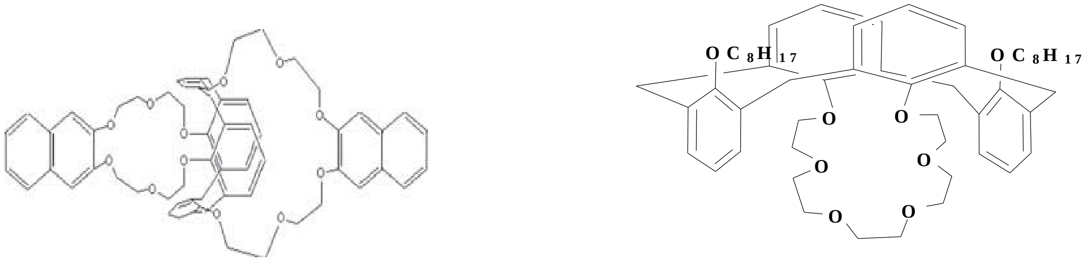
Calix[4]arene-bis-crown-6 (CC), calix[4]arene-bis-benzocrown-6 (CBC), calix[4]arene-bis-naphtho-crown-6 (CNC) were obtained from Across Organics, Belgium while bis(octyloxy) calix[4]arene-mono-crown-6 (CMC) was obtained from Orion Chemicals, Mumbai as a gift sample. Structural formulae of the calix[4]arene-crown-6 (or simply the calix-crown-6) ligands used are given in **Figure 1.**

2.2.1.2 Tri-*n*-butyl phosphate

Tri-*n*-butyl phosphate (TBP) was procured from M/s Bharat Vijay Chemicals, India and purified by contacting it with a 2% solution of sodium carbonate for the removal of the acidic impurities. It was then washed with distilled water and dried over anhydrous sodium sulphate.



Calix[4]arene-bis(crown-6) Calix[4]arene-bis(o-benzocrown-6)



Calix[4]arene-bis(napthocrown-6) bis-(octyloxy)calix[4]arene-mono-crown-6

Figure 2.1: Structural formulae of the calix-crown-6 ligands used in the present study

2.2.2 Diluents

2.2.2.1 *n*-Dodecane

n-Dodecane (C_{10}-C_{14}>95%, below C_{10}<2% and higher C_{14}<2%, specific gravity = 0.751, refractive index = 1.42, aromatics <0.1%, distillation range ~160-210°C), procured from M/s.Transware Chemia Handelsgeselschaf, Hamburg, Germany was used as the diluent in part of this study.

2.2.2.2 Phenyltrifluoromethylsulphone

Phenyltrifluoromethylsulphone (PTMS), was synthesized by a reported method from thioanisole through phenyltrifluoromethyl sulphide which was subsequently oxidized following a literature report (64) and was used as diluent in part of the studies carried out under this Thesis work. Its purity was ascertained by NMR, IR and MS.

2.2.2.3 Isodecanol

Isodecanol (99.0%), procured from Sigma Aldrich, was used as received. This diluent was used as a phase modifier in some of the solvent extraction studies involving *n*-dodecane as the diluent.

2.2.3 Radiotracer

Radiotracer ^{137}Cs, separated and purified from PUREX stream was used. Its radiochemical purity was checked by gamma ray spectrometry using an HPGe detector (vide infra).

2.2.4. General reagents

Nitric acid used in this Thesis work was procured from S. D. Fine Chem. Limited Mumbai and was of AR grade. Double distilled water was used to prepare the diluted HNO_3 solutions. Phenolphthalein (Merck) was used as indicator for acid base titrations involving standard alkali solution prepared from AR grade NaOH (BDH) pellets.

2.2.5 PTFE flat sheet membranes

For the supported liquid membrane studies, PTFE (polytetrafluoroethylene) flat sheet membranes (pore size: 0.45 µm; porosity: 64%; thickness: 85 µm), procured from Sartorius, Germany were used.

2.2.6 Hollow fiber membranes

The hollow fiber membrane contactor used in the present work involving transport studies using SHLLW was procured from Alting, France and made up of hydrophobic microporous polypropylene hollow fibers enclosed in a polypropylene shell. The module contained about 2,200 fibers of 0.03 µm pore size and 40% porosity (wall thickness of 30 µm and fiber outer diameter 300 µm) and had an effective surface area of 0.18 m^2. The complete specification has been given in **Table 2.1.**

Table 2.1: Hollow fiber membrane contactor, (LiquiCel Mini Module G543)

Parameter	Specification
Fibre material	Polypropylene
Number of fibers	2200
Fiber internal diameter (µm)	240
Fiber outer diameter (µm)	300
Fiber wall thickness (µm)	30
Effective pore size (µm)	0.03
Porosity (%)	40
Tortuosity	2.5
Effective fiber length (cm)	11.8
Effective surface area (m^2)	0.18

2.2.7 Hollow fiber membrane used for Cs recovery from actual HLLW

A hollow fiber contactor, containing 35 hydrophobic polysuphone fibers (active length: 26 cm; internal diameter: 0.562 mm; external diameter: 0.862 mm; average pore size: 0.01 μm), prepared at National Chemicals Laboratory, Pune was used for the studies involving radio-cesium recovery from actual HLLW. The hollow fiber module was operated in the recirculation mode with the help of metering pumps (Varicon, Model: QG20 – Q1CSCS) equipped with precise flow controller (vide infra).

2.3 Analytical techniques used

^{137}Cs and other fission products in the samples were analyzed by radiometry. Wherever experiments are carried out using pure ^{137}Cs tracer it was counted using a NaI(Tl) scintillation counter (Para Electronics) coupled to a multi-channel analyzer. The efficiency of the counter was ~10% as standardized against ^{137}Cs standard source. Individual fission products in feed as well as in product samples were assayed using gamma spectrometry employing HPGe detector (Baltic Scientific Instruments) coupled to a 4K multi-channel analyzer. Non radioactive elements were analyzed by ICP-AES. Appropriate volumes of the samples were diluted in 0.5 M HNO_3 and subjected to ICP-AES analysis. Details of the instruments and their operative specifications are described below.

2.3.1 NaI(Tl) detector

It is the most widely used inorganic scintillator for the assay of gamma ray emitting radionuclides. The main component of the detector is sodium iodide crystal activated with 0.1 – 0.2 % of thallium. Salient features of the detector include its low cost, ease of operation and ruggedness**.** The band gap in NaI crystal is of the order of 5-6 eV. When a charged particle (or gamma ray) falls on the detector, its energy is consumed in the crystal either for excitation of the electrons from the valence band to the conduction band or for the ionization of the atom. De-excitation of the electrons from conduction band to the valance band leads to the emission of photons in the UV region as the band gap is rather large. To shift the wavelength (or energy) of the emitted gamma photons to the visible region, which is required for detection by photo multiplier tube (PMT), NaI crystal is doped with an activator impurity like thallium (Tl) which forms the intermediate level conduction band. The resolution of NaI(Tl) detector is about 7 % at 661 keV. In the present work, a 3” x 3” well type NaI(Tl) detector coupled with a multi-channel analyzer (Electronics Corporation of India Limited) (**Figure 2.2**) has been used for gamma ray counting.

Figure 2.2: NaI(Tl) detector used for gamma counting

Nearly 100 % detection efficiency for moderate energy photons in a well type NaI(Tl) detector offers great advantages for the counting of low radioactive samples. Suitable aliquots (usually 0.1 mL) of the desired analyte solution were taken in glass counting tubes which were then placed in the well of the detector. Each sample was counted for sufficient time so as to get more than 10,000 counts to restrict the counting error to <±1%.

2.3.2 High purity germanium (HPGe) detector

In the present work, a high purity germanium (HPGe) detector (Baltic Scientific Instruments) 4K multi-channel analyzer has been employed for gamma ray spectroscopy to check the radiochemical purity of the radionuclides. The HPGe detector is made up of highly pure germanium crystal in which the impurity level is around 10^{10} atoms/cc of the crystal. This is referred to as high purity germanium which approaches the theoretically pure semiconductor. HPGe is one of the most widely used semiconductor detectors for gamma ray spectrometry and can be considered as the workhorse of gamma ray spectroscopy. The high energy resolution (typically 1.9 keV at 1332 keV) is the key feature of this detector due to low energy band gap (0.7eV). The major advantage of HPGe detector over Ge(Li) detector (another type of semiconductor detector) is that it can be stored at room temperature. However, while operating it has to be cooled to liquid nitrogen temperature. HPGe detectors are of two types, p-type and n-type. In case of a p-type detector, the outer surface of the germanium crystal is heavily doped with an n-type impurity. As a result, the detection efficiency falls drastically below 100 keV. On the other hand, the n-type detectors are sensitive to wider range of photon energy. The n-type detector has the added advantage in that it is more resistant to radiation damage in a neutron field as compared to a p-type detector. Analyses in samples generated during extraction and stripping studies from diluted and actual HLLW were carried out using

HPGe detector coupled to a multi-channel analyzer (**Figure 2.3**) after appropriately diluting the sample in 1 M HNO_3.

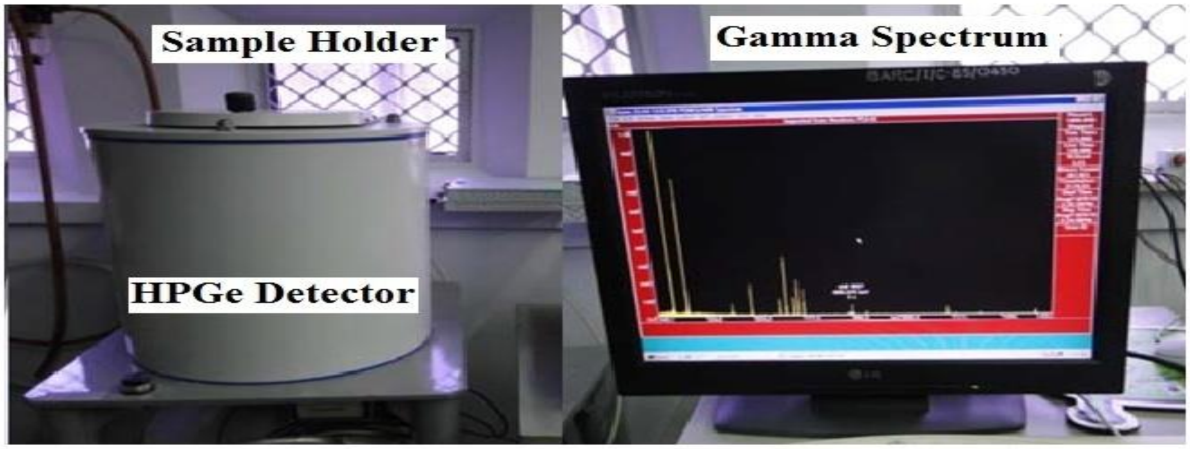


Figure 2.3: HPGe detector used for gamma spectrometry

2.3.3 Inductively coupled plasma-atomic emission spectroscopy

Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) is an emission spectrophotometric technique, working on the fact that the excited electrons emit energy at a given wavelength as they return to ground state after excitation by high temperature Argon Plasma. The fundamental characteristic of this process is that each element emits energy at specific wavelengths peculiar to its atomic character. The energy transfer for electrons when they fall back to ground state is unique to each element as it depends upon the electronic configuration of the orbital. The energy transfer is inversely proportional to the wavelength of the electromagnetic radiation.

$$E= hc/\lambda \qquad (2.1)$$

Where, h is Planck's constant, c the velocity of light and λ is wavelength, and hence the wavelength of light emitted is also unique.

Although each element emits energy at multiple wavelengths, in the ICP-AES technique it is most common to select a single wavelength (or a very few) for a given element. The intensity of the energy emitted at the chosen wavelength is proportional to the amount (concentration) of that element in the sample being analyzed. Thus, by determining which wavelengths are emitted by a sample and by determining their intensities, the analyst can qualitatively and quantitatively find the elements from the given sample relative to a reference standard. Block diagram of the instrument is given below (**Figure 2.4**).

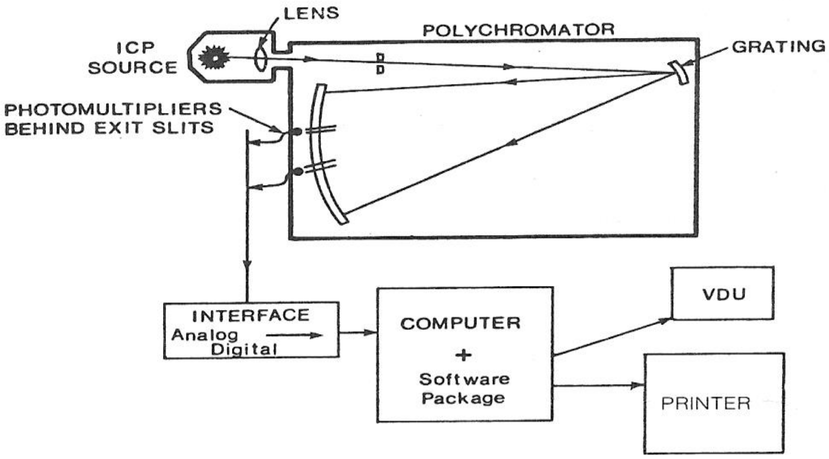


Figure 2.4: Simultaneous multi-element spectrometer

The wavelengths used in the AES measurements ranges from the upper part of the vacuum ultraviolet (160 nm) to the limit of visible light (800 nm). As borosilicate glass absorbs light below 310 nm and oxygen in air absorbs light below 200 nm, optical lenses and prisms are generally fabricated from quartz glass and optical paths are evacuated or filled by a non-absorbing gas such as Argon.

The spectroanalyser system of M/S Jobin Yvon comprising multi-channel (JY-48) and high resolution scanning monochromator (JY-38) was employed. A low resolution monochromator, JY-H20 with 0.2m focal length and a spectral range of 400-800 nm was also used. The instrumental and operating parameters are described in **Table 2.2**.

Table 2.2: Operating conditions for ICP-AES set up

Spectrometers	Jobin Y von(JY-48) 1 m simultaneous spectrometer having a grating with 2550 grooves per mm, Jobin Y von (JY-38) 1 m sequential spectrometer having grating with 3600 grooves per mm
RF generator	Model JY-2300
Frequency	40.68 MHz,
Forward power	1.25 kw,
Reflected power	0.05kw
Nebulizer	Pneumatic concentric type with stainless-steel needle and PTFE nozzle
Plasma torch	Demountable assembly with mermet configuration with three coaxial concentric tube; central injector alumina and other tube of silica glass
Argon gas	18.00 L/min,
Coolant,	0.45 L/min,
Sheathing	0.40 L/min
Aerosol carrier	Three periods of 10 s each
Integration	

2.3.4 GC-MS

Gas chromatography-mass spectrometry (GC-MS) spectra were recorded using Shimadzu GC–MS QP5050A spectrometer with GC-17A gas chromatograph (**Figure 2.5**). The samples were subjected for GC using column dimension J&W DB5-MS 60 m

(L) × 0.25 mm-(id), 0.25 mm (film thickness) to separate extractant compounds with high molecular weight with reasonably acceptable quantification.

Figure 2.5: GC-MS spectrometer

2.4 Preparation of Simulated PHWR-HLLW

The composition of SHLLW used in solvent extraction and membrane based studies is given in **Table 2.3**. The chemicals used in the preparation of the waste are also given in the same Table. Most of the compounds used for the preparation of this waste were of analytical reagent grade. Due to the difficulty in the procurement of some of the chemicals, they were substituted by their chemical analogues, e.g., palladium was replaced by nickel, technetium by molybdenum and promethium lanthanum. Yttrium, terbium and dysprosium were also replaced by lanthanum. Final acidity of the SHLLW was adjusted to 3.0 M which was confirmed by analyzing its free acidity by acid base titration in neutralized potassium oxalate medium. The composition of the prepared Simulated High Level Liquid Waste (SHLLW) was verified by ICP-AES. For verifying the elemental composition, 5 mL of the SHLLW was contacted successively four times with 30% TBP in *n*-dodecane for carrying out uranium depletion.

Table 2.3: Composition of the simulated PHWR- HLLW used in the present Thesis work, [HNO_3] = 3 M

Elements	Conc. (g/L)	Salt used
Fe	0.72	$Fe(NO_3)_3.\ 9H_2O$
Cr	0.119	CrO_3
Ni	0.107	$Ni(NO_3)_2.\ 6H_2O$
Na	5.5	$NaNO_3$
K	0.224	KNO_3
Mn	0.426	$Mn(NO_3)_2.\ 6H_2O$
U	6.34	$UO_2(NO_3)_2.\ 6H_2O$
Sr	0.067(9.5Ci/L)	$Sr(NO_3)_2$
Zr	0.042	$Zr(NO_3)_4.\ 5H_2O$
Mo	0.137	MoO_3
Ba	0.064	$Ba(NO_3)_2$
La	0.18	$La(NO_3)_3\ 6H_2O$
Ce	0.06	$Ce(NO_3)_3\ 6H_2O$
Pr	0.09	$Pr(NO_3)_3\ 5H_2O$
Nd	0.12	$Nd(NO_3)_3.\ 5H_2O$
Sm	0.0855	$Sm(NO_3)_3.\ 5H_2O$
Y	0.06	$Y(NO_3)_3.\ 6H_2O$
Cs	0.315 (9.135 Ci /L)	$CsNO_3$

Contact time of about 10 minutes was maintained for each contact. As uranium in HLLW is one of the major constituents and is a major interfering element, its removal is essential prior to the estimation of other elements in order to eliminate spectral interference due to uranium during the ICP-AES analysis. After four batch contacts its concentration gets reduced below 10 mg/L which dose not interfere in the analysis of metallic impurities by ICP-AES technique (65). The raffinate after fourth contact was diluted appropriately (generally 100 times) with 0.5 M HNO_3 to get the metal ion concentration by ICP-AES.

2.5 Solvent Extraction Experiments

2.5.1 Extraction experiments

For the distribution studies, suitable volume (0.5-5 mL) of the aqueous phase of the desired acidity containing the required radio tracer was equilibrated in stoppered Pyrex glass tubes with equal volume of the organic phase containing the desired concentration of the extractant (calix-crown-6) in the suitable diluent system. For all solvent extraction studies, except stated otherwise, the organic phases were pre-equilibrated with the respective acid solutions to eliminate the effect of acid uptake. The agitation of the two phases was carried out by rotating the sealed tubes in a thermostated water bath (**Figure 2.6**) maintained at 25 ± 0.1°C. After equilibration, the phases were centrifuged and assayed for the desired constituents by removing suitable volumes (20-50µL) from both the phases. The distribution ratios of the metal ions were calculated as the ratio of concentration of metal ion in the organic phase to that in the aqueous phase at equilibrium (expressed in the same unit). During the distribution studies, the hydrogen ion concentration in the organic solution was obtained by titration with standard alkali solution using phenolphthalein as the indicator. The reproducibility of the results was generally within ±5%.

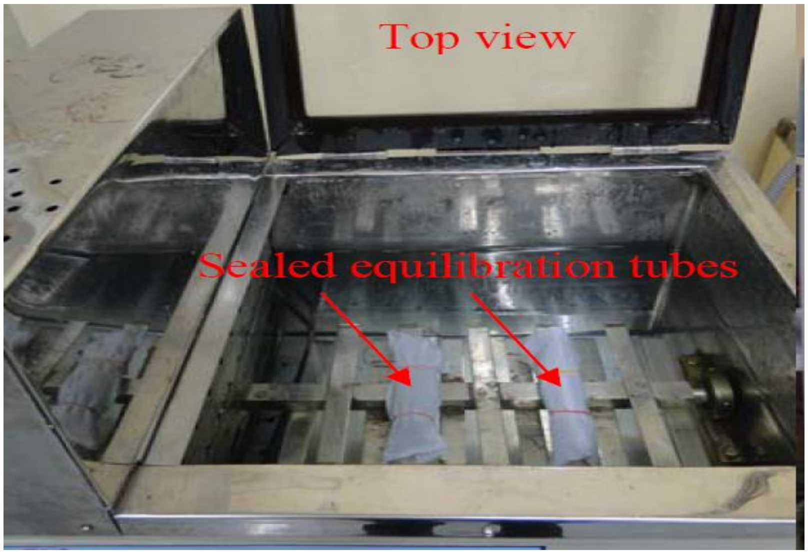


Figure 2.6: The thermostated water bath used in the solvent extraction studies

Different solvent extraction studies include extraction of Cs(I) (a) from varying concentrations of HNO_3 at a fixed ligand concentration, (b) using varying concentrations of calix-crown-6 ligand at a fixed concentration of HNO_3 and (c) studies involving simulated HLLW. Cs loading effect on the D_{Cs} (distribution ratio of Cs(I)) values was also investigated by using feed solutions containing varying concentrations of $CsNO_3$. The data obtained from the calix-crown-6 concentration variation studies were used to understand the nature of extracted species. Co-current extraction and stripping studies were also carried out which were relevant for the experiments pertaining to the recovery of radio-cesium from actual HLLW.

2.5.2 Extraction kinetics

In order to optimize the contact time for the attainment of equilibrium, solvent extraction experiments were carried out in the batch mode for different time intervals up to a maximum of 1 h. Samples, taken out of the equilibration tubes at different time intervals, were assayed for Cs activity to find the distribution ratio. A plot of *D vs* contact time was drawn and the time beyond which the *D* values appear to saturate is considered as the time required to attain equilibrium.

2.5.3 Effect of HNO_3

In order to find the effect of nitric acid concentration on the extraction of Cs (D_{Cs}) by various calix–crown-6 ligands, batch extraction experiments were carried out using feed solutions of varying nitric acid concentrations up to 4.0 M. Usually, a contact time of 10 minutes was maintained in each case. Samples from organic and aqueous phases were assayed for the ^{137}Cs activity to calculate the distribution ratios.

2.5.4 Effect of extractant concentration

The nature of the extracted species was determined by carrying out the solvent extraction studies by equilibrating the two phases at a fixed HNO_3 concentration but varying concentrations of the calix-crown-6 ligands.

2.5.5 Effect of varying concentration Cs in the feed

In order to study the effect of varying concentration of Cs in the feed, extraction experiments were carried out using feed solutions containing different concentration of Cs in feed up to 1g/L. Concentration of nitric acid in these experiments was maintained at

3 M. Samples from organic and aqueous phases were assayed for Cs activity to calculate the distribution ratio.

2.5.5 Stripping

The loaded organic phases containing the extracted metal ion were subjected to stripping (or back extraction) using de-ionized water as the strippant at desired organic to aqueous phase ratio. Generally, an organic to aqueous phase ratio of 1:1 was maintained in most of the studies carried out. Contact time of about 10 minutes was maintained during this step. Small quantity of Alamine 336 (0.5% v/v) was added to the organic phase during stripping.

2.5.6 Co-current extraction and stripping studies

In order to study the quantitative recovery of Cs, co-current extraction experiments were carried out using a ^{137}Cs tracer spiked feed solution containing 3 M HNO_3. In these experiments, known volume of a feed solution was given four successive contacts. The lean aqueous phase from the first contact was contacted with a fresh lot of the organic phase and so on. The samples from each stage of contacting were drawn and assayed for Cs activity to find out the percent extraction. The stripping studies were also carried out in an analogous manner using composite loaded organic phase from the extraction experiments. Organic to aqueous phase ratio of 1 was generally maintained in these experiments. In a separate set of experiments, extraction studies were also carried out by varying organic to aqueous phase ratio up to 4. Percent extraction (%E) values were evaluated from each contact to calculate the cumulative extraction.

2.5.7 Speciation studies

In order to find the nature of extracted species, i.e., the mole ratio of ligand to the extracted cesium nitrate a set of experiment was carried out wherein the D_{Cs} was obtained using varying concentrations of ligand (0.1×10^{-3} to 1×10^{-3} M in PTMS). The D_{Cs} values were calculated and plotted as a function of logarithm of ligand concentration. Slopes from these curves were found out to establish the equilibrium extraction reaction in nitric acid medium.

2.5.8 Determination of the ligand partition coefficients

The partition coefficients of the calix-crown-6 extractants were determined by equilibrating the ligand solution (1.0×10^{-3} M calix-crown-6 in PTMS) with 3 M HNO_3 (not containing the radiotracer) for 1 h at 25±0.1°C followed by which the phases were separated after centrifugation. The aqueous phase (usually 1 mL) was then mixed with a very small volume (about 10 μL) of the radiotracer (in 3 M HNO_3) and equilibrated with PTMS (1 mL) alone at 25±0.1°C. The distribution ratio value, thus obtained, was fitted into a calibration line (D_{Cs} *vs* ligand concentration) to calculate the concentration of the ligand which was used to calculate the partition coefficient of the ligands.

2.5.9 Solvent irradiation studies

In order to study the stability of the four calix-crown-6 ligands, used in the present study, towards gamma radiation, 10 mL solutions of each ligand (1×10^{-3}M in PTMS) were kept in contact with 10 mL of 3 M HNO_3 separately in stoppered glass vials for irradiation in a gamma chamber **(Figure 2.7)** at a dose rate of 2.5 kGy/h. These solution mixtures were kept in the chamber for the predecided time to get the desired radiation dose. Irradiation experiments were carried out for 100, 200, 350, 600 and 1000 kGy absorbed dose values wherein the ligand solutions were kept in contact with 3 M HNO_3 to simulate the more realistic conditions.

Figure 2.7: ^{60}Co Gamma irradiation chamber

After irradiation, all the organic samples were subjected to solvent extraction studies for Cs(I) ion extraction. Speciation studies were also carried out using irradiated solvents for 1000 kGy. Extraction behaviour of various metal ions present in the HLLW by the irradiated solvent systems was also assessed by carrying out batch partitioning experiments using uranium depleted SHLLW and compared with those obtained with the unirradiated solvent systems. The assaying of the metal ions present in the SHLLW was done by ICP-AES. The irradiated solvents were subjected to GC-MS studies to find the possible degradation products.

2.65 Recovery of Radio-Cesium from Actual HLLW

2.6.1 Cs recovery using simulated high level liquid waste

In order to assess the possibility of radio-cesium recovery from actual HLLW, test solvent experiments were carried out from ^{137}Cs spiked SHLLW (simulated high level liquid waste) feed solutions. In these experiments, 5 mL of the tracer spiked SHLLW was contacted with 5 mL of the organic phase for about 1 h. Afterwards, the aqueous phases were assayed for Cs. Extraction experiments were also carried out from three different types of ^{137}Cs spiked waste feed solutions, *viz.*, containing uranium (6.34 g/L), no uranium and after depleting uranium to below 10 mg/L using 30% TBP in *n*-dodecane as described above in Section 2.2.

2.6.2 Recovery using actual HLLW

Radio-cesium recovery experiments using selected ligands were carried out from actual HLLW solutions. In these experiments, 1×10^{-3} M CBC solution in PTMS was used. Composition of the actual HLLW used in present study is given in **Table 2.4**. The analysis of each constituent was carried out following standard methods of analyses. This is a typical waste composition generated from the reprocessing of spent fuel from research reactor. This was given two contacts for uranium depletion and used for Cs recovery as mentioned above. The recovery studies were carried out in two steps; first a 100 times diluted HLLW was used and subsequently, a lot of undiluted HLLW was used. Both experiments involved four stages of extraction and two stages of stripping carried out in the co-current mode. Recovery of radio-cesium was calculated and its purity was ensured by gamma spectrometry using HPGe detector coupled to a 4 K multi-channel analyzer.

Table 2.4: Radiochemical composition of a typical HLLW used for the solvent extraction and hollow fiber SLM studies

Constituents	Concentration after 2 contacts with 30% TBP	Concentration after dilution[a]
[HNO_3]	1.96 M	3.0 M
[U]	0.08 g/L	0.8 mg/L
[Pu]	0.06 mg/L	0.6 µg/L
Gross β	92.46 Ci/L	0.93 Ci/L
Gross γ	30.18 Ci/L	0.30 Ci/L
Fission Products		
^{144}Ce	10.94 Ci/L	0.11 Ci/L
^{106}Ru	6.80 Ci/L	0.07 Ci/L
^{137}Cs	5.06 Ci/L	0.05 Ci/L
^{95}Zr	2.18 mCi/L	0.02 mCi/L
^{95}Nb	26.04 mCi/L	0.26 mCi/L

a:Analysed concentrations in 100 times diluted HLLW in 3M HNO_3

2.7 Supported Liquid Membrane Experiments

2.7.1 Flat sheet membrane experiments

2.7.1.1Preparation of SLM

The supported liquid membranes (SLM) were prepared by dipping the PTFE membrane supports in the desired concentration of ligand solution for overnight (ca. 12 h). Subsequently, the membranes were washed with distilled water mildly prior to its use.

During impregnation, 0.5% v/v of Aliquot 336 was also added to the solvents, i.e. 1×10^{-3} M in PTMS.

2.7.1.2 Transport studies

The supported liquid membrane (SLM) experiments were carried out using a two-compartment transport cell (20 mL capacity for each of the compartment) made from Pyrex glass. SLM containing the desired solvent system containing the extractant carrier solvent was introduced in between the feed and the receiver compartment (the latter containing the strippant) and the cell was made leak proof by tightly wrapping a small length of Parafilm (ca. 15 cm) at the rim joining the two compartments. A stainless steel clip was used for holding the cells firmly. The cell was placed on a magnetic stirrer unit where the solutions were stirred using a magnetic spin bar at about 200rpm. Aliquots (generally 20µL) were drawn through the sample ports from each compartment at the desired time interval for assaying the ^{137}Cs activity or any other constituents. The transport experiments were carried out at ambient temperature under different experimental conditions. Various parameters such as concentration of nitric acid in the feed compartment, concentration of Cs in the feed etc. were measured using standard procedure described here. Transport of the metal ion was calculated by assaying ^{137}Cs in the feed as well as in the receiver phase at any given time intervals. The cumulative percent transport (% T) of the metal ions at any given time was calculated using equation 2.2.

$$\text{Per cent transport (\%T)} = (A_t / A_o) \times 100 \qquad (2.2)$$

where, A_t is the activity at time interval 't' in the receiver compartment and A_o is the initial activity taken in the feed compartment. Schematic presentation of a transport cell is given in **Figure 2.8** whereas the transport cell housed in fume-hood is shown in **Figure 2.9**.

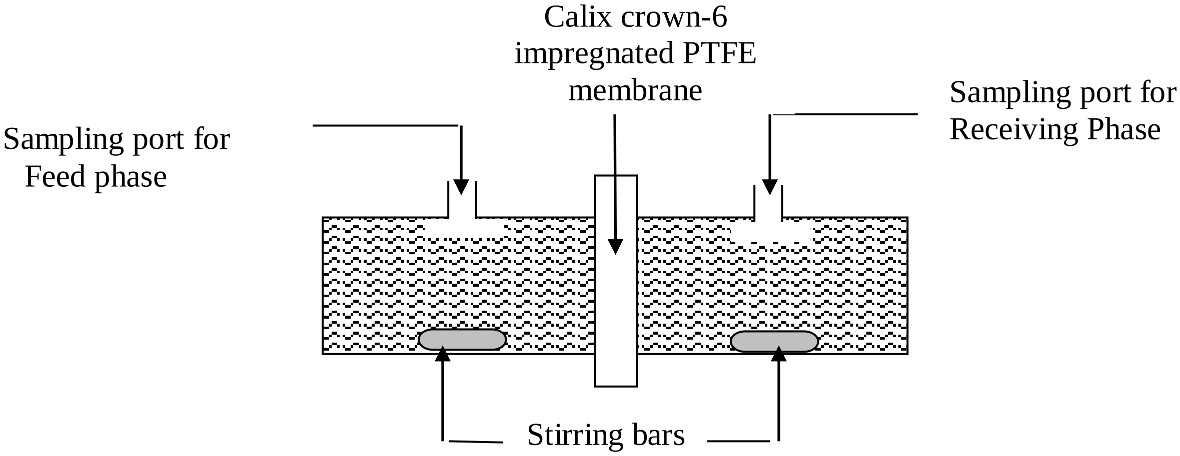


Figure 2.8: Schematic diagram of a transport cell used in the present Thesis work

Figure 2.9: Transport cell housed in fume hood

2.7.1.3 Calculation of permeability coefficient

In the case of transport studies involving flat sheet SLMs, the permeability coefficient (P) of the transported Cs(I) was obtained from linear plots of the following equation (66).

$$-\ln (C_t/ C_o) = P . (A/V_F). t \quad (2.3)$$

where P is the permeability coefficient, C_t and C_o are the respective concentrations of the Cs(I) in the feed solution at the elapsed time ‘t’ and at ‘zero time’, and V_F is the total volume of the feed solution. Here, the parameter ‘A’ represents the total effective surface area of the membrane, which was calculated to be 3.14 cm^2. A linear plot of $\ln(C_t/C_o)$ vs. t yields straight line, and the value of P is calculated from the slope.

2.7.1.4 Calculation of permeation flux

Membrane flux (J_M) was determined by monitoring the ^{137}Cs radioactivity (obtained by gamma ray counting) in the receiving phase as a function of time. The flux is computed using the following equation (67).

$$J_M = [Cs(I)]_r \times V_r/(A\times t) \quad (2.4)$$

where, $[Cs(I)]_r$ = Cs(I) concentration in the receiving phase in mole dm^{-3} while V_r, A and t refer to the volume of receiving phase in dm^3, effective area of the membrane in m^2 and time elapsed (in s), respectively.

2.8 Hollow Fiber Supported Liquid Membrane Experiments

2.8.1 Preparation of HFSLM

The hollow fiber supported liquid membrane (HFSLM) was prepared by passing the desired concentration of the ligand solution (1.0×10^{-2} M CMC in 40% iso-decanol / *n*-dodecane) through the lumen side of the module. A pressure of about 20 kPa was applied at the other end of the module to ensure the percolation of the ligand solution from the lumen side to the shell side. About 100 mL of the ligand solution was circulated using a peristaltic pump equipped with precise flow controller till small droplets of the solvent appeared in the shell side. Complete soaking of the membrane pores was ensured by circulating the solvent for about 15 minutes. After this, about 200 mL of distilled water was passed through the shell side as well as the lumen side of the contactor to remove the excess of ligand solution. The feed solutions were passed through the tube side while the strip solutions were passed through the shell side of the contactor **Figure. 2.10**.

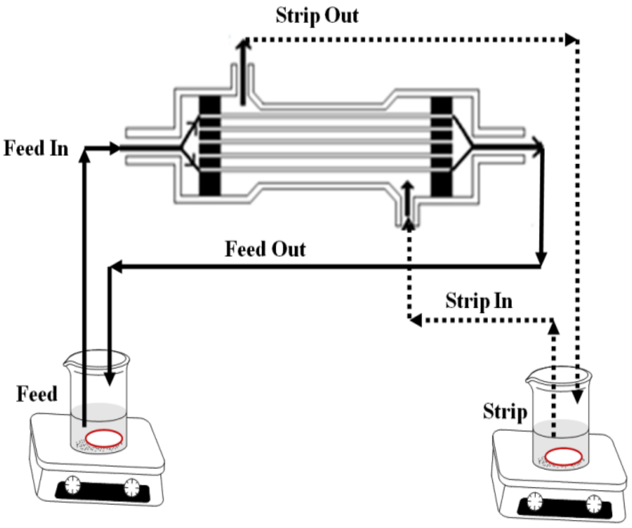


Figure 2.10: Schematic diagram of the hollow fiber membrane set-up

2.8.2 Effect of feed acidity on Cs(I) transport

In order to study the effect of acidity, Cs(I) transport experiments were carried out from ^{137}Cs tracer spiked feed solutions containing different concentration nitric acid in the range of 1-6 M. Samples from feed and strip solutions were drawn at different time intervals and assayed for ^{137}Cs activity up to 2 h. Transport data were used to plot $Ln(C_t/C_o)$ vs. t graph for calculating permeability coefficient (P*) values.

2.8.3 Effect of solute concentration on Cs(I) transport

In order to study the effect of solute concentration on Cs(I) mass transfer rates, transport experiments were carried out from 4 M HNO_3 feed solutions containing varying concentrations of Cs up to 300 mg/L. As mentioned above, the feed solutions were spiked with ^{137}Cs tracer. The transport data were used for calculating permeability coefficient (P*) values.

2.8.4 Experiments using simulated HLLW

To study the transport of Cs(I) from SHLLW, experiments were carried out using a hollow fiber contactor procured from Alting, France. The details of this hollow fiber membrane contactor are given above in this chapter in **Section 2.1.6**.

2.8.5 Hollow fiber contactor studies for radio-cesium recovery from actual HLLW

The hollow fiber contactor used for the radio-cesium recovery studies from the diluted HLLW solution was indigenously made at National Chemicals Laboratory, Pune as described above in **Section 2.1.7**. The membrane was impregnated with a 0.01 M solution of CMC in 60% *n*-dodecane + 40% iso-decanol. Actual photograph of the experimental set-up used in the present work is given in **Figure 2.11**. The feed solution (100 mL of diluted HLLW) was processed using the hollow fiber and the results are discussed below. For all the experiments, the feed solution was circulated through the lumen side while strip solution was circulated through the shell side of the module in counter-current flow direction. The flow rates of the feed and strip solutions were maintained constant at 200 mL/min with the help of gear pumps equipped with precise flow controllers. The volumes of the feed (diluted HLLW) and the strip solutions were 100 mL each. The transport of Cs(I) was obtained by radiometric assay of the feed as well as the strip phase samples at regular intervals.

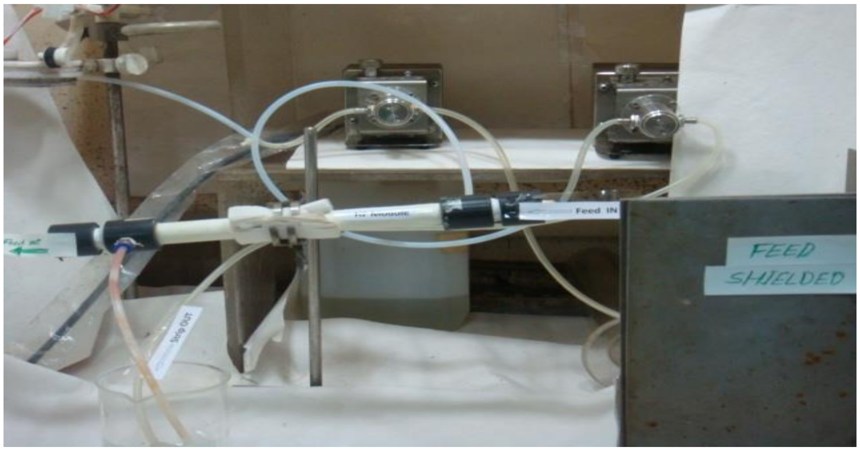


Figure 2.11: Separation of ^{137}Cs from 100 times diluted HLLW using a hollow fiber contactor

2.8.6 Calculation of permeability coefficient

In HFSLM, the overall permeability coefficient (P^*) of the metal ion was calculated using the following equation (68-70).

$$-\ln\left(\frac{C_t}{C_o}\right) = P^* \cdot \left(\frac{A}{V}\right) \cdot \left(\frac{\phi}{\phi+1}\right) \cdot t \tag{2.5}$$

Here, the parameter *A* represents the total effective surface area of the hollow fiber (cm^2), which is calculated as follows,

$$A = 2\pi r_i l N \varepsilon \tag{2.6}$$

Where, r_i is the internal radius of the fiber (cm), *l* is the length of the fiber (cm), *N* is the number of fibers and $\in$ is the membrane porosity. The parameter, ϕ for a module containing N number of fibers is expressed as follows:

$$\phi = \frac{Q_T}{P^* \mathrm{r}_i l N \pi \varepsilon} \tag{2.7}$$

Where, Q_T is the volumetric flow rate of the feed solution (mL/min).

EXTRACTION OF CESIUM USING CALIX-CROWN-6 LIGANDS

3.1 Introduction

Cesium(I) being an alkali metal ion, its recovery from aqueous solutions containing another alkali metal ion as well as metal ions of other groups has always been a challenging task for the separation scientists and technologists. Several reagents have been reported for the recovery of radio-cesium from acidic / alkaline waste solutions which include ion-exchange materials such as ammonium molybdophosphate(AMP) coated resins (71,72,34-36), zeolites (31), resorcinol formaldehyde polycondensate resin (RFPR) (73), crystalline sillicotitanate (CST) (75,76), etc. On the other hand, solvent extraction methods include chlorinated cobalt dicarbollide (76,77), crown ethers (55,78) and calix-crown-6(79,80,59), etc. A detailed literature on Cs(I) separation using such reagents has already been described in the Chapter 1. Major problems with AMP include peptization and difficulties in back extraction indicating poor reusability. Calix-crown-6 ligands have been particularly interesting due to the presence of a crown ether type chain in their frame work (80,59,81,82). The unusually high selectivities of the calix-crown-6 extractants for Cs(I) as compared to the other alkali metal ions have been attributed to the cation-pi interaction (52). The selectivities of the complexation for metal ions depend on the conformation adopted by the rigidified calix[4]arenes (83).

3.2 Calix-crown-6 ligands

The word calixarene was coined by Gutsche for cyclic oligomers obtained by the condensation of formaldehyde with *p*-alkyl phenols by a template reaction (81,82). The number of benzene units in a calixarene ring is used inside a square bracket in the nomenclature (such as calix[4]arene, calix[6]arene, etc.) and is decided by the metal ion size used in the template reaction. Calixarenes offer several advantages *viz.* low aqueous solubility, formation of neutral complexes by exchanging a metal ion with proton, potentiality of coupling metal ion transport and reverse proton transport, etc. Calix-crowns are the moieties obtained by grafting crown ether rings on to the phenyl rings of the calixarene (52). Recent studies have indicated, that substituted calix crown ligands with six 'O' donor atoms (termed as calix-crown-6) are more attractive due to high separation factors obtained for cesium over other alkali metal ions and possibility of easy stripping(83). While calix[4]arene-crown-6 is more selective for Cs(I) ion extraction, calix[4]arene-crown-5 is more selective for K(I) ion. The cavity size of the calix-crown-6 ligands (cavity radius: 3.2-3.5Å) is highly complementary to the size of the Cs(I) ion as compared to the other alkali metal ions making them Cs(I) ion selective. Other studies employing x-ray crystallography have shown the cation–pi interaction between metal-arene rings and thus, explain the exceptional selectivity of these calix[4]arene-crown-6 ligands for cesium(57,84-86). This indicates the favorable interaction of the calix[4]arene moiety with the cesium ion that enables the selective separation of Cs(I) with a reasonably high separation factor with respect to other metal ions. Calix-[4]-arene-bis-crown-6 molecules in 1,3-alternate conformation have been reported to be selective for Cs(I) ion in the presence of large concentration of sodium ions and the separation factor is reported to be $>10^4$(70). The complimentarily between crown ether ring size and Cs(I) ion have been reported to be quite important for the selectivity observed in case of calix[4]arene-crown-6 molecules(87). Any increase or decrease in the crown ether ring size resulted in a lower cesium extraction.

As mentioned in Chapter 2, **c**ommercially available calix[4]arene-crown-6 ligands in phenyl trifluro methyl sulphone (PTMS) diluents were used as extractant in present work. Typically, ligand concentrations of 1×10^{-3} M in PTMS are used in batch mode for Cs(I) extraction from nitric acid medium. Results of various extraction parameters those influences the

Cs(I) extraction *viz.* concentrations of nitric acid and Cs concentration in the feed, concentration of ligand, organic to aqueous phase ratio etc. are discussed. Nature of the extracted species is established using slope analysis method. Results from the co-current extraction and stripping are also described in this chapter. In view of the poor solubility of the ligands namely calix[4]arene-bis-crown-6 (CC), calix[4]arene-bis-benzocrown-6 (CBC), calix[4]arene-bis-napthocrown-6 (CNC) and bis(octyloxy)calyx[4]arene-mono-crown-6 (CMC), in non-polar diluents such as *n*-dodecane, a mixture of *n*-dodecane and iso-decanol has been suggested as the diluent for bis(octyloxy)calyx[4]arene-mono-crown-6 (CMC). The results are found to be encouraging for the application of these solvents for supported liquid membrane studies (Chapter 5) for which PTMS based solvent systems show poor stability over a prolonged period. Results of the solvent extraction experiments using the four calix[4]arene-crown-6 ligands under different experimental conditions are described in this chapter.

3.3 Optimization of the Equilibration Time

Usually, the extraction of Cs(I) by the calix-crown-6 ligands is expected to be relatively faster as the crown ether rings are in a pre-organized conformation. As described in Chapter 2, in order to optimize the contact time for the attainment of equilibrium, Cs(I) ion extraction experiments were carried out from aqueous feed solutions containing ^{137}Cs tracer spiked 3 M HNO_3. The extraction studies were at varying time intervals up to a maximum of 1 h. Samples drawn at different time intervals, both aqueous and organic, were assayed radiometrically for the estimation of ^{137}Cs. The distribution ratio values (D_{Cs}) were calculated using the standard procedure and plotted as a function of time. The results from these studies for all the four calix-crown-6 ligands are presented in **Figure 3.1.** It can be seen from these results that the D_{Cs} values increases rapidly in the beginning and reaches to a plateau within 5 minutes. This indicates that the Cs(I)-HNO_3-calix-crown-6 system attains equilibrium within 5 minutes of mixing of the aqueous and the organic phases. Therefore, in all subsequent experiments, a contact time of 10 minutes was maintained so as to ensure the attainment of extraction equilibrium.

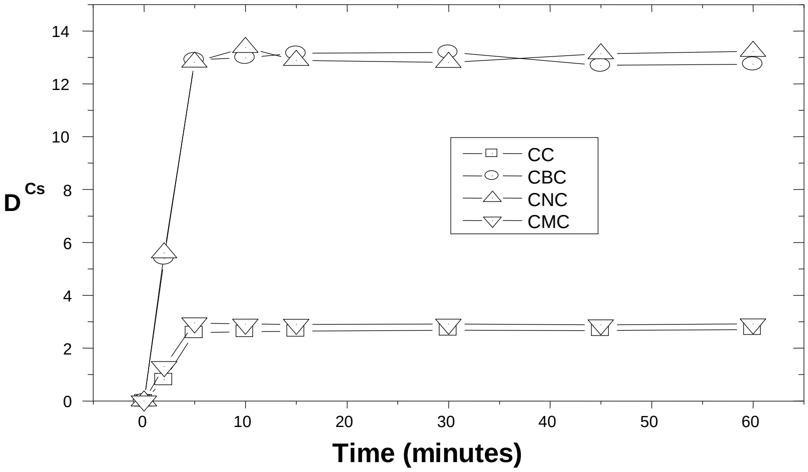


Figure 3.1: D_{Cs} as a function of equilibrium nitric acid concentration; Aqueous phase: ^{137}Cs spiked 3 M HNO_3; Organic phase: Calix-crown-6 ligands (1×10^{-3} M in PTMS) ; Volume ratio: 1; Volume of each phase: 2 mL

3.4 Effect of Nitric Acid Concentration

The extraction of Cs(I) from varying concentrations of nitric acid can throw light on the extraction and stripping conditions. In view of this, the extraction of Cs(I) was carried out from aqueous feed solutions of varying HNO_3 concentrations containing ^{137}Cs tracer with the four calix–crown–6 ligands. Concentration of each ligand used in these studies was 1.0 × 10^{-3} M in PTMS. As mentioned above, a contact time of about 10 minutes was maintained in each case keeping the organic to aqueous phase volume ratio of 1:1. Figure 3.2 gives the distribution ratio data plotted as a function of nitric acid concentration up to 4.0 M.

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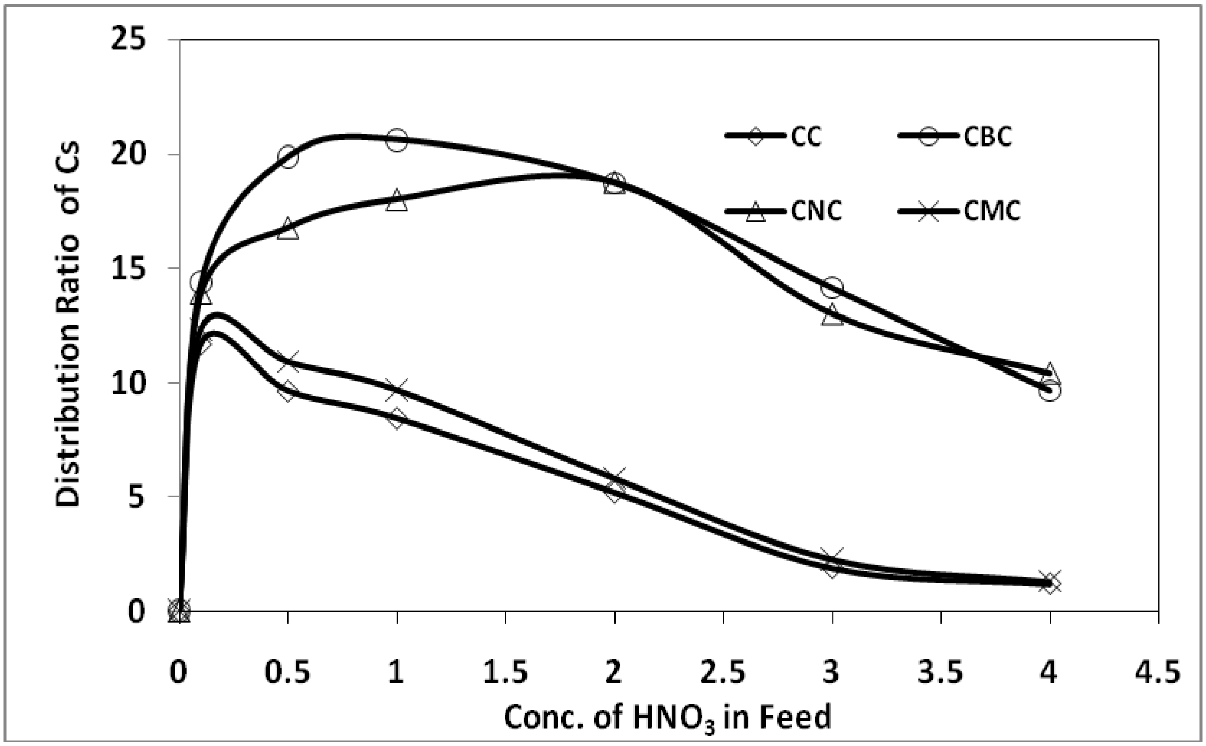

Figure 3.2: Distribution ratio of Cs as a function of HNO$_3$ in the feed.

Aqueous phase: ^{137}Cs spiked HNO$_3$ solutions; Organic phase: 1×10^{-3} M calix–crown-6 ligands in PTMS; Volume ratio: 1, Volume: 2 mL, Contact time: 10minutes

The results indicate that the D_{Cs} values increase initially with increasing concentration of nitric acid in the feed and thereafter it decreases for all the four ligands. At any given concentration of nitric acid in the feed, the extraction ability of the calix-crown-6 ligands follows the trend of CBC >CNC >CMC~CC. As the extraction is mainly due to the crown-6 ring(s) attached to the calix[4]arenes, the distribution coefficient values may be governed by the overall lipophilicity of the complexes which in turn is based on the partition coefficient values of the individual ligands.

To understand the observed trend, experiments were carried out to find out the partition coefficient for all the four calix-crown-6 ligands. Concentration of each ligand was maintained at 1×10^{-3} M in PTMS. The partition coefficients of the extractants were determined by equilibrating the ligand solutions with 3 M HNO_3 (not containing the radiotracer) for 1 h at 25°C followed by which the phases were separated after centrifugation. The aqueous phase (usually 1 mL) was subsequently mixed with a very small aliquot (about 10 μL) of the radiotracer (in 3 M HNO_3) and equilibrated with pure PTMS (1 mL) at 25°C. The distribution ratio value, thus obtained, was fit into a calibration line (D_{Cs} *vs* ligand concentration) to calculate the concentration of the ligand which was used to calculate the partition coefficient of the ligands. The partition coefficient data obtained for all the ligands are given in **Table 3.1**.

Table 3.1: Partition coefficient data for the ligands in 3 M HNO_3

Aqueous phase: Pre-equilibrated 3 M HNO_3 solution; Organic phase: 1×10^{-3} M calix-crown-6 ligands in PTMS; Volume ratio:1; Volume: 1 mL each; Contact time: 10 minutes.

Ligand	D_{Cs}	Equivalent total ligand concentration	Partition coefficient
CC	0.012	1.10×10^{-5} M	91
CBC	0.006	2.73×10^{-7} M	3.7×10^{3}

CNC	0.008	4.49×10^{-7} M	2.2×10^{3}
CMC	0.010	9.84×10^{-6} M	1.0×10^{2}

The parallel between the partition coefficient and the D_{Cs} values is clearly seen from the above results. While lower extraction with CC is attributed to higher aqueous solubility of the ligand (this ligand does not have any lipophilic substituents unlike the other ligands used in the present study), CNC and CBC are better extractants based on their higher lipophilicity. On the other hand, lower Cs(I) extraction with CMC may be attributed to the presence of only one crown-6 moiety. It was observed that the extraction of Cs(I) decreased with increasing nitric acid concentration suggesting competitive interaction of the calix-crown-6 ligands with nitric acid, i.e., the hydronium ion (H_3O^+) probably gets encapsulated in the crown ether ring (88). Similar behavior has been reported earlier using a toluene–nitrobenzene mixture (89). Reasonably good D_{Cs} values are observed in the acidity range of 1-2 M HNO_3 which is the expected acidity of HLLW after the first cycle of partitioning using PUREX solvent for uranium and plutonium depletion (90). On the other hand, the present studies have indicated that while the Cs(I) extraction decreased continuously with nitric acid concentration for both CMC and CC, the peak values of D_{Cs} were observed at 1-2 M HNO_3, respectively, for CBC and CNC. This suggested that CBC is the preferred extractant for feeds at ~1 M HNO_3 while CNC can be used for feed solutions at higher acidity (2 M). On the other hand, both CC and CMC may not find much use with PTMS as the diluent. In view of the previously published results using CNC and CMC in toluene–nitrobenzene as the diluent which suggested peak D_{Cs} values at 3 M and 2 M nitric acid, respectively (91), it may be concluded that the diluents have a very significant role to play in the extraction of Cs(I) from nitric acid feeds which is based on viscosity, nature of extracted species, etc.

3.5 Loading Studies

The high level liquid waste contains large concentrations of Cs (about 300 mg/L as shown in Table 1.1) in Chapter 1. As the concentration of the ligand used in the present studies is 1.0×10^{-3} M, it can extract only an equivalent amount of Cs(I), i.e., about 135 mg of Cs if the entire amount of the extractant molecules are employed for Cs(I) extraction, i.e., under the assumption that the extraction of other metal ions and hydronium ion is negligible. Moreover, the presence of large concentrations of Cs in the feed can drastically change the D_{Cs} values.

In view of this, it was required to investigate the effect of Cs loading in all these extractants. Batch experiments were carried out from ^{137}Cs spiked 3M HNO_3 solution containing varying concentration of Cs up to 1000 mg/L as the feed. Concentration of ligand for each ligand used was 1×10^{-3} M in PTMS. Contacts time of about 10 min was maintained at organic to aqueous phase ratio of 1:1. After the attainment of equilibrium, the aqueous and the organic phases were assayed for Cs activity using radiometry. Distribution ratio values were calculated for each experiments and the results are presented in **Table 3.2** which indicate that the extraction of Cs(I) is highly influenced by the change in concentration of Cs in the feed solution. As the concentration of Cs increases in the feed solution, the D_{Cs} values are found to decrease. This can be attributed to the fact that as the concentration of Cs increases in the feed, the free available solvent concentration decreases in the organic phase due to higher Cs loading. Above fact can be explained based on the following equilibrium extraction reaction.

$$K_{ex}$$

$$Cs^{+}_{(aq)} + NO_{3}^{-}{}_{(aq)} + x\,L_{(org)} \rightleftharpoons (Cs{\cdot}xL)(NO_{3})_{(org)} \quad (3.1)$$

where, the subscripts (aq) and (org) represent the species present in the aqueous and the organic phases, respectively while L represents the calix-crown-6 ligand.

Equilibrium constant for this can be represented as

$$K_{ex} = ([Cs{\cdot}xL(NO_{3})_{org}])/([Cs^{+}_{(aq)}].[NO_{3}^{-}{}_{(aq)}]\ .[x\,L_{(org)}]\ ) \quad (3.2)$$

$$D_{Cs} = ([Cs{\cdot}xL(NO_{3})_{org}])/\ ([Cs^{+}_{(aq)}]\ ) \quad (3.3)$$

$$K_{ex} = D_{Cs}/\ \ ([NO_{3}^{-}{}_{(aq)}]\ .[x\,L_{(org)}]\ ) \quad (3.4)$$

$$D_{Cs} = K_{ex}.\ [NO_{3}^{-}{}_{(aq)}][x\,L_{(org)}] \quad (3.5)$$

From equation 3.5, it can be concluded that as the concentration of Cs in the feed increases the free ligand concentration in organic phase is consequently decreased resulting in the reduction in the D_{Cs} values.

Table 3.2: D_{Cs} as a function of Cs concentration in feed; Aqueous phase: ^{137}Cs spiked 3M HNO_3 solution containing varying concentration of Cs; Organic Phase: 1×10^{-3} M in PTMS for each; Volume ratio: 1; Volume of each phase: 2 mL; Contact time: 10 minutes.

Conc. of Cs in feed (g/L)	D_{Cs}			
	CC	CBC	CNC	CMC
0	2.06	13.14	12.19	1.98
0.05	1.90	12.41	11.82	2.00
0.1	1.82	11.57	10.58	1.83
0.2	1.71	11.33	10.29	1.74
0.5	1.52	9.50	6.81	1.45
1.0	1.19	4.06	3.50	1.06

As mentioned above, the D_{Cs} values can be enhanced by increasing the ligand concentration. Therefore, higher concentrations of the ligands should be employed when the extraction of Cs(I) is required to be carried out from aqueous nitric acid medium/HLLW containing higher amounts of Cs.

3.6 Nature of the Extracted Species

In order to find out the nature of the extracted species, extraction of Cs(I) was carried out from an aqueous phase containing 3.0 M HNO_3 (spiked with the ^{137}Cs tracer) as a function of the ligand (calix-crown-6 ligands) concentration. As described in Chapter 2, the concentrations of the calix-crown-6 ligands in the organic phase were varied in the range of 2.0×10^{-4} to 1.0×10^{-3} M. The volume ratio was maintained as 1 while the contact time was kept as 10 minutes. The distribution ratio values were determined at each concentration of the ligand. To understand the nature of the extracted complex, the 'slope analysis' method was used which is done by taking the logarithm of Equation 3.5.

$$\text{Log } D_{Cs} = \text{Log } K_{ex} + \text{Log } [NO_3^-]_{(aq)} + x \text{ Log}[L]_{(org)} \tag{3.6}$$

In equation 3.6, the values of Log K_{ex} and Log $[NO_3^-]_{(aq)}$are constant and hence, it can get modified to the following equation

$$\text{Log } D_{Cs} = x \text{ Log}[L_{(org)}] + C \tag{3.7}$$

Equation 3.7 represents a straight line with intercept at Y axis given as 'C'. Plotting Log D_{Cs} vs Log $[L]_{(org)}$ (**Figure 3.3**) gives such straight plots for all the four ligands and the slope values can give an idea on the nature of the extracted species.

The straight line plots (**Figure 3.3**) with slopes close to 1 for all the four ligands suggest that one mole of the ligand molecule is participating with one mole of the $CsNO_3$ in the extraction of Cs(I) by an ion-pair mechanism in each case.

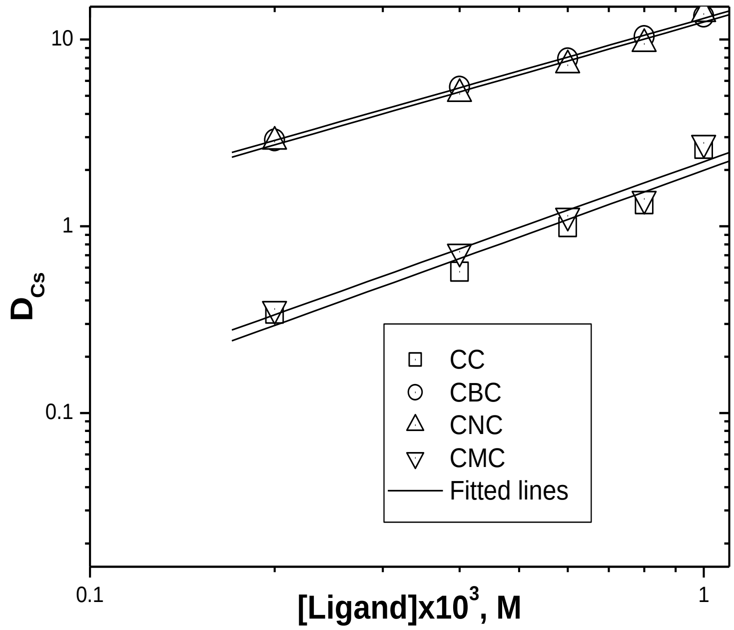

Fig. 3.3: Ligand dependence of Cs with calix-crown-6 ligands; Aqueous phase: ^{137}Cs spiked 3 M HNO_3 solution; Organic Phase: Varying concentration of the calix-crown-6 in PTMS; Volume ratio: 1; Volume of each phase: 2 mL; Contact time: 10 minutes.

Thus, the equilibrium reaction (Eq. (3.1)) in the solvent extraction process taking place at the liquid-liquid inter phase can be represented as:

$$Cs^{+}_{(aq)} + NO_3^{-}{}_{(aq)} + L_{(org)} \rightleftharpoons (Cs \cdot L)(NO_3)_{(org)} \qquad (3.8)$$

Using the above equilibrium reaction, the extraction constant (K_{ex}) can be calculated. The extraction of Cs(I) by the calix–crown-6 ligands in PTMS has shown an extraction mechanism similar to the one reported previously with other polar diluents (75). This is also true from the fact that the presence of more than one extractant molecule in the extracted species is rather unfavorable due to possible steric crowding.

3.7 Stripping Studies

It has been reported that de-ionized water cannot be used for the stripping of the extracted Cs(I) from the organic phase containing the calix-crown-6 extractants as significantly large D values were obtained (92). However, the addition of a small fraction of a tertiary amine such as Alamine 336 has shown to improve the stripping efficiency of distilled water tremendously (89). Therefore, the stripping of the metal ion from the loaded organic phase was attempted using a solvent containing 0.5% (v/v) Alamine 336 which corresponds to ~0.02 M. The D_{Cs} values were found to be slightly affected by the presence of Alamine 336. The results are encouraging as >98% stripping was observed in a single contact. The stripping efficiency was found to be significantly higher as compared to that observed previously with nitrobenzene as the diluent where ~96% stripping was reported.

3.8 Co-Current Studies in Batch mode

3.8.1 Extraction studies

In order to check the number of contacts required for the quantitative recovery of Cs(I), co-current extraction experiments were carried out in batch mode using1.0×10^{-3} M solutions for all the four calix-crown-6 ligands in PTMS as the organic phase. The aqueous phase containing ^{137}Cs tracer spiked 3.0 M HNO_3solutions were used as the feed. Four contacts were given successively keeping the same aqueous phase (feed). After the attainment of equilibrium, the organic extracts from each extraction experiment were separated after centrifugation. All the four extracts from each of the experiments were sampled and subjected to radiometric assay. The percent extraction in each case after each contact was calculated using following equation:

$$\% \text{ Extraction} = [C_o / C_i] \times 100 \quad (3.9)$$

where, C_o is the extracted radioactivity in the organic phase (cpm/mL) and C_i is the initial ^{137}Cs activity present in the feed solution (cpm/mL). The results of the co-current extraction studies are presented in **Table 3.3.**

Table 3.3: Co-current extraction data using 1×10^{-3} M calix crown in PTMS; Feed: ^{137}Cs tracer spiked with 3 M HNO_3; Volume ratio: 1; Volume of each phase: 2 mL; Contact time: 10 minutes.

Calix-crown-6 ligands	Extraction (%) in each contact				Raffinate activity after 4 contacts (%)
	I	II	III	IV	
CC	67.80	20.0	9.80	2.30	<0.01
CBC	90.70	5.00	4.10	0.17	<0.01
CNC	90.95	5.60	3.25	0.19	<0.01
CMC	68.20	20.30	9.40	2.00	<0.01

As expected from the batch distribution data, the extraction of Cs(I) was more efficient with CBC and CNC which resulted in 90.0% and 90.6% extraction in a single contact. On the other hand, about 67.0% and 67.7% extraction of Cs(I) was possible in a single contact while using CC and CMC, respectively. However, more than 99% extraction was possible in four contacts with CC, CBC, and CNC while about 98.5% extraction was possible with CMC. However, the raffinate activity showed almost no ^{137}Cs count above the background level suggesting no further extraction stages were required. However, it is required to carry out counter-current extraction studies in the future using simulated high level liquid waste solution as the feed to make a more realistic evaluation of these solvent systems.

3.8.2 Stripping studies

Cesium loaded organic phases from the extraction experiments were collected separately to get the composite organic phases for the four ligands. After radiometric assay, 2 mL each of the composite organic phase was subjected to Cs(I) stripping studies after adding 0.5% (v/v) Alamine 336 using an equal volume of distilled water. A contact time of about 10 minutes was maintained in each case. The aqueous phases containing the stripped radio-cesium were assayed for ^{137}Cs activity using radiometry (using an HPGe detector). The lean organic phases from each of the experiments after two contacts were also assayed for Cs activity. Results of stripping experiments are given in **Table 3.4.**

Table 3.4: Co-current stripping data for four calix-crown-6 ligands using distilled water Organic phase: Composite organic phase after adding 0.5 volume % Alamine 336 from extraction experiments; Volume ratio: 1; Volume: 2 mL; Contact time: 10minutes.

Calix-crown-6 ligands	Stripping (%)		Activity in Lean organic After 2 contacts (%)
	Contact-1	Contact-2	
CC	97.80	2.18	<0.01
CBC	98.02	1.88	<0.01
CNC	98.26	1.75	<0.01
CMC	98.15	1.80	<0.01

Results from the stripping experiment are found to be highly encouraging as about 98% or higher stripping is found in a single batch contact while >99.9% stripping was observed in two contacts. The pH of the aqueous phase after stripping was lower than the strippant solution suggesting stripping of the co-extracted acid as well. The mechanism of stripping has been reported for analogous solvent system in the literature (93). The organic phase was devoid of any measurable^{137}Cs activity after two stages of co-current stripping suggesting that the lean organic phase can be subsequently reused for another cycle of extraction and stripping.

In view of the better extraction and stripping performance of CNC, though it may be marginally higher than CBC, further stripping studies with varying volume ratio were carried out using this solvent system. The volume ratio (O/A) was varied from 1 to 4 and the stripping results (**Table 3.5**) suggest that the % stripping decreased with increasing volume ratio. However, in view of very high stripping percentage with the volume ratio of 4 which may result in significant concentration of the metal ion, this can be used in subsequent counter-current extraction studies.

Table 3.5: Results of stripping studies with ^{137}Cs loaded CNC based solvent system (contains 0.5% (v/v) Alamine 336) ; Volume ratio: varying from 1 to 4; Strippant: distilled water; Contact time: 10 minutes.

Phase ratio (O/A)	Stripping (%)	Phase ratio (O/A)	Stripping (%)
1	97.26	3	91.24
2	97.06	4	85.19

The present study reports, for the first time, the extraction of Cs(I) using calix-crown-6 ligands in the fluorinated solvent, PTMS. Though similar studies with these extractants were reported (**Table 3.6**) in diluents such as nitrobenzene, its mixture with toluene and 2-nitrophenyloctyl ether (NPOE) and its mixture with *n*-dodecane, the results obtained with the present solvent systems were strikingly different as nitrobenzene is toxic and NPOE is highly viscous and were highly encouraging as compared to those reported previously (89,91). The stripping of the extracted radio-cesium is more facilitated when the organic phase was spiked with 0.5% (v/v) Alamine336 as a modifier which facilitates stripping. Batch co-current extraction/stripping results as well as those from loading studies are highly encouraging. The favorable extraction and stripping data suggested possible application of these ligands for the recovery of radio-cesium from acidic radioactive wastes such as the HLLW. In view of a higher amount of Cs present in the HLLW, it is proposed to enhance the concentration of the extractant.

Table 3.6: Comparative Cs(I) extraction and stripping data with different diluents

Ligand	Diluent	Aqueous phase	D_{Cs}	Ref.
CNC	Nitrobenzene	3 M HNO_3	7.71	15
CC	Nitrobenzene	3 M HNO_3	1.04	15
CMC	Nitrobenzene	3 M HNO_3	1.8	51
CNC	Nitrobenzene	Distilled water	56.4	14
CNC	Nitrobenzene[a]	Distilled water	0.039	14
CNC	NPOE + Dodecane[b]	3 M HNO_3	2.53	16
CNC	NPOE + Dodecane[b]	Distilled water	0.08	16
CMC	PTMS	3 M HNO_3	2.0	This study
CNC	PTMS	3 M HNO_3	12.2	This study

Note: [a]: The organic phase contained 0.5% Alamine 336; [b]: The diluent composition is 80% NPOE + 20% *n*-dodecane

Though PTMS has been used in the work presented in this chapter, attempts to use the calix-crown-6 ligands in a process diluent such as *n*-dodecane were not successful. In view of the poor solubility of the ligands viz. CC, CNC, CBC, CMC in n-dodecane, a mixture of *n*-dodecane and *iso*-decanol was used as the diluent (94,95). However, the diluent mixture was found compatible only with CMC in terms of solubility and hence was not used for the other three calix-crown-6 ligands.

3.9 Extraction studies using CMC in *n*-dodecane and iso-decanol mixture

Preliminary extraction studies were carried out by dissolving CMC in different diluents such as chloroform, nitrobenzene and iso-decanol (IDA) as well as in the diluent mixture containing iso-decanol and n-dodecane. The results indicated significantly higher extraction with iso-decanol which prompted us to use the modifier diluent along with n-dodecane in varying fractions. It was also noted that CMC was not soluble in n-dodecane alone probably due to its bulky nature containing 8 oxygen atoms. In order to facilitate its solubility, iso-decanol was mixed with *n*-dodecane at varying proportions and the distribution ratio values for Cs(I) were evaluated. The diluent mixtures consisting of 20% to 60% iso-decanol in *n*-dodecane were used to prepare 1×10^{-2} M CMC solutions and the solvent systems were used to extract Cs(I) from feeds containing varying concentrations of HNO_3 (up to 6.0 M). The two phases were contacted for about 10 minutes at an organic to aqueous phase volume ratio of 1. After equilibrium, the phases were centrifuged and separated for subsequent radiometric assay. Results from these experiments showing D_{Cs} as a function of HNO_3 concentration using varying proportions of iso-decanol are given in **Fig. 3.4.**

These results show that at any given solvent composition, the D_{Cs} value increase with increasing concentration of nitric acid in the feed. The increase in the D_{Cs} values is several folds from 0.01 M to 6 M HNO_3. This behaviour can be best explained based on Eqn. (3.8), which predicts higher D_{Cs} value with increased nitrate concentration arising from the nitric acid. Results given in **Figure 3.4** also show that at any given feed acidity, the enhancement in the D_{Cs} value did not show much effect with increasing iso-decanol fraction in the diluent mixture, except at 0.01 M HNO_3 where the increase in the D_{Cs} value was ~7 times higher from 20% to 60% iso-decanol.

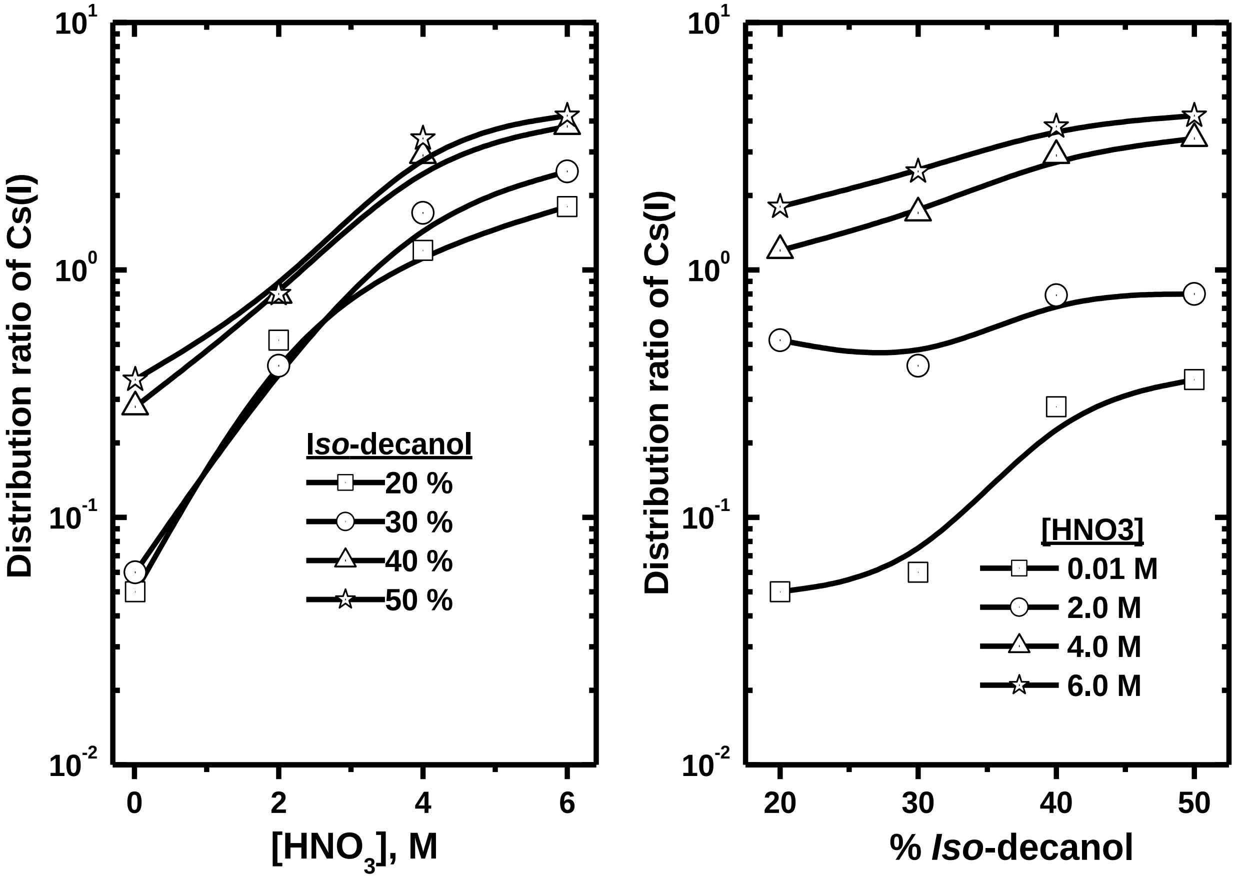

Figure 3.4: Solvent extraction data showing the effect of solvent composition on distribution behaviour of Cs(I) by CMC, Feed: ^{137}Cs spiked nitric acid solutions; Organic phase: 1.0×10^{-2} M CMC in the diluent mixture containing varying proportions of iso-decanol; Volume ratio: 1; Contact time:10 minutes.

In case of other feed acidities (2-6 M HNO_3), the enhancement in the D_{Cs} value is only about two times under a similar solvent composition. A similar 2-3 times increased in the D_{Cs} values have been shown previously by CMC with increasing fraction of iso-decanol in the diluent mixture (36). Owing to the feed condition of the HLLW (2 - 4 M HNO_3), which is a rich source of radio-cesium, 40 - 50 % iso-decanol shows the best extraction results.

It is well known that the long chain alcohols can extract nitric acid on their own. However, < 0.06 M HNO_3 extraction was observed when the diluent mixture as CMC (comprising of 40-50% iso-decanol) when equilibrated with 3.5 M HNO_3(96). Even in the presence of 0.03 M CMC, the acid extraction in the organic phase was found to be < 0.1 M HNO_3 when extraction was carried out from feed solution containing 3.5 M HNO_3. Due to significantly low acid extraction, the stripping of the extracted ^{137}Cs was carried with distilled water and it took less than 5 minutes to get steady D_{Cs} values (< 0.01) suggesting fast back extraction of the metal ion.

RADIOLYTIC STABILITY STUDIES

4.1 Introduction

As described in Chapter 1, solvent extraction is the most commonly used process-scale separation technique for nuclear fuel cycle applications. Tri-*n*-butyl phosphate (TBP) in the most widely used extractant used in solvent extraction processes relevant for nuclear fuel cycle which include the Plutonium Uranium Redox EXtraction (PUREX) (97) process. Subsequently, there are many solvent extraction based processes developed in various laboratories for possible application. These include the TRans Uranic EXtraction (TRUEX) (98,99), DIAMide EXtraction (DIAMEX) (100,101), TALSPEAK (Trivalent Actinide Lanthanide Separation by Phosphorous reagent Extraction from Aqueous Komplexes) (102), etc. Deployment of the above mentioned separations process flow-sheets is now almost nearing maturity. However, these solvent systems will be used in highly radioactive environment that prevails in acidic high level liquid waste. Radiation chemistry of the ligands and their diluents will play a big role in determining extraction and stripping efficiencies, decontamination factors and solvent-recycle longevity. Any process, eventually adopted, must be robust under conditions of high radiation dose-rates and acid hydrolysis. The effect of irradiation on solvent extraction formulations may result in-

1. decreased ligand concentrations resulting in lower metal distribution ratios,
2. decreased selectivity due to the generation of ligand radiolysis products that are themselves complexing agents,
3. decreased selectivity due to generation of diluents radiolysis products that are complexing agents, and
4. altered solvent performance due to films, precipitates and increased viscosity.

These altered complexing agents may also have differing solubilities in the organic/aqueous phases that affect metal ion extraction efficiency and separation factors. In the previous chapter, results of the solvent extraction studies on Cs extraction from aqueous nitrate medium are described in batch mode using four calix–crown-6 ligands *viz.* calix[4]arene-bis-crown-6 (CC), calix[4]arenebenzo-bis-crown-6 (CBC), calix[4]arene-naphtho-bis-crown-6 (CNC), and bis-(octyloxy) calix[4]arene-mono-crown-6 (CMC) dissolved in phenyl trifluoromethylsulphone (PTMS). Very few data are available in the literature on the radiation stability of these ligands (103-107). Radiolytic degradation of some calix[4]arene-crown-6 ligands as well as their solvent, o-nitrophenyloctyl ether (NPOE), was studied using electrospray ionization mass spectrometry as well as by chemical ionization tandem mass spectrometry (103). The stability of crown ethers was also studied under mild radiolysis nuclear cycle simulations (104,105) wherein it was reported that though the crown ethers displayed relatively good radiation stability, it was drastically affected in the presence of nitric acid due to several modifications which include oxidation and nitration. Effect of irradiation on Cs-selective calix [4]-bis-2,3-naphtho-crown-6 (CNC) was studied by Raut et al (107) in a mixed diluent system and the irradiated solvent was subsequently used in solvent extraction as well as in supported liquid membrane studies. While an increase in the distribution ratio values for Cs were observed with the irradiated CNC, the transport studies indicated a decrease in the permeability coefficient values.

From the point of view of separating radio-cesium from PUREX-HLLW, this chapter describes the results on the radiolytic stability of these four ligands under the influence of gamma radiation in the presence of nitric acid.

4.2 Solvent Irradiation Experiments

In view of the long term use of the solvent systems, it was decided to carry out the irradiation studies for all the solvent systems containing the calix-crown-6 ligands by exposing to varying doses *viz.* 100, 200, 350, 600 and 1,000 kGy. As described in Chapter 2, the solvents in separate vials were kept for irradiation in contact with 3 M nitric acid in a gamma chamber having a ^{60}Co source. After irradiation for the assigned dose was complete, the organic phases were separated and used for the subsequent investigations as mentioned above.

4.2.1 Extraction of Cs(I) using irradiated solvent

D_{Cs} values were determined with all the four irradiated solvents containing the calix-crown-6 ligands in PTMS. Under identical conditions, the D_{Cs} values were also determined for all the four unirradiated solvents. The results are listed in **Table 4.1** which indicate that the extraction of Cs(I) is not affected significantly when the solvents were exposed up to an absorbed dose of 100 kGy. Distribution ratio values were found to decrease by < 8 percent as shown inside the parentheses in each case. The metal ion extraction (D_{Cs}) was found to decrease sharply thereafter with increasing gamma ray exposure. The results showed that the D_{Cs} values were affected to a very large extent after exposure to 1000 kGy gamma ray dose.

Table 4.1 also lists the percent degradation of the solvents as a function of absorbed dose for the extraction of Cs(I) using the unirradiated solvents. CBC shows highest stability among the calix-crown-6 ligands studied which showed D_{Cs} of about 3 even after the exposure to 1000 kGy radiation dose.

Table 4.1: Cs(I) extraction and percent degradation with irradiated calix-crown ligands Aqueous feed: ^{137}Cs spiked 3 M HNO_3; Organic Phase: 1×10^{-3} M irradiated/unirradiated ligands in PTMS; Volume ratio: 1; Contact time: 10 minutes.

Extractant	Unirradiated	D_{Cs} (% Degradation)				
		100kGy	200kGy	350 kGy	600 kGy	1,000 kGy
CC	2.60	2.39(8)	2.00(23)	0.89(66)	0.72(73)	0.64(75)
CBC	13.35	12.68(5)	10.35(22)	5.5(59)	4.68(65)	3.23(76)
CNC	13.70	12.76(7)	11.10(19)	3.64(73)	2.78(80)	1.54(89)
CMC	2.80	2.61(7)	2.34(16)	0.76(73)	0.51(82)	0.27(90)

4.2.2 Instability index

The above data are also explained based on the “instability index” which is a novel way of comparing the performance of the solvents after exposing to a given dose of radiation and has direct relevance with respect to the extraction property of the solvent. **Figure 4.1** gives a pictorial presentation of the D_{Cs} values obtained with unirradiated as well as irradiated (absorbed dose of 1,000 kGy) solvent systems containing calix-crown-6 ligands in PTMS. The instability index is defined as the ratio of the D_{Cs} values obtained with the unirradiated solvent to that obtained with the irradiated solvent (exposed to 1000 kGy dose) is also plotted in **Figure 4.1** which suggests comparable stability of CC and CBC. Two general observations can be made from these results. Firstly, the relative resistance of the ligands to gamma ray irradiation follows the order: CBC ~ CC >CNC ~ CMC. Secondly, the largest change in solvent performance is seen during the initial stages, i.e., up to 350 kGy of absorbed dose. Though the relative resistance of CC and CBC appear to be similar with an absorbed dose of 1,000 kGy, CBC was chosen as a better choice in view of higher aqueous partitioning of CC as described in Chapter 3.

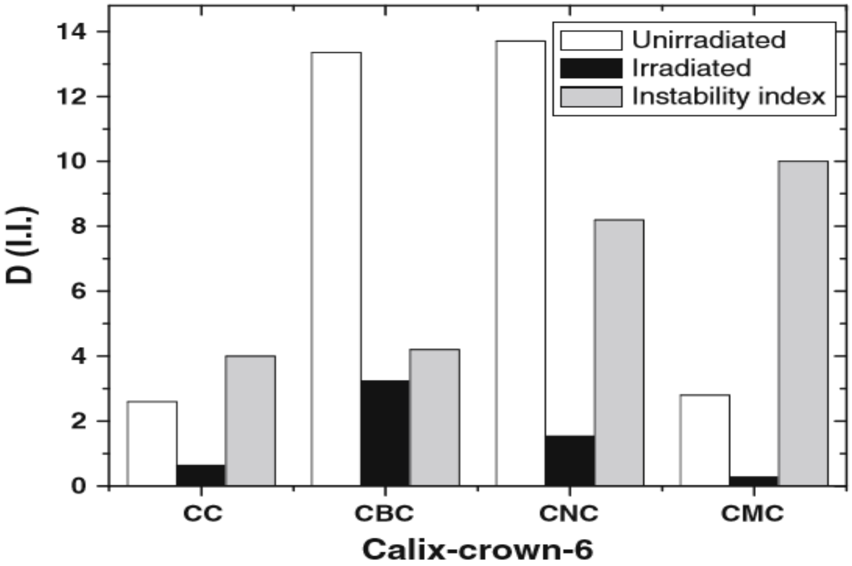

Figure 4.1: Distribution ratio (*D*$_{Cs}$) as well as the instability index (I.I.) of the solvents containing calix-crown-6 ligands in PTMS

It was interesting to note that the present results were in sharp contrast to the results reported with the solvent containing CNC in nitrobenzene - toluene mixture as the diluents where several fold increase in the D$_{Cs}$ values were seen $^{(107)}$. The opposite trend observed in the present solvent system is not understood clearly. The calix-crown-6 ligands show formation of a complex having a metal to ligand stoichiometry of 1:1 which is explained in Chapter 3. The irradiated solvents of various concentrations up to 1000 kGy were also subjected to slope analysis methods to understand the nature of the extracted species. **Figure 4.2** shows the log-log plots of *D*$_{Cs}$ as a function of ligand concentration for all the four calix-crown-6 ligands used in the present study. The figure shows data obtained with the irradiated as well as the unirradiated solvent systems. Slope values and regression coefficients for unirradiated and irradiated ligands under identical experimental conditions are given in **Table 4.2**. The present results on the radiolytic stability are the first reports on the stability of calix–crown-6 ligand containing solvents in PTMS.

Table 4.2 : Comparison of slope analysis data using irradiated and unirradiated solvents in PTMS diluents

Ligand	Unirradiated ligand		Irradiated ligand (1,000 kGy)	
	Slope	R^2	Slope	R^2
CC	1.22 ± 0.22	0.953	0.74 ± 0.04	0.995
CBC	0.93 ± 0.02	0.999	1.08 ± 0.14	0.976
CNC	0.94 ± 0.06	0.994	1.45 ± 0.19	0.974
CMC	1.17 ± 0.15	0.977	0.56 ± 0.73	0.978

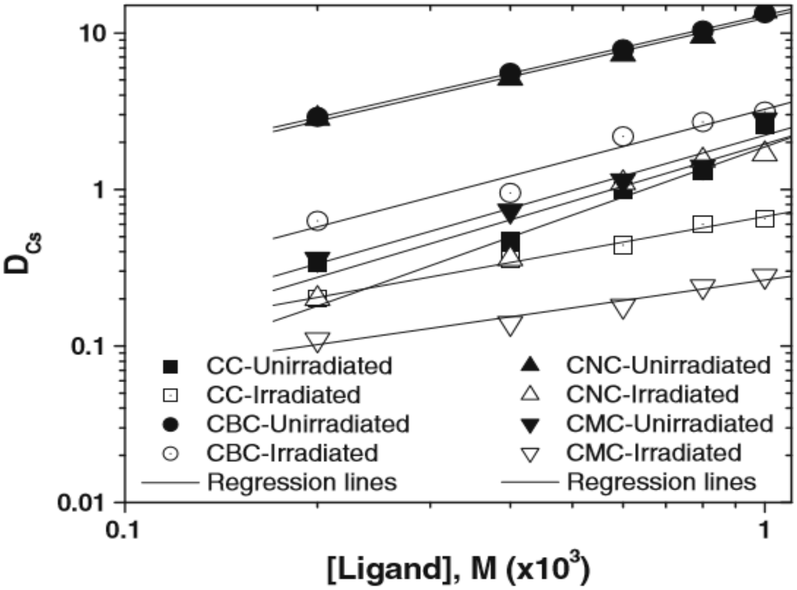

Figure 4.2: Log-log plots of D_{Cs} versus ligand concentration at 3 M HNO_3 using unirradiated as well as irradiated solvents

As seen from **Table 4.2**, the slope values decreased significantly in the case of CMC (to almost half) and CC, suggesting that these extractants are not suitable for long term use under actual radioactive waste conditions. On the other hand, the slope value increased by about 50% with CNC while it remained roughly unchanged with CBC suggesting that the extracted species do not change with the latter. In view of the instability data as well as the slope value data, it appeared that the solvent system containing CBC in PTMS is the most suitable for radio-cesium recovery from the acidic radioactive wastes. Overall, the results can be considered encouraging as reasonably good selectivity was seen even with the irradiated solvents.

Further studies were taken up to identify the degradation path way and degradation products for all the four calix–crown-6 ligands using gas chromatography coupled with mass spectrometry and the results are discussed below.

4.3 GC–MS studies

To elucidate the plausible mechanism for the radiolytic degradation of the extractant or the diluent, GC-MS chromatograms were taken for each of the calix–crown-6 ligands after exposure to 1000 kGy gamma ray dose. The GC–MS spectra and respective mass spectra (for finding out the mass fragmentation patterns due to radiolytic degradation) for all the irradiated samples from the four calix-crown-6 ligands are shown in **Figures 4.3** to **4.4 (see Annexure 1).**

The possible degradation products, identified using the GC-MS spectral information for CC, CBC, CNC, and CMC in PTMS, are listed in **Table 4.3.** Generally, the radiolytic degradation of the calix[4]arene-crown-6 extractants in polar media, leads to the formation of calix[4]arene moiety, nitro derivatives of the calix[4]arene, and the crown ethers, due to cleavage of alkyl groups. These products mentioned above are possible due to different pathways such as radical cleavage at alkyl or crown ether linkage, oxidation, aromatic substitution at aromatic rings. The representative reaction pathways can be explained as follows (**Figure 4.3**).

Table 4.3: Possible degradation products for the calix-crown-6 ligands and their GC-MS analysis

Sample	GC (retention time, min)	MS (m/z) base peak	Fragment identified	% fragment formed
CC	5.10	238	1,14-dihydroxy-[3,6,9,12]-tetraoxa-tetradecane	7.75
	5.10	202	[3,6,9,12]-tetradecane	7.75
	13.74	410	Nitro-calix[4]-arene	1.66
CBC	6.16	281	Ortho-di-[(5-ol)-3-oxapentoxy]-benzene	9.33
	6.16	415	Hydroxy, nitro-calix[4]arene	9.33
CNC	7.26	335	2,3-di-[(5-ol)-3- oxapentoxy]-naphthalene	3.56
	10.24	417	Hydroxy, nitro-calix[4]arene	2.52
CMC	4.84	202	[3,6,9,12]-tetradecane	7.63
	4.84	235	1,14-dihydroxy-[3,6,9,12]-tetraoxa-tetradecane	7.63
	5.90	410	Nitro-calix[4]-arene	0.95
	11.74	418	Hydroxy, nitro-calix[4]arene	11.52
	17.22	603	Bis-(octyloxy)-calix[4]-arene	2.08

$$\mathrm{RCMC\text{-}H} \xrightarrow{\gamma\ \text{radiation}} \begin{array}{l} \mathrm{RCMC}^{\bullet} + \mathrm{H}^{\bullet} \\ \mathrm{CMC}^{\bullet} + \mathrm{R}^{\bullet} \\ \mathrm{RCM}^{\bullet} + \mathrm{R}^{\bullet} \\ \mathrm{RCMC}^{\bullet} + {}^{\bullet}\mathrm{NO_2} \end{array}$$

CMC = Calix[4]arene, R = Alkyl or crown ether chain

Figure 4.3: Plausible generic degradation pathways for the calix-crown-6 extractants

The degradation mechanism for calix[4]arene crown extractants has been found similar to that earlier reported radical degradation mechanism of similar class of compounds (**Figure 4.4**) (108).

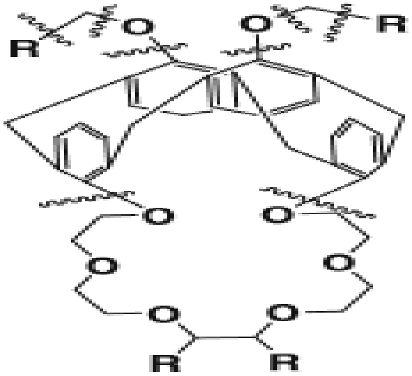

Figure 4.4: Schematic for radiolytic degradation of calix-crown extractants

However, the radiation stability is found to be relatively better as compared to other class of extractants such as malonamides and diglycolamides, within similar range of absorbed radiation dose (109). The stability of calix[4]arene skeleton can be attributed to the presence of 4 aromatic rings. Also, in the case of CBC and CNC, additional stability can be anticipated in view of presence of O-benzo and O-naptho group, helping in stabilization of ionizing radicals. As compared to earlier literature, these aromatic hydrocarbons act as the radical stabilizers or quenchers and eventually minimize the extractant degradations in non-polar systems (110). But similar behaviour is not observed in polar medium such as ionic liquids in case of malonamide extractants (109).

In summary, the above study reports the results obtained from the radiolytic stability of the solvents made from the four calix-crown-6 ligands in PTMS. These results have great relevance if applied for the recovery of radio-cesium from actual HLLW solutions. The solvent containing CBC has shown higher resistance to degradation possibly due to the aromatic substituents though analogous behavior was not seen with CNC which also contains aromatic naphtha groups. The solvent containing CBC was reported to be best amongst the four calix-crown-6 ligands when one takes into consideration the results from the batch solvent extraction studies as reported in Chapter 3. An attempt has been made to identify the degradation products from GC-MS studies. The major conclusion of the present work is that the observed degradation per unit dose absorbed is maximum when the absorbed dose is lower which was found to be true in all the solvents. Furthermore, the degradation slows down at higher absorbed dose values and solvents irradiated to 1,000 kGy dose gives reasonably good D_{Cs} values for CBC. The present study indicates that CBC in PTMS can be used as a solvent for radio-cesium recovery with good recycling possibilities.

SUPPORTED LIQUID MEMBRANE STUDIES

5.1 Introduction

As has been described in Chapter 1, there are several disadvantages of the solvent extraction method which include formation of third phase during extraction, phase entrainment, flooding, phase separation issues beside the requirement of large volumes of volatile organic compounds. All these can be alleviated by the use of liquid membrane based separation techniques which have several unique advantages such as simple to operate, simultaneous extraction and stripping, lesser space, solvent inventory requirements, etc. Among the various membrane based separation techniques, hollow fiber supported liquid membranes are particularly promising for large throughput and have been demonstrated for the selective separation of actinides and fission product elements (111).

In view of this, four calix-crown-6 ligands *viz.*, calix[4]arene-bis-crown-6 (CC), calix[4]arene-bis-benzocrown-6 (CBC), calix[4]arene-bis-napthocrown-6 (CNC) and bis(octyloxy)calix[4]arene-mono-crown-6 (CMC) have been studied as carrier extractants in PTMS (phenyltrifluromethyl sulphone) as the diluent for Cs transport studies from nitric acid medium under different experimental conditions. Previously, calix-crown-6 ligands were used for the transport of Cs(I) from acidic feeds in diluents such as nitrobenzene (80) and a mixture of NPOE (2-nitrophenyloctyl ether) and n-dodecane (59) , while nitrobenzene was a good diluent for the solvent extraction studies (79), its performance in the flat sheet supported liquid membrane studies was not up to the mark (80). On the other hand, the mixture of NPOE and *n*-dodecane has led to interesting results though the mass transfer rates were rather slow. In view of this, it was of interest to evaluate the performance of PTMS as the diluent in the transport studies. After evaluating the performance of all the four SLMs in flat sheet configurations, CBC and CMC were pursued for selective transport of Cs in hollow fiber supported liquid membrane configuration. Results from various experiments at tracer concentrations, as well as at, large concentrations of cesium up to 0.32 g/L in feed are summarized here. Apart from these, results on the stability of the SLMs are discussed in this Chapter. Transport parameters such as permeability coefficient, mass transfer coefficient, diffusion coefficient, etc. are determined from the experimentally obtained mass transfer data.

5.2 Evaluation of Transport Performance of the Calix-Crown-6 Ligands

Solvent extraction data are basic requirement to understand the transport parameters for supported liquid membrane techniques which are described in Chapter 3. As described, a small fraction of Alamine 336 was added to facilitate the of stripping of Cs(I) from the Cs loaded organic phase. In view of this, 0.5% (v/v) Alamine 336 was added to organic phases containing calix-crown-6 solutions in PTMS during stripping.

5.3 Distribution Data for Extraction and Stripping of Cs using various Calix-Crown-6 Ligands

To validate the distribution data, solvent extraction experiments were carried out using tracer spiked (^{137}Cs) feed solutions (3.0 M HNO_3 as well as from 0.01 M HNO_3) solution under identical experimental conditions. Contact time of about 10 minute was maintained in each case as followed in solvent extraction experiments described earlier. D_{Cs} values were calculated and the results of forward and back extraction using 1.0×10^{-3} M ligand in PTMS as the organic phases are given in **Table 5.1**.

Table 5.1: D_{Cs} data for extraction and stripping using various calix-crown-6 ligands Organic phase: 1.0×10^{-3} M calix crowns in PTMS +0.5% Alamine-336; Contact time: 10 minutes; Volume ratio:1; Volume: 2mL each

Ligand	D_{Cs}-Extraction	D_{Cs}-Stripping
CC	2.61	0.02
CMC	2.80	0.02
CBC	13.40	0.03
CNC	13.70	0.03

The single stage solvent extraction results carried out in batch mode clearly explain the extraction and stripping possibility of Cs under experimental conditions. However, it was decided to use higher concentrations of the ligands (4.0×10^{-3} M, as compared to that used in the liquid-liquid extraction studies mentioned above and earlier in Chapter 4 for the transport studies to result in better mass transfer rates which may have relevance while carrying out studies involving HLLW. The results given in the above table explain that CNC is the most efficient among the various calix- crown-6 ligands studied under experimental conditions. Further studies were therefore taken up to understand the transport behavior of Cs(I) from 3 M HNO_3 solutions.

5.4 Transport Experiments

Using the solvent extraction data as presented above and in Chapter 3, Cs transport studies were carried out from nitric acid feed solutions. A transport cell of 20 mL feed and receiver compartment capacity was used in all the FSSLM (flat sheet supported liquid membrane) transport studies under different experimental conditions. The feed and the receiver phases were separated by a PTFE support containing fixed concentrations of the calix-crown-6-ligands. The experimental set up used for the transport studies is shown in Chapter 2 (**Figure 2.4**). As described previously, the solutions in the feed as well as the receiver compartments were stirred using magnetic stirring bars to reduce the aqueous diffusion layer thickness as well as to make the phases homogeneous. Transport was studied from the feed phase containing ^{137}Cs radiotracer spiked in 3 M HNO_3 solution to the receiver phase containing water as strip solution. Samples were drawn at predetermined time intervals and assayed for the ^{137}Cs activity. These experiments were carried out up to 6 h and the percent Cs(I) transport were calculated as a function of time for all the four calix-crown-6 ligands. The results presented in **Fig. 5.1** indicate increased transport of Cs(I) with increasing ligand concentration and time. Though the distribution data for the extraction and the stripping of Cs(I) using various calix–crown-6 ligands suggested (**Table 5.1**) that CNC be the most efficient carrier extractant, the results from the transport studies, under comparable experimental conditions, did not followed the expected trend in the present study due to its limited solubility in PTMS. Hence, while 4.0×10^{-3} M solutions of CC, CBC and CMC were used for the transport studies, a lower concentration i.e., 1.0×10^{-3} M was used as carrier concentration for analogous studies involving CNC. For comparison purpose, Cs(I) transport studies were also carried out using 1.0×10^{-3} M CBC in PTMS and the data are included in **Fig.5.1** as well. The trend of Cs(I) transport efficiency, observed with the calix-crown-6 ligands, was found to be: CNC $\geq$ CBC > CC $\geq$ CMC (CNC data were on the basis of relative transport behavior with respect to CBC).

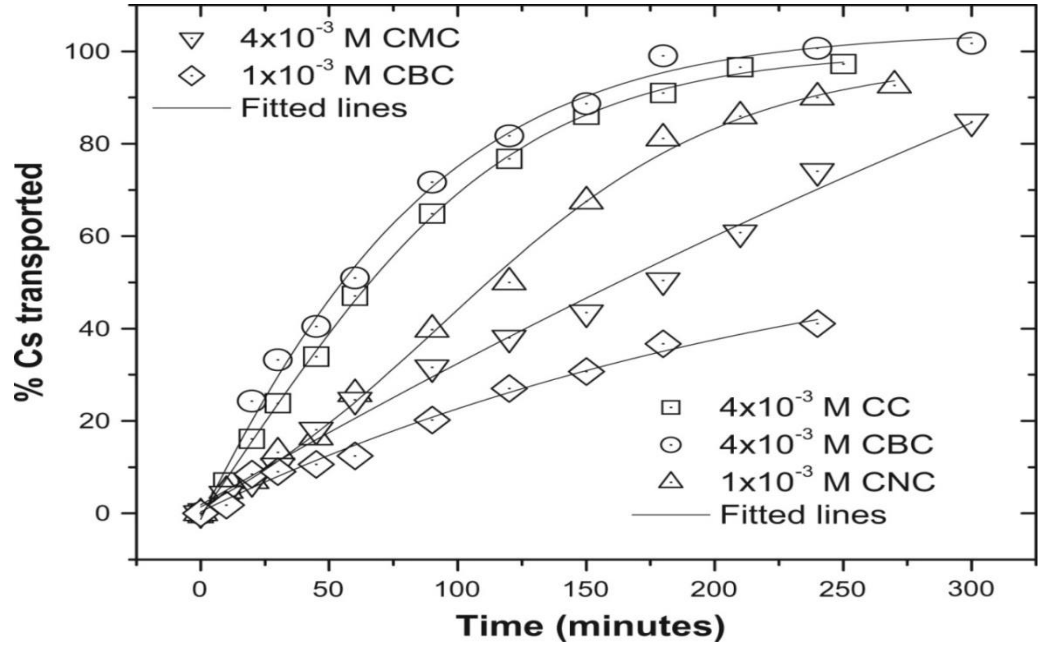

Figure 5.1: Comparative transport behavior of Cs from 3 M HNO_3, Feed: ^{137}Cs spiked 3 M HNO_3 solution; Receiver phase: distilled water; Carrier solvent: 4.0×10^{-3} M calix-crown-6 ligands in PTMS + 0.5% Alamine 336; Transport profiles with 1.0×10^{-3} M CBC and CNC are also included.

The above transport results also explain quantitative transport (>99%) of Cs(I) in the solvent system containing CBC after about 4 h. Such results are not reported so far using a calix-crown-6 ligand. These results are significantly superior (>85% in 4h) to those reported previously (80% in 24h) where a mixture of NPOE + *n*-dodecane was used as the diluent(59).

The calix-crown-6 ligands are reported to transport significant amounts of nitric acid due to the complex formation with the hydronium ions present in the acidic aqueous feed phase (112). Therefore, it was required to measure the acid transport also from the feed to the receiver compartment. As shown in **Figure 5.2**, the acid transport rates were < 3% after 2 h, but increased rather steeply beyond that to result in nearly 8% transport after 5 h. It was rather surprising to note ~25% HNO_3 transport after 24 h which would affect the metal ion transport significantly. However, this may not be very relevant as the bulk of the metal ions got transported in about 5-6 h. CBC, which showed maximum Cs(I) transport also showed most efficient HNO_3 transport.

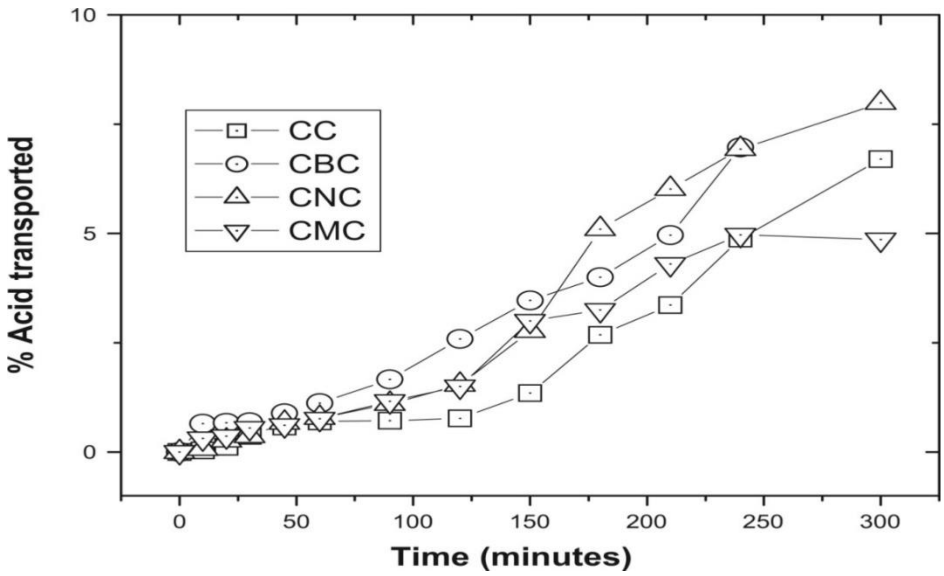

Figure 5.2: Acid Transport profile of various calix-crown-6 ligand,Feed: ^{137}Cs spiked 3.0 M HNO_3 solution; Receiver phase: distilled water; Carrier concentration in PTMS: 4.0×10^{-3} M for CC, CBC and CMC and 1.0×10^{-3}M for CNC; The carrier solvent also contained 0.5% Alamine 336.

However, in view of the acid transport seen with CNC (even with four times lower concentration of the extractant), it was reasonable to assume that it may show much higher acid transport as compared to CBC at extrapolated concentration of 4.0×10^{-3} M. On the other hand, CC and CMC showed lower acid transport rates. Though CC has showed reasonably high Cs(I) transport rates and less favorable HNO_3 transport rates, it was not chosen for subsequent transport studies due to higher aqueous partitioning (as reported previously in Chapter 3 and hence, CBC was used instead as the carrier extractant.

5.5 Effect of Feed acidity

Concentration of nitric acid in feed compartment is found to have a significant effect in the metal ion transport. Hence, its effect needs to be investigated in more detail. Solvent extraction studies using the four calix-crown-6 ligands in PTMS indicated extraction maxima values (the acid concentration where the maximum D_{Cs} value was obtained) at different HNO_3 concentrations. While CC and CMC showed higher Cs(I) extraction at lower HNO_3 concentration indicating a continuous decline in the D_{Cs} values starting from 0.1 M HNO_3, CBC and CNC showed maximum Cs(I) extraction at 1 M and 2 M HNO_3, respectively. In another study (80,113) involving CNC and CMC in nitrobenzene as the solvent systems, while the peak D_{Cs} value with CBC was still observed at 1 M HNO_3 as the feed, the same with CNC was shifted to 3 M HNO_3 suggesting that diluents have a very important role to play in metal ion extraction. It is understood that the diffusion of the metal-carrier complex is one of the key steps in the supported liquid membrane transport studies, thereby suggesting the peak Cs(I) transport may not be at the same acid concentration as indicated in the solvent extraction studies. As explained in Chapter 2, Cs(I) transport studies were carried out from the feed compartment with varying concentrations of HNO_3 in the range 1-4 M. Percent Cs(I) transport as a function of time using 4.0×10^{-3} M CBC in PTMS carrier are shown in **Figure 5.3**. These results show that the transport of Cs(I) increases with time under the experimental conditions as studied up to 5 h. Cs(I) transport rates were found to be most favorable up to 2 h with 3 M HNO_3 as the feed, while those with 2 M HNO_3 were only marginally lower in this time period. After 2 h, however, the 2 M HNO_3 data were slightly higher at 82.2% as compared to the 3 M HNO_3 data (81.7%) and the trend continues up to 5 h (**Table 5.2**). This could be attributed to higher acid co-transport at 3 M HNO_3 which affected the mass transfer after certain period of time.

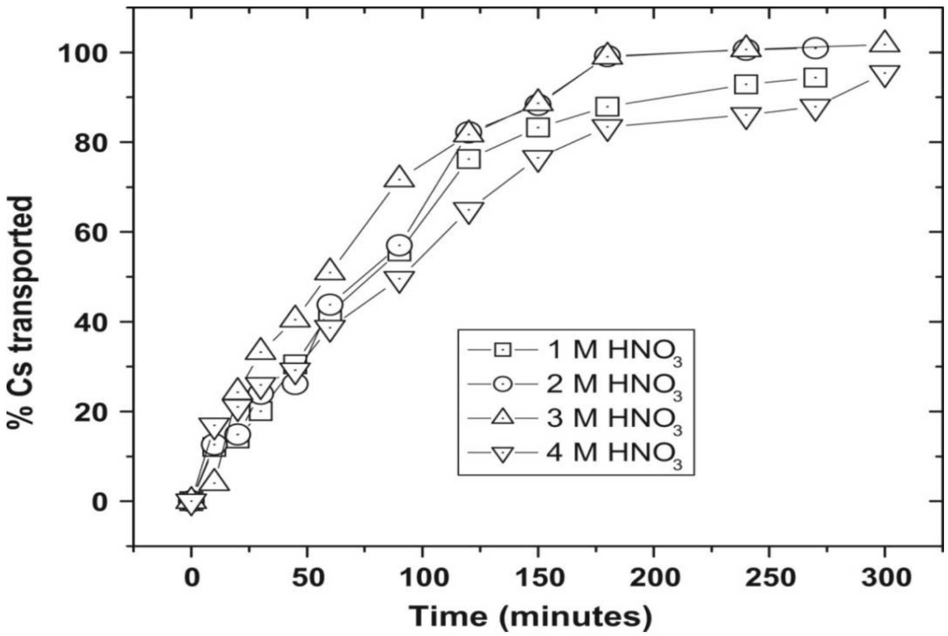

Figure 5.3: Effect of aqueous phase [HNO_3] on Cs transport using CBC ; Carrier phase:4.0×10^{-3}M CBC in PTMS +0.5% Alamine-336(v/v); Receiver phase: distilled water.

The Cs(I) transport rates were significantly lower with 4 M HNO_3 as the feed which was attributed to very high acid co-transport which was proven in a separate experiment (**Figure 5.4**). While using 2 M HNO_3, the acid co-transport was ca. 3% after 4.5 h, it nearly doubled when 3 M HNO_3 was used as the feed. However, 15% acid co-transport was seen in the same time period when 4 HNO_3 was used as the feed (**Figure 5.4**). This acid co-transport increased to about 50% after 24 h suggesting strong competition between Cs(I) and H_3O^+ ions for the calix-crown-6 ligand at higher feed nitric acid concentrations. The permeability coefficient data for Cs(I) transport were also calculated using the Danesi equation (114) and are given in **Table 5.2**.

Table 5.2: Cs(I) transport data as a function of nitric acid concentration.

Feed: varying concentrations of HNO_3; strippant: distilled water;

Flat sheet support: PTFE; carrier solvent: 4.0× 10^{-3} M CBC + 0.5% alamine 336.

HNO_3, M	2 h - %Cs(I) transport*	$P \times 10^3$ (cm/s)	2 h - % Acid transport[a]
1	76.3 (93.9)	0.92±0.06	0.6
2	82.2 (499.9)	1.06±0.04	1.14
3	81.7 (499.9)	1.00±0.05	2.59
4	64.9 (96.8)	0.88±0.02	5.88

*Values in parenthesis indicate % transport after 24 h.

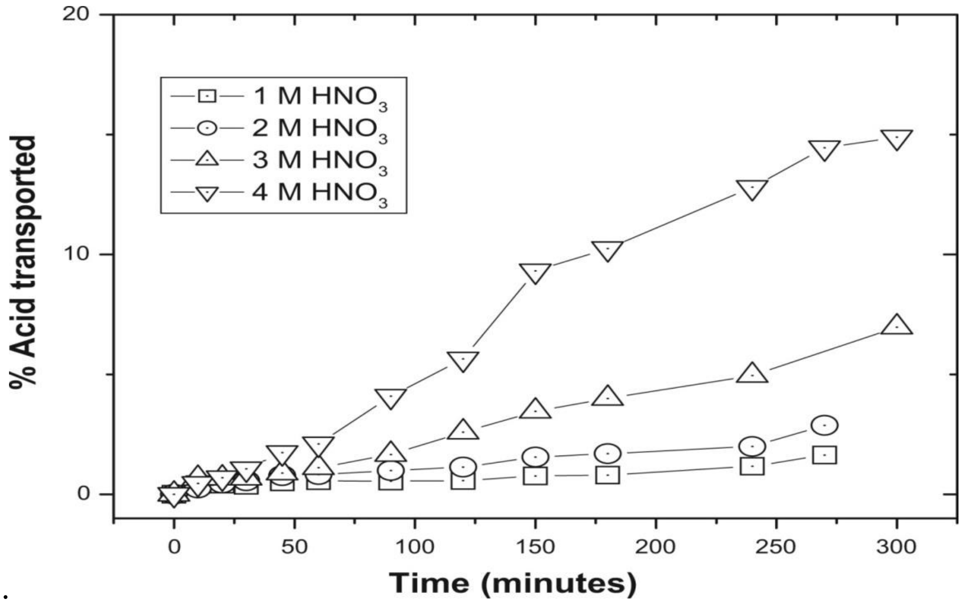

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Fig. 5.4: Acid transport profiles with varying feed phase nitric acid concentration

Carrier: 4.0×10^{-3} M CBC in PTMS +0.5% alamine-336(v/v); Receiver: distilled water.

5.6 Calculation of diffusion parameters

When the extraction and stripping conditions are favorable, the mass transfer in the liquid membrane systems is governed by the diffusion rate of the metal-carrier complex. In view of the bulky nature of the calix-crown-6 ligands used in the present study and significant variation in their size, for example, CC and CNC or even CMC have large difference in their molar volumes. The diffusion coefficient, D_o, can be calculated as per the empirical Wilke-Chang equation(115) given below:

$$D_o = 7.4\times10^{-8}\ (\chi^{0.5}M^{0.5}T)\ /\ (\eta V_m^{0.:6}) \qquad (5.1)$$

where, M, V_m, χ, η and T are the molecular weight, molar volume, solvent association parameter, viscosity of the solvent, respectively and temperature (in degree K). Usually, the solvent association parameters can be taken as unity (114). The molar volumes of CC, CBC, CNC and CMC were calculated using literature data (116) to be 897.6, 1002.1, 1098.2 and 921.0 $cm^3\ mol^{-1}$, respectively. Considering, the molecular weights of the ligands as 829.0, 925.1, 1025.2 and 851.2, respectively the D_o values can be calculated easily (**Table 5.3**) The diffusion coefficient values are higher for CC as compared to those for CNC and CBC though the observed transport efficiencies showed an opposite trend. This is attributed to the fact that faster diffusion is expected for a ligand with lower molar volume (CC). On the other hand, higher transport rates for CNC and CBC are due to higher extraction efficiency of these ligands. The observed transport rates were also due to interference by the nitric acid co-transport.

Table 5.3: Comparison of diffusion coefficient values for Cs-ligand complex Obtained experimentally by lag-time method and theoretically by Wilke-Chang equation

Ligand	Lag time (s)[a]	Molar volume[b]	Diffusion coefficient (D_o) × 10^6 (cm^2/s)	
			Lag time data	Wilke-Chang equation
CC	19	897.57	0.406	3.10
CMC	30	920.97	0.257	3.06
CBC	60	1002.13	0.128	3.05
CNC	60	1098.23	0.128	3.09

[a] [CC], [CBC] and [CMC]= 4.0 $\times 10^{-3}$ M;[CNC]= 1.0×10^{-3} M; the carrier solvent also contained 0.5 % Alamine 336, [b]Calculated using Ref. [112].

The diffusion coefficient values can also be obtained experimentally using the lag-time method (117-118), i.e., from the time taken to detect the metal ion in the receiver compartment from the start of the experiment (t_{lag}) using the following formula:

$$D\text{o} = \text{do}^2\varepsilon / 6t_{lag} \tag{5.2}$$

Where, ε is the membrane porosity and d_o is the membrane thickness. The D_o values were calculated using Eq. (5.2) and the results are also included in **Table 5.3** along with the lag-time data. It was rather surprising to note that the D_o values experimentally obtained by the lag-time method were about one order magnitude lower than those obtained by calculations. Though one may be tempted to attribute this lowering to some attractive interactions between the diffusing complexes, no evidence is available to suggest this.

5.7 Membrane Stability

Practical application of a supported liquid membranes based separation system is dependent on many factors out of which the stability of the membrane is of great relevance (119). It is required to make a comparison of the stability of the calix-crown-6 based SLM systems reported previously as well as the present system. Apart from poor mass transport rates, the stability of the nitrobenzene based supported liquid membranes (80,123,79) reported for Cs(I) transport using calix-crown-6 ligands was poor to make any practical applications to nuclear waste management. On the other hand, SLMs based on *n*-dodecane + NPOE displayed reasonably good stability (59). A comparative stability data of different supported liquid membrane systems is given in **Table 5.4**.

Table 5.4: Comparative stability data of different supported liquid membrane systems

Diluent-Ligand system	Stability (d)	Reference
80%NPOE+20% *n*-dodecane - CNC	20	59
Nitrobenzene - CNC	Not stable	59
PTMS- CBC	Not stable	Present work
40% Isodecanol+60% *n*-dodecane -CMC	50	Present work

Though the present solvent system has showed significantly faster mass transfer rates as compared to the *n*-dodecane + NPOE based liquid membranes, it was of interest to ascertain the membrane stability for any practical applications. For this purpose, the same SLM was used over a period of 10 days by changing the contents of the feed and receiver compartments on every day. The transport rates showed gradual deterioration over a period of time (**Table 5.5; Figure 5.6**). However, though the % Cs transport after 4 h decreased by about 13% and 52% after two and five days of operation, respectively and the SLM was relatively stable thereafter as the 10 days transport data were found to be little above 40%.

Table 5.5: Supported liquid membrane stability data using 4.0×10^{-3} M CBC, Carrier: CBC+ 0.4% Alamine 336 in PTMS; Feed: 3 M HNO_3; Strippant: distilled water.

Time (day)	4 h - %Cs(I) transport[a]	2 h - % Acid transport	$P \times 10^4$ (cm/s)
1	>99.9 (>99.9)[a]	2.59	10.00±0.05
2	87.0 (97.2)[a]	1.07	7.55±0.04
5	48.0 (61.0)[a]	12.20	1.85±0.05
10	43.0 (47.7)[a]	15.39	3.12±0.03

[a] Values in parenthesis indicate % transport after 24 h.

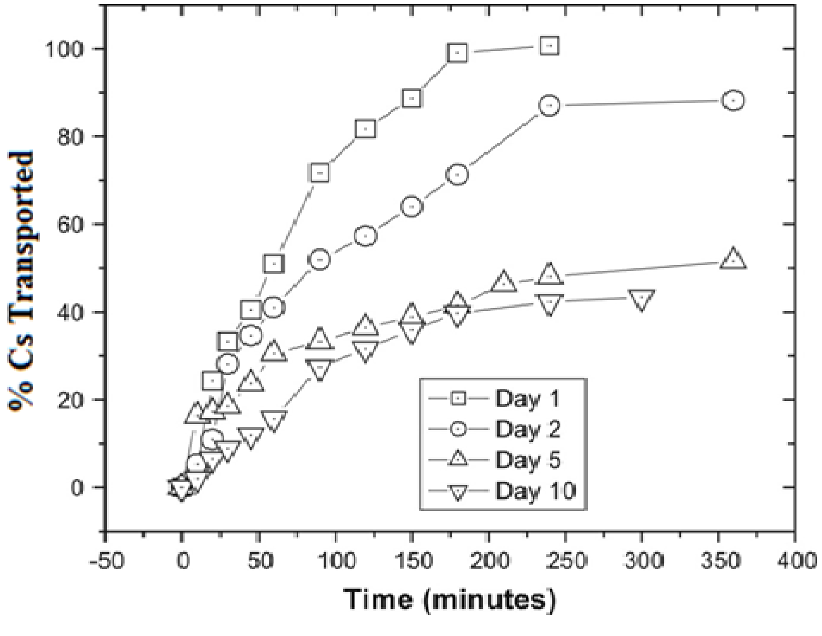


Figure 5.6: Stability of the SLM over 10 day's time period; Carrier: 4.0×10^{-3}M CBC+ 0.5% Alamine-336 (v/v) in PTMS; Feed: 3 M HNO_3; Receiver: distilled water.

The permeability as well as the acid transport data are included in **Table 5.5**. As evident from the permeability data, the stability of the membrane decreased with time. Poor stability of PTMS based supported liquid membranes has been reported in a previous study involving CCD (chlorinated cobalt dicarbollide) as the carrier extractant (120) and the observations made in the present study are in the same line. However, the membrane stability is acceptable in the initial period and it is suggested to use fresh membranes after two days of continuous operation. In view of the very low ligand inventory used in the SLM studies, it would still be a viable alternative to the solvent extraction based separation systems being proposed (121).

Above transport data suggests that CBC is the most suitable out of the four calix-crown-6 ligands evaluated in the present study. Overall, the transport rates are faster than those reported previously using calix-crown-6 ligands in other diluents such as nitrobenzene or the *n*-dodecane and NPOE mixture (59). The diluent viscosity is attributed to be the major cause for faster mass transfer rates in the present work. The acid co-transport rates were reasonably acceptable up to 5 h, beyond which a sharp increase was observed suggesting long term use of the membranes may be marred by the presence of nitric acid in the receiver compartment. This can be alleviated by destroying the nitric acid in the receiver compartment to make the transport system sustainable.

Studies with SHLLW appeared encouraging due to relatively higher mass transfer rates (as compared to those reported previously) and also very good selectivity to make the transport system highly promising for application in nuclear waste remediation. The Cs(I) transport rates from SHLLW can be improved even further by increasing the calix-crown-6 concentration in the SLM. However, studies with SLM stability has shown mixed results as the liquid membranes can be used for a couple of days only with marginal loss in transport rates beyond which a sharp fall in Cs(I) transport rates was noticed. In order to increase the throughput one needs to evaluate the solvent system (4.0×10^{-3} M CBC in PTMS) in the hollow fiber mode.

A recent solvent extraction study used bis-(octyloxy)-calix[4]arene-mono-crown-6 dissolved in 30% iso-decanol in *n*-dodecane as the diluent for the extraction of cesium from acidic feeds solutions (121). However, owing to the large ligand inventory in the solvent extraction method, it is imperative to explore hollow fiber based membrane technique, where the ligand inventory is extremely low. In the present work, therefore, attempt was made to explore the possible application of bis-(octyloxy) calix[4]arene-mono-crown-6 for the recovery of radio-cesium utilizing the hollow fiber membrane based technique. Various experimental conditions and diffusional parameters were optimized for efficient recovery of cesium.

5.8 Flat Sheet Membrane Transport of Cs(I) using CMC as Carrier

Transport profiles of Cs(I) in flat sheet SLM using CMC as the carrier are presented in **Figure 5.7.** The transport of Cs(I) increased with *iso*-decanol content from 20% to 30%, and remained nearly constant beyond 30% of iso-decanol. There is also co-transport of nitric acid to a much lower extent than the Cs(I) transport and the results are presented in **Figure 5.8.**

The permeability coefficients were calculated using the standard transport equation discussed in Chapter 2 and the results are listed in **Table 5.6**.

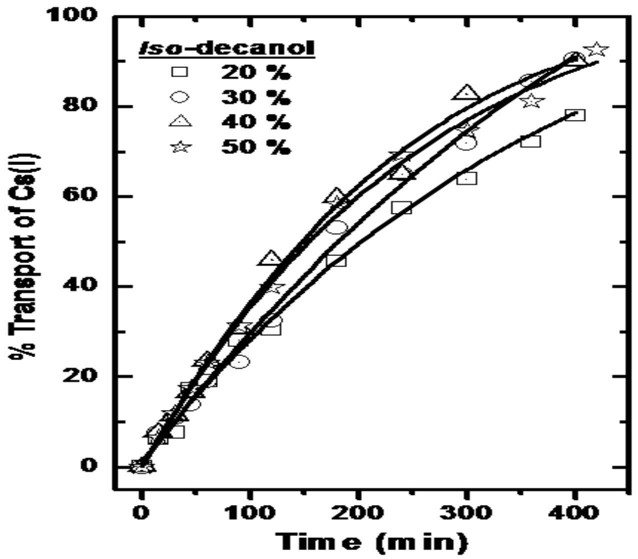


Figure 5.7: Flat Sheet SLM transport data showing the effect of solvent composition on the transport of Cs(I); Carrier: 1.0×10^{-2} M CMC in iso-decanol/*n*-dodecane mixed solvent; Feed: 4 M HNO_3 spiked with ^{137}Cs (20 mL); Receiver phase: dist. water (20 mL).

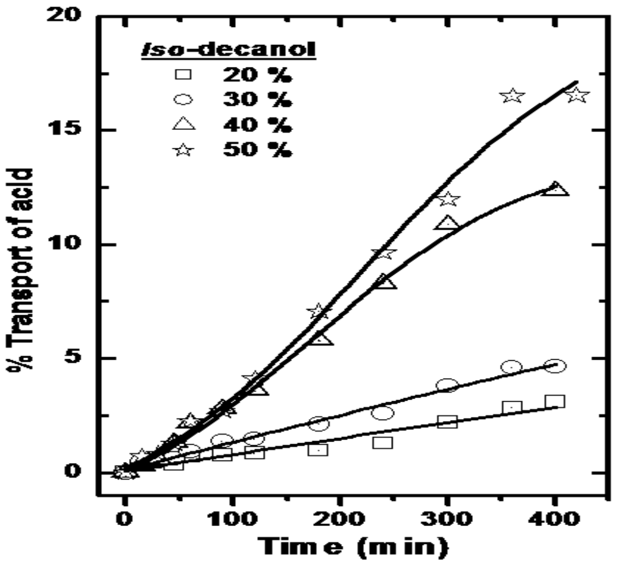


Figure 5.8: Flat Sheet SLM transport data showing the effect of solvent composition on the transport of nitric acid; Carrier: 1.0×10^{-2} M CMC in iso-decanol/*n*-dodecane mixed solvent; Feed: 4 M HNO_3 spiked with ^{137}Cs (20 mL); Receiver phase: dist. water (20 mL).

Table 5.6: Effect of iso-decanol on the transport data of Cs(I) in flat sheet SLM; Ligand: 1.0×10^{-2} M CMC in varied fractions of isodecanol in *n*-dodecane; Feed acidity: 3 M HNO_3.

% iso-decanol	$P\times10^4$ (cm/s)	%Transport of Cs(I) in 5 h	%Transport of acid in 5 h
20	2.97 ± 0.01	63.9	2.2
30	4.40 ± 0.02	71.8	3.8
40	4.69 ± 0.01	82.7	10.9
50	4.17 ± 0.08	74.6	12.0

As seen from the table, the permeability coefficient of Cs(I) was not affected with iso-decanol content in the solvent between 30-50%. After 7 h, the transport of Cs(I) with 30-40% iso-decanol was about 20% higher than the transport data obtained with 20% iso-decanol in the same time period. On the other hand, the transport of acid increased significantly with increased iso-decanol content. Since, long chain alcohols are known to extract acid (69), the effect is also seen with increase in the acid transport in the presented transport data. It should be noted that higher transport of acid at the receiver phase will have an adverse effect on metal ion decomplexation, which will reduce the stripping efficiency. Furthermore, lower feed acidity can have an impact on the metal ion extraction at the feed – membrane interface and hence, a concomitant reduction in transport efficiency. By looking into the D_{Cs}, transport of Cs(I) and co-transport of acid data, the solvent composition of 40% iso-decanol + 60% *n*-dodecane was considered as the optimum diluent composition for CMC, and all the further studies were carried out with this solvent.

Long chain alcohols, such as 1-decanol, show finite solubility in the aqueous phase (122). Due to the presence of significant amount of iso-decanol in the present solvent (40%), it may lead to leaching of the solvent from the membrane support, which in turn may cause damage to the SLM. The stability of the SLM was, therefore, investigated by measuring the transport of Cs(I) over a period of 12 days. In order to establish the SLM stability, the transport of Cs(I) was monitored for 8 h, and then feed and strip solutions were replaced with the fresh one and the transport experiment was repeated with the same membrane. As shown in **Table 5.7**, the transport was not affected even after 12 days of continuous use of the membrane.

Table 5.7: Transport data of Cs(I) in flat sheet SLM to evaluate the stability of membrane [Ligand]: 1.0x10^{-2} M CMC in 40% iso-decanol / *n*-dodecane; Feed acidity: 3 M HNO$_3$.

Time (days)	P×10^4 (cm/s)	%Transport of Cs(I) in 5 h	%Transport of acid in 5 h
1	4.99 ± 0.01	74.8	6.3
2	4.68 ± 0.02	74.2	8.1
6	4.82 ± 0.01	76.5	6.0
12	4.87 ± 0.08	73.3	6.8

Excellent reproducibility of the transport data over a period of 12 days (**Figure 5.9**) is an indication of possible scale up of the transport system using HFSLM.

Using the above mentioned basic information further studies were carried out using hollow fiber supported liquid membrane which are described in the following section.

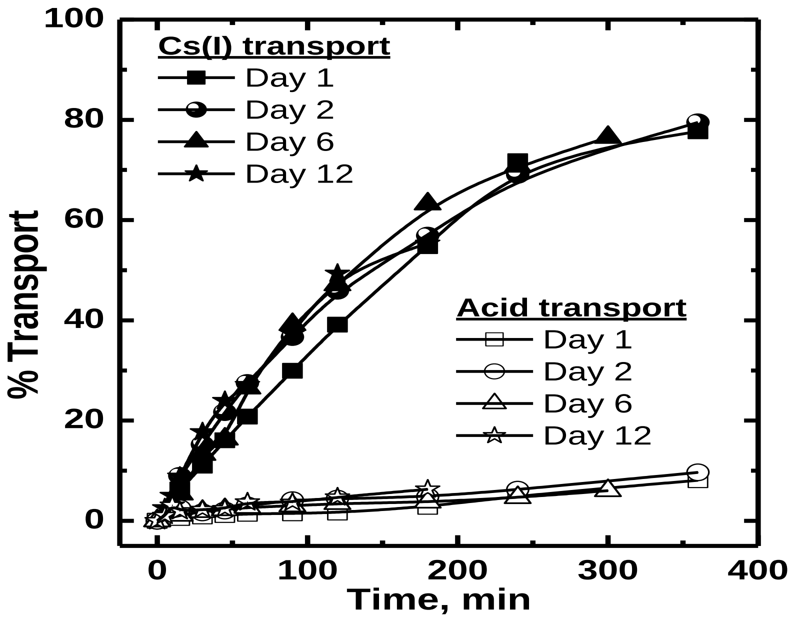


Figure 5.9: Flat sheet SLM transport of Cs(I), showing its stability over a period of 12 days; Carrier: 1.0×10^{-2} M CMC in 40% iso-decanol in *n*-dodecane; Feed: 4 M HNO_3 spiked with ^{137}Cs (20 mL); Receiver phase: Distilled water (20 mL).

5.8 Hollow Fiber Supported Liquid Membrane (HFSLM) Studies

After evaluating the four calix-crown-6 ligands in PTMS as the carrier solvent in the flat sheet supported liquid membrane studies, further work was carried out on the selective transport of Cs(I) using HFSLM. Initially, a few parameters which influence the transport of Cs(I) were investigated which are discussed below.

5.8.1 Effect of feed acidity on Cs(I) transport

After optimization of various conditions in solvent extraction and FSSLM, HFSLM studies were carried out with 15 times higher feed and receiver solution volumes (300 mL). In order to quantify the effect of feed acidity on the transport of Cs(I), experiments were performed from feed solutions of varying acidity (1-6 M HNO_3). The results from these studies are given in **Figure 5.10** These results clearly indicate the enhanced permeation rate of Cs(I) with increasing concentration of HNO_3 in feed. With increased nitric acid concentration, the concentration of nitrate ion is increased and, therefore, equilibrium reaction is favored due to the salting out effect. The P^* values calculated from the fitted slopes of the straight line plots presented in **Figure 5.11** are given in **Table 5.7**.

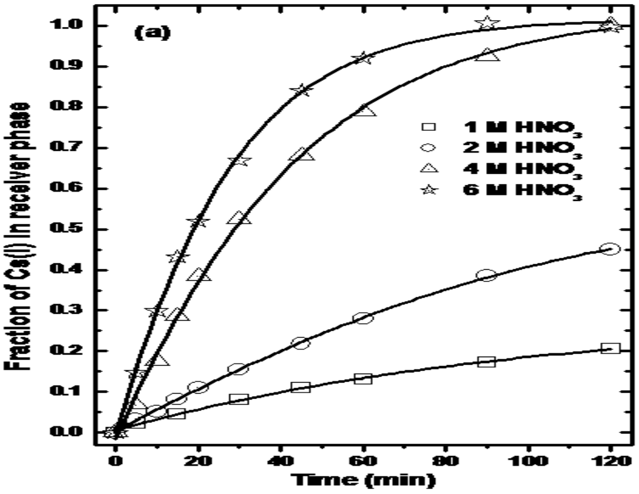


Figure 5.10: HFSLM transport profile of Cs(I) with HNO_3 concentration in the feed solution, Carrier: 1.0×10^{-2} M CMC in 40% isodecanol/*n*-dodecane; Feed: Varying HNO_3 concentration spiked with ^{137}Cs tracer (300 mL); Receiver phase: dist. water (300 mL); Flow rate: 200 mL/min.

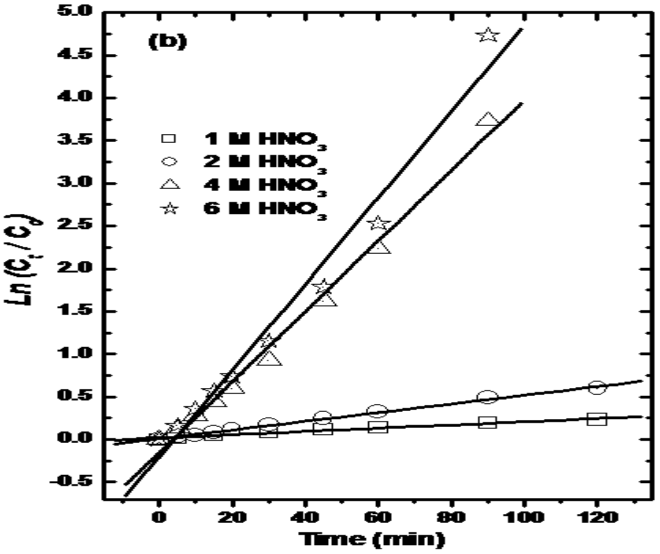


Figure 5.11: Plot of Ln(C_t/C_o) vs. time as function of HNO$_3$ concentration in the feed; Carrier: 1.0×10^{-2} M CMC in 40% iso-decanol/*n*-dodecane; Feed: Varying HNO$_3$ concentration spiked with ^{137}Cs tracer (300 mL); Receiver phase: dist. water (300 mL); Flow rate: 200 mL/min.

It was interesting to observe that near quantitative (> 99%) transport of Cs(I) could be achieved in 2 h of operation from the feed solution of 4 M HNO$_3$. It should be noted that under identical conditions of feed and strip solutions in FSSLM, only about 90% Cs(I) transport was recorded after 7 h when the feed and strip solutions were 20 mL. Higher transport of Cs(I) in the case of HFSLM is very obvious due to large surface area of the membrane. The *P** value increased gradually with feed acidity from 1.21×10^{-5} cm/s at 1 M HNO$_3$ to 3.27×10^{-4} cm/s at 6 M HNO$_3$ **(Table 5.7)**

5.8.2 Effect of solute concentration on Cs(I) transport

Since, HLLW contains significant concentration of Cs (~0.32 g/L), it was of interest to investigate its concentration effect on transport of Cs(I) using the CMC based solvent system by the hollow fiber liquid supported membrane. Results of the transport studies carried out using 1.0×10^{-2} M CMC in 40% isodecanol/*n*-dodecane are presented in **Figure 5.12.**

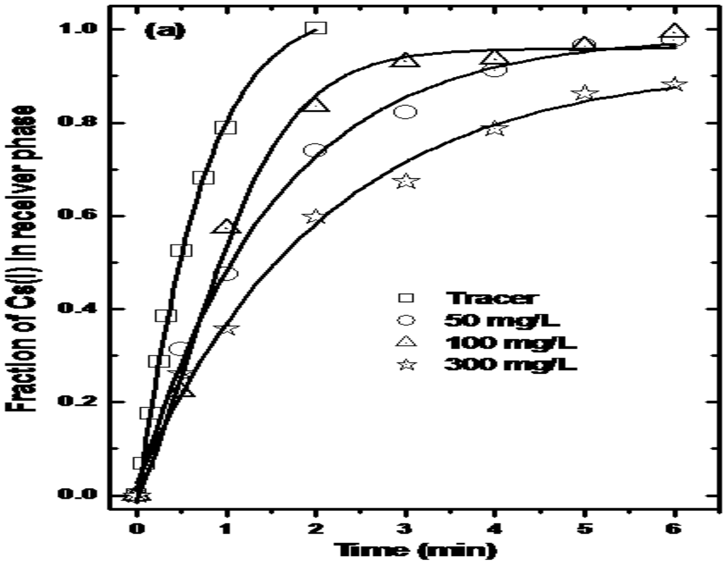


Fig. 5.12: HFSLM transport profile of Cs(I) transport with Cs conc. in the feed solution; Carrier: 1.0×10^{-2} M CMC in 40% iso-decanol/*n*-dodecane; Feed: 4 M HNO_3 spiked with ^{137}Cs (300 mL); Receiver phase: distilled water (300 mL); Flow rate: 200 mL/min.

It is evident from these results that the near quantitative transport of Cs(I) is possible in about 2 h when it is present at tracer concentrations. As the concentration of Cs(I) in the feed solution increases, its permeation rate decreases. However, decrease in the transport rate was not sharp, indicating that the effect is not much pronounced. After 5 h of operation, the transport values of Cs(I) were: 100% , 96%, 95% and 86% for tracer, 50 mg/L, 100 mg/L and 300 mg/L feed solutions, respectively.

The P^* value of the transported Cs(I) decreased from 2.67×10^{-4} cm/s at tracer concentration to 4.11×10^{-5} cm/s at 300 mg/L. **(Table 5.8).**

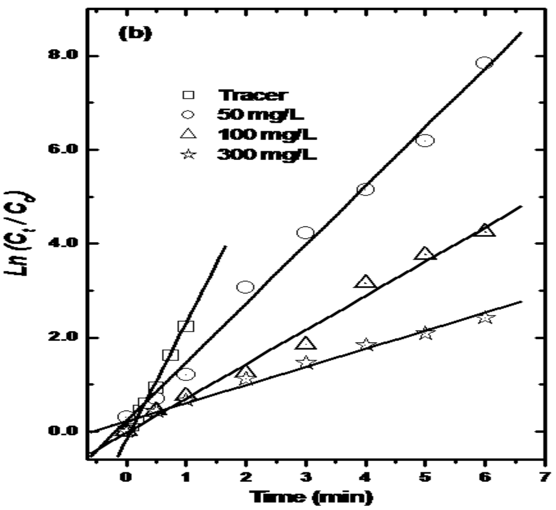


Fig. 5.13: Plot of Ln(C_t/C_o) vs. time as a function of Cs conc. in the feed solution; Carrier: 1.0×10^{-2} M CMC in 40% isodecanol/*n*-dodecane; Feed: 4 M HNO$_3$ spiked with ^{137}Cs (300 mL); Receiver phase: distilled water (300 mL); Flow rate: 200 mL/min.

Table 5.8: Distribution behaviors and permeability coefficient of Cs(I) by CMC in HFSLM; [Ligand]: 1.0×10^{-2} M in 40% isodecanol + 60% *n*-dodecane.

[Cs], mg/L	Feed Acidity	P*×10^5 (cm/s)	%T in 2 h
Tracer	1 M HNO$_3$	1.21 ± 0.04	20.6
Tracer	2 M HNO$_3$	3.26 ± 0.11	45.0
Tracer	4 M HNO$_3$	26.7 ± 0.87	100.2
Tracer	6 M HNO$_3$	32.7 ± 1.2	99.7
50 mg/L	4 M HNO$_3$	13.4 ± 0.63	83.5
100 mg/L	4 M HNO$_3$	7.78 ± 0.47	73.9
300 mg/L	4 M HNO$_3$	4.11 ± 0.22	59.8

5.9 Diffusional Parameters

It is well known that (122,123,67), the permeation of the Cs(I)-CMC complex

($(Cs{\cdot}L)(NO_3)_{(org)}$) across the liquid membrane takes place in the following three steps: (i) extraction of Cs(I) at feed-membrane interface, (ii) diffusion of the Cs(I) - CMC complex across the liquid membrane, and (iii) back extraction of Cs(I) at membrane-strip interface. Therefore, the permeability of the transporting species, $(Cs{\cdot}L)(NO_3)_{(org)}$, in the HFSLM depends upon the following three mass transfer resistances (67) (i) resistance due to flowing feed solution inside the lumen of the hollow fiber, (ii) resistance due to diffusion of the metal-ligand complex across the liquid membrane which is immobilized in the porous wall of the fiber, and (iii) resistance due to flowing strip solution outside the lumen (shell side). The overall permeability coefficient (P^*) is related with these resistances by the following equation. (125)

$$\frac{1}{P^*} = \frac{1}{k_f} + \frac{r_i}{r_{lm} \cdot k_m \cdot K_{ex} \cdot [NO_3^-] \cdot [L]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 5.3$$

where, r_i, and r_{lm} are the internal radius, and log-mean radius of the hollow fiber tube, respectively. Furthermore, k_m is the membrane mass transfer coefficient, and k_f is the aqueous feed mass transfer coefficient in the tube side. Above relation has been derived base on the equilibrium reaction at the feed-membrane and strip-membrane interfaces, and by assuming that the stripping reaction is instantaneous (vide supra) at the membrane-strip interface which neglects the shell side aqueous phase resistance.

A plot of $1/P^*$ vs $1/K_{ex} \cdot [NO_3^-][L]$ yielded a straight line **(Figure 5.14)** and the k_f value was obtained from the intercept of the plot. Similarly, the k_m value was obtained from the slope of the same plot (i.e. $slope = r_i / r_{lm} {\cdot} k_m$) as radius of the hollow fiber is known. The values of k_f and k_m were experimentally determined to be 3.68×10^{-4} cm/s and 6.68×10^{-5} cm/s, respectively. The value of k_f was an order of magnitude higher as compared to k_m, suggesting that the membrane mass transfer coefficient is the rate controlling step in the overall transport process. The membrane diffusion coefficient (D_o) for the [(CsL)(NO$_3$)] complex in the liquid membrane phase is related to the solid support properties by $D_o = K_m.d_o. \tau$, where d_o is the fiber wall thickness (3×10^{-3} cm) and τ is the tortuosity factor (2.5). The D_o value for the present system was calculated to be 5.01×10^{-7} cm^2/s. The D_o value calculated using the Wilke-Chang equation (115) was found to be 3.09×10^{-7} cm^2/s and that obtained from lag-time experiment (117) the value was found to be 2.57×10^{-7} cm^2/s suggesting good agreement.

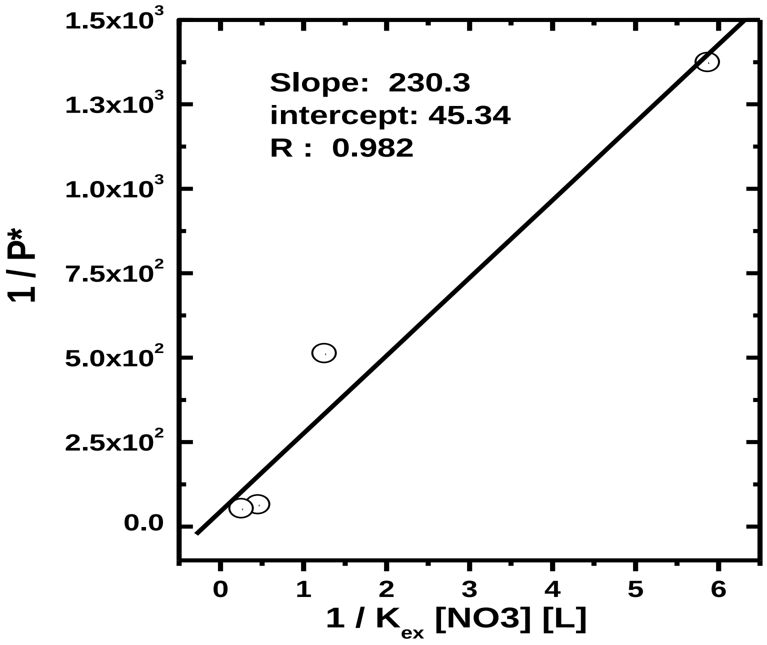


Figure 5.14: Plot of *1/P vs 1/*K*$_{ex}$[L][NO$_3^-$] for the calculation of mass transfer coefficients**

In summary, the results presented in this chapter are from the supported liquid membrane transport studies using the four calix-crown-6 ligands (CC, CNC, CBC and CMC) in the fluorinated diluent, PTMS. The transport data in PTMS suggested CBC being the most suitable out of the calix-crown-6 ligands evaluated in the present study. Overall, the transport rates are faster than those reported previously (80,81,79) using calix-crown-6 ligands in other diluents such as nitrobenzene or the n-dodecane and NPOE mixture. The diluent viscosity is attributed to be the major cause for faster mass transfer rates in the present work. The acid co-transport rates were reasonably acceptable up to 5 h, beyond which sharp increase was seen. This can be alleviated by destroying the nitric acid in the receiver compartment. Studies with SHLW appeared encouraging due to relatively higher mass transfer rates (as compared to those reported previously) and also very good selectivity to make the transport system highly promising in application for nuclear waste remediation. The Cs(I) transport rates from SHLW can be improved even further by increasing the calix-crown-6 concentration used in the SLM studies. However, studies with SLM stability has shown mixed results as marginal loss in transport rates was seen in the first couple of days beyond which a sharp fall in Cs(I) transport rates was noticed. In order to increase the throughput one needs to evaluate the solvent system (4.0×10^{-3} M CBC in PTMS) in the hollow fiber mode.

In the second part of the SLM studies, FSSLM studies were carried out using solutions of bis-octyloxy-calix[4]arene-mono-crown-6 (CMC) in a mixed diluents system of 40 % iso-decanol and 60 % *n*-dodecane. In view of the encouraging stability data over a period of 12 days, the FSSLM studies were extended to those involving a hollow fiber contactor.

A hollow fiber supported liquid membrane (HFSLM) based method was developed for selective recovery of radio-cesium from HLLW selective carrier ligand. The permeation of cesium increased with nitric acid concentration from 1 M to 6 M HNO_3. At moderate acidity of 3-4 M HNO_3, near quantitative transport of Cs(I) was possible within 2 h of operation at 300 mL feed scale. The efficiency of the transport process could be improved in HFSLM system by increasing the surface area of the hollow fiber module. The present work explored the possible application of exotic ligands such as CMC in HFSLM technique for radioactive waste treatment where the ligand inventory is very low.

SEPARATION STUDIES FROM ACTUAL HLLW

6.1 Introduction

Separation methods for radio-cesium recovery have been developed from acidic feed solutions using calix-crown-6 ligands in different diluent systems and the results are discussed in Chapters 3 and 5. This chapter utilizes two methods for the separation of radio-cesium from actual HLLW using these calix[4]arene-crown-6 based solvent systems. While the solvent extraction method involved calix[4]arene-bis-benzo-crwon-6 (CBC) in PTMS (phenyltrifluoromethyl sulphone), the hollow fiber supported liquid membrane (HFSLM) method used bis-octyl-benzo-calix[4]arene-mono-crown-6 (CMC) in 40% iso-decanol + 60% *n*-dodecane as the carrier extractant. Selective extraction of Cs(I) with almost no contamination from the associated fission product radionuclides is achieved using both the techniques. The HFSLM results in the Chapter 5 were based on modules containing polypropylene fibers. However, polypropylene fiber based contactor is not suitable in view limited radiolytic stability of the polymer. On the other hand, polysulphone (PS) based hollow fiber contactor has been reported to have better radiation resistance. PS fiber containing hollow fiber contactor was used in the present work involving actual HLLW. The results indicate that the radiolytic stability of the hollow fibers is excellent with good reproducibility of mass transfer data suggesting efficacy of this method for radioactive waste remediation. Results from the experiments carried out using waste solutions, simulated as well as real, are described below.

6.2 Solvent Extraction Studies

6.2.1 Studies with simulated HLLW

The composition of the simulated HLLW used in present study is given in **Table 2.1** of Chapter 2. The final acidity of the simulated HLLW was maintained at 3.0 M HNO_3, as estimated by titration against standard NaOH solution in pre-neutralized potassium oxalate (10%) medium using a pH meter. This is the acidity generally maintained for HLLW generated from PUREX process.

In order to understand the extraction behaviour of Cs(I), initial extraction experiments were carried out using 1.0×10^{-3} M CBC diluted in PTMS from ^{137}Cs tracer spiked simulated HLLW as the feed. Extraction of Cs(I) was also studied from uranium depleted SHLLW as well as a synthetic waste solution containing no uranium. The depletion of uranium from the simulated HLLW was carried out by solvent extraction method using 30% TBP in *n*-dodecane. As described in the experimental chapter, 2 mL lots of the SHLLW solutions of different nature with respect to uranium were contacted with 2 mL of the extractant separately for about 10 minutes in all these experiments. The phases after centrifugation were separated and subjected to radiometric assay for the assay of ^{137}Cs using NaI(Tl) scintillation counter. Percent extraction of Cs(I) for each case was calculated and the results are given in **Table 6.1.**

Table 6.1: Extraction of Cs from simulated HLLW feed solution spiked with ^{137}Cs tracer; Extractant: 1.0×10^{-3} M CBC diluted in PTMS. Contact time: 10 minutes; Volume ratio: 1; Volume of each phase: 2 mL.

Feed details	^{137}Cs activity cpm per 100μL			Extraction (%)
	Feed	Organic Phase	Aqueous phase	
Simulated HLLW	44350	18023	25884	40.64
Uranium depleted simulated HLLW	43807	17986	25884	41.06
Simulated HLLW without uranium addition	44540	18820	26518	42.50

The above results show that Cs(I) extraction from the simulated HLLW solutions are only to the extent of ~40% with all the three types of feed solutions. As reported in Chapter 3, when ^{137}Cs tracer solution in 3 M HNO_3 was contacted with 1.0×10^{-3} M CBC solution in PTMS, a single contact carried out with a volume ratio of 1 (organic to aqueous phase volume ratio = 1), resulted in ~91% extraction of Cs. Lower extraction of Cs(I) from HLLW is attributed to the higher concentration of Cs (0.3 g/L) in the SHLLW. This can be explained based on higher loading of Cs(I) ion in the organic phase resulting in a decrease in the free ligand concentration. However, it is expected that the extraction of the metal ion can be improved using higher concentrations of the extractant. Such loading effect has been explained in Chapter 3 when feeds containing varying concentrations of Cs were used for the extraction studies. Above results clearly show that the concentration of Cs in the feed has great impact on the extraction of the former.

Results given in **Table 6.1** also indicate that the presence of uranium does not interfere in the extraction of Cs(I) ion by the calix–crown-6 ligands as the distribution ratio of Cs(I) is not affected by the presence of uranyl ion which is poorly extracted by these ligands. Since the depletion of uranium and plutonium by the PUREX solvent (30% TBP in *n*-dodecane) is one of the mandatory steps during the partitioning of actinides from HLLW, further studies were carried out using uranium depleted HLLW solutions as the feed. Prior to employing the calix-crown-6 ligands for Cs(I) ion recovery, the extraction behaviour of other metal ions present in HLLW was studied which is discussed below.

6.2.2 Extraction behaviour of metal ions present in HLLW

As already mentioned in Chapter 2, HLLW is a highly complex matrix. Besides the actinides, it contains many metal ions which are present as fission products or are from the structural materials or impurities from the chemicals added during the reprocessing operations. Concentrations of the metal ions present in the HLLW depend upon factors such as the fuel burn up, cooling period, efficiency of the PUREX process and the volume of the waste that gets generated per tonne of the fuel reprocessed. The extraction behaviour of metal ions from the simulated HLLW solution was studied using solvents containing all the four calix–crown-6 ligands. As described in Chapter 2, exactly 2 mL of the simulated HLLW feed solution was contacted with 2 mL each of the solvents (1×10^{-3} M solutions of CC, CBC, CNC and CMC in PTMS) in separate vials for about 10 minutes. After contacting, the phases were centrifuged and separated. Aqueous phases from each vial were diluted to 200 times accurately in 0.5 M HNO_3 and subjected to elemental analysis using ICP-AES. In each case, the concentrations of the individual elements in each raffinate phase and feed were analyzed and compared. The results of the analysis for feed as well as raffinate phase for each ligand are presented in **Table 6.2.** These results clearly indicate that the extraction of metal ions other than Ba, La, Mo and Mn is almost negligible indicating the selectivity of the calix–crown-6 ligands for Cs(I) ion recovery from the simulated PUREX-HLLW. Small contamination of any metal ion, if any, observed during extraction can be removed by incorporation a scrub step using 3 M HNO_3 from the organic phase which is a common practice in solvent extraction processes. This step helps to get the desired purity of radio-cesium without any loss during the extraction step. Encouraged by these results, further studies were carried out using actual HLLW solution and the results of these studies are described below.

Table 6.2: ICP-AES analysis results for SHLLW and the aqueous phases obtained after extraction using the irradiated solvents containing the calix-crown-6 ligands (1.0×10^{-3} M) in PTMS

Element	SHLLW (μg/mL)	CC (μg/mL)	CBC (μg/mL)	CNC (μg/mL)	CMC (μg/mL)
Ba	57 ± 6	34 ± 2	30 ±3	38 ±4	50 ±5
Ce	2.8 ±0.3	2.8± 0.3	2.7 ±0.3	2.7 ±0.3	2.8 ±0.2
Co	10.5 ±1	10.7±1	10.0 ±1	10.5 ±1	10.5 ±1
Cr	11.0 ± 1	10.2+1	10.6 ±1	10.1 ±1	10.2 ±1
Cu	2.5 ±0.2	2.3 ± 0.2	2.2 ±0.2	2.2 ±0.2	2.2 ±0.2
Fe	87 ±9	88 ±8	85 ±9	84 ±8	88 ±0.9
La	3.4 ±0.3	1.7 ±0.2	1.9 ±0.2	2.2 ±0.2	2.7 ±0.3
Mn	52 ±5	47 ±0.5	45 ±0.5	44 ±4	45 ±4
Mo	19.2 ±2	14.1 ±1	14.9 ±1.5	15.6 ±1.6	17.4 ±2
Nd	7.6 ±0.8	7.2 ±0.7	7.0 ±0.7	7.0 ±0.7	7.1±0.7
Ni	8.6 ±0.8	9.0 ±0.9	8.5 ±0.9	8.1 ±0.8	8.2±0.8
Sm	12.2 ±1.2	12.2 ±1	12.5 ±1.2	12.0 ±1.2	11.8±1.1
Sr	2.5 ±0.3	2.6 ±0.3	2.4 ±0.2	2.3 ±0.23	2.4±0.2
Y	11.2 ±1.1	11.9 ±1	11.2 ±1.1	10.8 ±1.1	10.8±1
Zr	4.8 ±0.5	4.4 ±0.4	4.2 ±0.4	4.3 ±0.4	4.3±0.4

6.2.3 Studies with actual HLLW

The HLLW used in the present studies was a composite waste obtained from a laboratory engaged in process control analytical tasks involving PUREX process samples. The composition of which is given in **Table 2.4** after uranium depletion. The actual waste was contacted with 30% TBP in *n*-dodecane twice for depletion of uranium and plutonium and used as feed for radio-cesium recovery. The initial recovery studies were carried out using 100 times diluted HLLW to establish the co-current batch process which was later extended to studies using the undiluted waste. As described above, 1.0×10^{-3} M CBC diluted in PTMS was used as the solvent system. The results from these studies are described below.

6.2.4 Studies with diluted HLLW

As stated above, the first set of studies with actual HLLW (composition given in Table 2.2 in Chapter 2) was carried out with a 100 times diluted solution. For dilution purpose, 3 M HNO_3 solution was used so as to maintain its acidity to 3 M which is the acidity of the actual HLLW. These studies were carried out in a fume hood with adequate shielding facility so as to reduce the dose rate at fume hood panel below the specified 1 mR/h level. Though our studies with simulated HLLW suggested insignificant role of uranium on the Cs(I) extraction, two consecutive contacts with 30% TBP in *n*-dodecane reduced uranium to 80 mg/L without any significant loss of Cs from the feed.

As described in the experimental section, four contacts of 10 minutes each were given while maintaining the organic to aqueous phase volume ratio as 1:1. For reducing the MANREM exposure, contact time of only 10 minutes was maintained in this case as this was enough to get the equilibrium as seen from a trial study carried out previously. Each time after equilibration, the phases were centrifuged and the organic phase was carefully taken out and kept in another vial retaining the aqueous phase in the first vial. Fresh lots of the organic phase were introduced for the subsequent contacts. The extracted organic phases from all the four contacts and the final raffinate phase were subjected to individual fission product analyses using gamma ray spectrometry using an HPGe detector coupled to a multi-channel analyzer. Results expressed as mCi/L for each of the organic phases and the final raffinate phases are given in **Table 6.3.**

Table 6.3: Extraction data with diluted HLLW: Extractant: 1.0×10^{-3} M CBC in PTMS; Feed: uranium depleted HLLW after diluting 100 times; Volume ratio: 1, Volume: 2 mL of each phase; Contact time: 10 minutes.

Constituents	Activity (in mCi/L)				
	Organic (1st contact)	Organic (2nd contact)	Organic (3rd contact)	Organic (4th contact)	Raffinate
^{144}Ce	ND	ND	ND	ND	108.5
^{106}Ru	0.18	0.20	0.16	0.17	67.2
^{137}Cs	31.4	16.1	2.5	0.5	<0.1
^{95}Zr	ND	ND	ND	ND	0.019
^{95}Nb	ND	ND	ND	ND	0.256

As shown in the table, the radio-cesium, ^{137}Cs and ^{134}Cs (not shown in the table) recovery was near quantitative with very little loss towards the raffinate phase while the other fission product radionuclides such as ^{144}Ce, ^{95}Zr and ^{95}Nb were not extracted at all. Very small fraction of ^{106}Ru was seen to be extracted suggesting the specificity of the solvent system. The raffinate after the fourth contact contained < 0.1 mCi/L of Cs activity suggesting a fifth contact was not necessary. Results of this extraction experiment are presented in **Table 6.3** which suggest quantitative radio-cesium recovery. Though the data presented shows only ^{137}Cs, the recovered radio-cesium also contained ^{134}Cs and ^{135}Cs. As expected, these results clearly suggest that radio-cesium can be quantitatively extracted using CBC in four contacts. To improve the purity of the radio-cesium with respect to Ru (co-extracted to a small extent), a separate experiment was carried out which is described below.

In a separate experiment, the small amount of Ru contamination seen in the organic phase could be removed by a scrubbing step using 3 M HNO_3 at an organic to aqueous phase volume ratio of 1 in a single stage without any significant Cs loss. To validate this, a scrubbing experiment was carried out using Ru containing organic phase generated from the fourth contact from co-current extraction studies explained above which had only 0.5 mCi/L Cs activity and Ru contamination of 0.17 mCi/L level. In single contact using 3 M HNO_3, organic phase was found to have no Ru activity indicating the efficacy of scrubbing stage.

In order to recover the loaded radio-cesium from the organic phase, the loaded solvents containing the radio-cesium from the first three contacts were mixed together to obtain a composite organic phase. The extract obtained from the fourth contact was discarded in view of the very low amount of the radio-cesium content (0.5 mCi/L) in it. It has been reported that the stripping of Cs(I) from the loaded organic phase containing the calix[4]arene-crown-6 ligands is not so straight forward and as reported by Delmau et al.,$^{(126)}$ the addition of a tertiary amine to the solvent has been beneficial. This finding was used for the stripping of the extracted radio-cesium from the organic phase. It was observed that the addition of a small amount of Alamine-336 to the organic solvent enhances the stripping efficiency of Cs(I) from the organic phase and these results are already described in Chapter 3. For radio-cesium recovery, the composite organic phase, after adding 0.5% (v/v) Alamine-336, was analysed for individual fission products and used for the subsequent stripping contact using distilled water at an organic to aqueous phase volume ratio of 1:1. For this purpose, an accurately measured 5 mL lot of the scrubbed organic phase was subjected to stripping by contacting with 5 mL of distilled water for about 5 minutes. Results from two successive contacts are presented in **Table 6.4**. Results clearly explain that about 94% Cs(I) can be stripped in the first contact under the experimental conditions described above. The remaining amount of the radio-cesium present in the organic extract could be stripped in the second contact (**Table 6.4**). The lean organic phases did not show any Cs activity above background level indicating quantitative recovery of radio-cesium.

Table 6.4: Stripping data using composite organic phase; Feed: 5 mL of organic extract (first three extracts after adding 0.5 % V/V Alamine-336); Strippant: distilled water; Volume ratio: 1; Contact time: 5 minutes.

Radionuclide detected	Activity in mCi/L			
	Composite organic extract	Strip fraction-1	Strip fraction-2	Lean organic
^{137}Cs	16.5	15.45	1.12	ND

The above results clearly indicate that the CBC is very selective for Cs(I) extraction and the extracted Cs(I) from the organic phase can be quantitatively stripped in two contacts.

6.2.5 Studies using actual HLLW

Encouraged by the above results, an attempt was made to recover radio-cesium from an actual HLLW sample. However, in view of very high dose (>100 R/h), the studies were carried out by taking only 2 mL of the actual HLLW solution. As mentioned above, uranium depleted HLLW by 30% TBP in *n*-dodecane was used as the feed. The actual HLLW was successively contacted with fresh 2 mL lots of 1.0×10^{-3} M CBC in PTMS (which also contained 0.5% Alamine 336) and this was done four times as after that the raffinate contained <0.02 mCi/L of ^{137}Cs activity. The extraction experiments were carried out in the dilution cell of a hot cell area using remotely operated tongs. These experiments were carried out in leak proof plastic vials of about 15 mL capacity. Contact time of about 10 minutes was maintained in each contact a manner similar to that carried out in the case of extraction studies from the diluted waste (vide supra). The organic and the aqueous phases were separated remotely using 1 mL capacity Metrohm Tele Dosimat pipetting set up. Organic extracts from each contact were preserved in separate vials. After four contacts, all the four organic extracts as well as the fourth contact raffinate were assayed for individual fission products. Results of this extraction experiment are presented in **Table 6.5** which suggested quantitative radio-cesium recovery from the HLLW. Though the data presented shows only ^{137}Cs, the recovered radio-cesium also contained ^{134}Cs and ^{135}Cs. As expected, these results clearly suggest that radio-cesium can be quantitatively extracted using CBC in four contacts in a manner similar to the diluted HLLW case reported above. No other fission product was detected in any of the organic phase fractions during the extraction experiment (**Table 6.5**).

Table 6.5: Radio-cesium extraction from actual HLLW; Aqueous feed: Uranium depleted actual HLLW, Extractant: 1.0×10^{-3}M CBC in PTMS; Volume ratio: 1; Volume: 2 mL for each phase; Contact Time:10 minutes.

Constituents	Activity (in Ci/L for ^{144}Ce, ^{106}Ru and ^{137}Cs; in mCi/L for ^{95}Zr and ^{95}Nb)				
	Organic (1st contact)	Organic (2nd contact)	Organic (3rd contact)	Organic (4th contact)	Raffinate
^{144}Ce	ND	ND	ND	ND	10.89
^{106}Ru	0.020	0.018	0.024	0.019	6.72
^{137}Cs	3.07	1.83	0.14	0.05	<0.02
^{95}Zr	ND	ND	ND	ND	2.2
^{95}Nb	ND	ND	ND	ND	24.82

First three organic phases from the extraction cycles were mixed to obtain 5 mL of loaded composite organic phase as described in the previous section and was subsequently used for the stripping studies. Under similar experimental conditions of stripping mentioned above, quantitative recovery of ^{137}Cs was observed when contacted with 5 mL distilled water in two contacts. The results from the stripping studies are shown in **Table 6.6**. These studies show quantitative recovery of radio-cesium using CBC in PTMS as the solvent system.

In order to check the purity of the product, a suitable aliquot from the recovered Cs product was subjected to gamma ray spectrometry using HPGe detector coupled to a 4k multi-channel analyzer. The gamma ray spectra of the untreated HLLW and the recovered radio-cesium are presented in **Figures 6.1** and **6.2.**

Table 6.6: Stripping data using composite organic phase from the extracts obtained with undiluted HLLW, Feed: 5 mL of ^{137}Cs loaded organic extract (first three organic extracts were mixed), Strippant: distilled water; Volume ratio: 1; Contact time: 5 minutes

Radionuclide detected	Activity (in mCi/mL)			
	Composite organic extract	Strip fraction-1	Strip fraction-2	Lean organic
^{137}Cs	1.71	1.6	0.12	ND

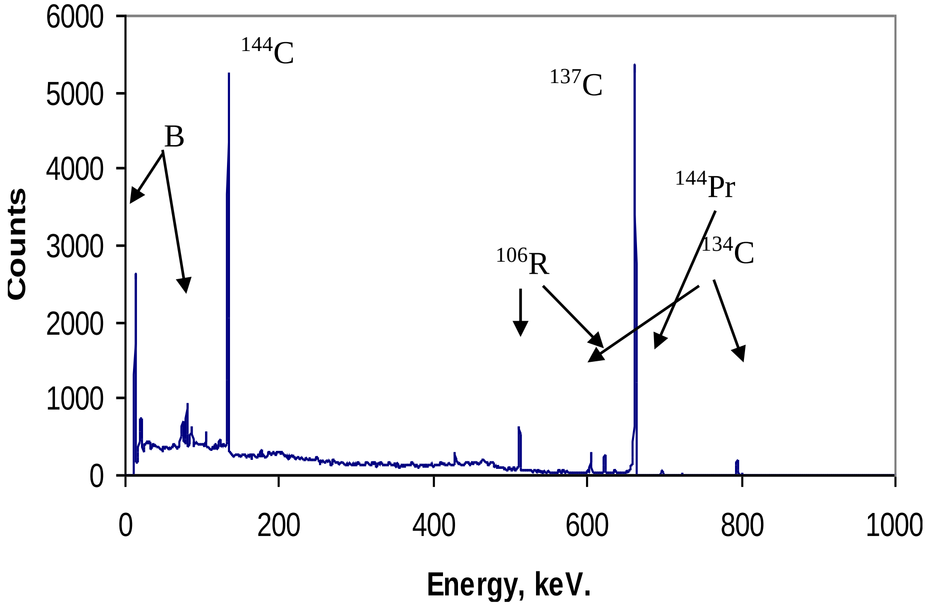


Figure 6.1: Gamma ray spectra of untreated HLLW

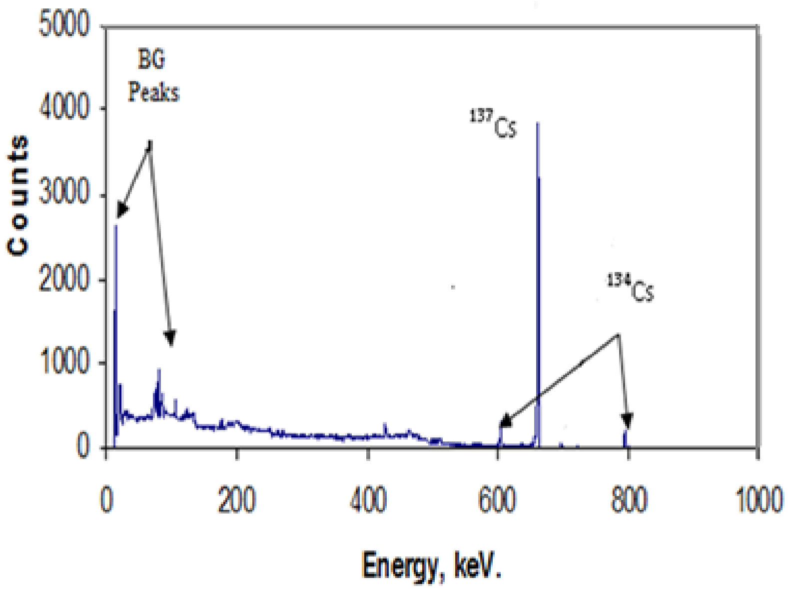


Figure 6.2: Gamma ray spectra of recovered Cs product from HLLW

As seen from the gamma ray spectra of the untreated HLLW and the strip fraction, the presence of other radionuclide is not detected in recovered Cs product. This suggests that the present method can be deployed for the selective separation of high purity radio-cesium from the actual HLLW. After establishing the extraction and stripping parameters of Cs(I) from HLLW using CBC in PTMS studies were extended for the recovery of radio-cesium using supported liquid membrane by a hollow fiber contactor. Advantages of such membrane techniques are already explained in Chapter 1 of this thesis.

6.3 Supported Liquid Membrane Studies

After establishing the transport parameters of Cs(I) (Chapter 5) from nitric acid medium, studies were extended to separate radio-cesium from simulated HLLW (spiked with ^{137}Cs) as well as actual HLLW using the calix-crown-6 ligands.

6.3.1 Transport studies involving simulated HLLW

Results of Cs(I) transport studies as described in Chapter 5 appear promising for the separation of the metal ion from nitric acid feeds. Further studies were carried out for Cs(I) recovery from simulated HLLW (SHLLW) solutions using SLM containing CBC in PTMS. The feed solutions, (SHLLW) spiked with ^{137}Cs radiotracer, were used for the transport studies using 4.0×10^{-3} M CBC and 0.5 % Alamine 336 in PTMS as the carrier solvent. The Cs(I) transport profiles are presented in **Figure 6.3** which show ~60% mass transfer in 5 h as against quantitative transport seen when the feed solution contained ^{137}Cs tracer spiked acid solution (3 M HNO_3).

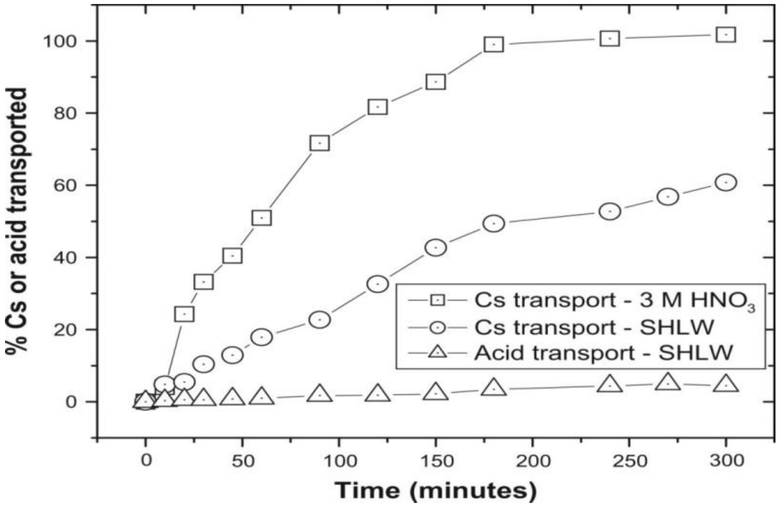


Figure 6.3: Comparative transport behaviour of Cs(I) from tracer spiked feeds of 3.0 M HNO_3 and SHLLW (3.0M HNO_3); Carrier: $4.0{\times}10^{-3}$ M CBC + 0.5 % Alamine-336(v/v) in PTMS; Receiver: distilled water.

The transport rates are significantly higher than that obtained using CNC in nitrobenzene (80) as the carrier solvent which resulted in a little over 20% Cs transport after 5 h as against 60% reported in the present study. The nitric acid co-transport during the study involving

SHLLW as the feed (with 3 M HNO_3) was found to be ~ 4.5% which was significantly lower than ~7% acid co-transport observed when ^{137}Cs tracer in 3 M HNO_3 was used as the feed **(Figure 6.3)**. The lower nitric acid co-transport in the case of SHLLW as the feed is attributed to larger fraction of the calix-crown-6 ligands in the membrane phase being engaged in Cs(I) transport (due to the presence of about 300 mg/L Cs carrier in the SHLLW). The other components of SHLLW were also monitored by measuring their concentrations as a function of time in the feed as well as the receiver compartment by ICP-AES analysis and the results are presented in **Table 6. 7**. It is clear from the data presented in **Table 6.7** that most of the components (other than K(I)) of SHLLW are not transported under the experimental conditions employed implying very high selectivity for Cs (I) transport with respect to the other metal ions present in the SHLLW. This makes the present transport system highly effective for the recovery of radio-cesium from radioactive wastes. It may be emphasized here that only 4.0×10^{-3} M CBC has been employed in the present study as against a recent claim of using 0.01 M CMC in a solvent extraction study (121). As the transport rates are guided by the ligand concentration, increasing the ligand concentration from 4.0×10^{-3} M to 0.01 M will result in a much higher transport rates. Furthermore, the solvent inventory in the case of the SLM based separation method will be significantly lower as compared to the solvent extraction method.

Studies with SHLLW appeared encouraging due to relatively higher mass transfer rates (as compared to those reported previously) and also very good selectivity to make the transport system highly promising for application to nuclear waste remediation. The Cs(I) transport rates from SHLLW can be improved even further by increasing the calix-crown-6 concentration in the

Table 6.7: Transport data of components of SHLLW as a function of time

Carrier: 4.0×10^{-3} M CBC+ 0.5 % Alamine336 in PTMS; Feed: SHLLW (3 M HNO_3).

Metal ion	Metal ion concentrations (ppm) as indicated after different time intervals						
	Concentration in feed				Concentrations in receiver		
	Initial	1 h	4 h	24 h	1 h	4 h	24 h
Ba(II)	3.6±0.1	3.6±0.1	3.6±0.1	3.6±0.1	<0.05	<0.05	<0.05
Mo(VI)	96±5	96±5	96±5	97±5	<0.05	<0.05	<0.05
Sr(II)	2.5 ±0.1	2.5 ±0.1	2.5 ±0.1	2.5 ±0.1	<0.05	<0.05	<0.05
Fe(III)	16±1	15±1	16±1	16±1	<0.05	<0.05	<0.05
Mn(VII)	9.3±0.5	8.7±0.5	8.8±0.5	9.1±0.5	<0.05	<0.05	<0.05
Cr(VI)	4.5±0.2	4.7±0.2	4.7±0.2	4.7±0.2	<0.05	<0.05	<0.05
K(I)	5.3±0.2	5.1±0.2	4.8±0.2	3.6±0.2	<0.05	<0.05	0.3±0.2
Na(I)	92±5	92±5	90±5	82±5	<0.05	<0.05	<0.05
Sm(III)	2.1 ±0.1	2.1 ±0.1	2.2 ±0.1	2.2 ±0.1	<0.05	<0.05	<0.05
Nd(III)	3.1 ±0.2	3.0 ±0.2	3.1 ±0.2	2.9 ±0.2	<0.05	<0.05	<0.05
Pm(III)	2.5 ±0.1	2.4 ±0.1	2.4 ±0.1	2.3 ±0.1	<0.05	<0.05	<0.05
Ce(III)	1.6 ±0.1	1.8 ±0.1	1.8 ±0.1	1.7 ±0.1	<0.05	<0.05	<0.05
La(III)	2.9±0.2	2.8±0.2	2.9±0.2	2.8±0.2	<0.05	<0.05	<0.05
Y(III)	1.9±0.1	1.8±0.1	1.9±0.1	1.8±0.1	<0.05	<0.05	<0.05
Zr(IV)	2.1 ±0.1	2.0 ±0.1	2.1 ±0.1	1.6 ±0.1	<0.05	<0.05	<0.05

Note: The samples were diluted 10 times for ICP-AES

SLM. However, studies with SLM stability has shown mixed results as the liquid membranes can be used for a couple of days only with marginal loss in the transport rates (Chapter 5) beyond which a sharp fall in the Cs(I) transport rates was noticed. In order to increase the throughput one needs to evaluate the solvent system (4.0×10^{-3} M CBC in PTMS) in the hollow fiber mode.

As has been discussed in Chapter 5, after evaluating calix[4]arene-benzo-biscrown-6 (CBC) in PTMS as the carrier solvent in flat sheet supported liquid membrane, further optimization studies were carried out using bis(octyloxy)calix [4]arene-mono-crown-6 dissolved in 40% iso-decanol / *n*-dodecane as the diluent for the extraction of cesium from acidic feeds solutions. In view of the large ligand inventory required in the solvent extraction method(70), it is imperative to explore supported liquid membrane based method in general and hollow fiber supported liquid membrane in particular, where the ligand inventory is extremely low. In the present work, therefore, an attempt was made to explore the possible application of bis-(octyloxy)calix [4]arene-mono-crown-6 (CMC); (**Figure 2.1, Chapter 2**) for the recovery of radio-cesium using hollow fiber contactors. Various experimental conditions were optimized for efficient recovery of cesium and the transport parameters were measured.

6.3.2 Studies involving CMC based SLM using SHLLW

Transport profiles of Cs(I) and nitric acid were measured from SHLLW using ^{137}Cs tracer spiked waste solution. The results are shown in **Figures 6.4 and 6.5**. As expected, the transport rate of Cs(I) from SHLLW was slow (~65% in 7 h) as compared to acidic feed containing pure tracer where >90% transport was recorded under identical experimental conditions.

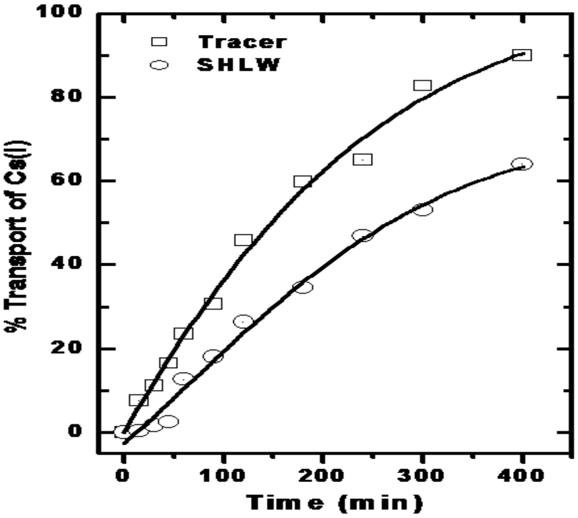


Figure 6.4: Flat sheet SLM showing the transport of Cs(I), Carrier: 1.0×10^{-2} M CMC in 40% iso-decanol/*n*-dodecane; Feed: 4 M HNO_3 / SHLLW spiked with ^{137}Cs (20 mL); Receiver phase: distilled water (20 mL); Membrane surface area: 3.14 cm^2.

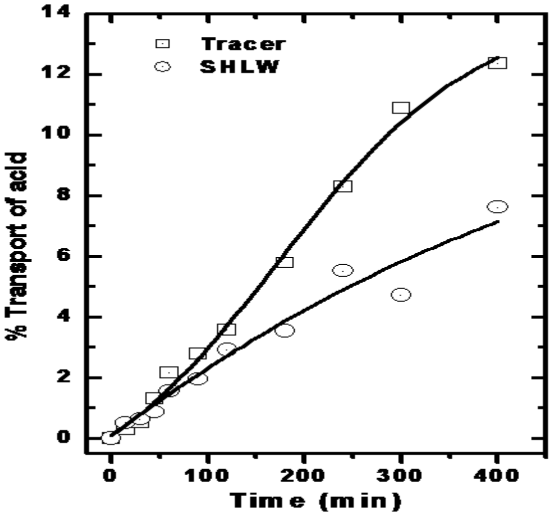


Figure 6.5: Flat sheet SLM showing the transport of nitric acid, Carrier: 1.0×10^{-2} M CMC in 40% iso-decanol/*n*-dodecane; Feed: 4 M HNO_3 / SHLLW spiked with ^{137}Cs (20 mL); Receiver phase: distilled water (20 mL); Membrane surface area: 3.14 cm^2.

It should be noted that the simulated waste solution contained 0.32 g/L of Cs and the presence of such a large concentration of the metal ion in the feed suppressed the transport rate under SHLLW condition due to carrier loading effect. Though the transport of Cs(I) under the SHLLW condition was incomplete, it gave an opportunity to use the ligand under similar feed and strip conditions in HFSLM, where process optimization is possible due to its large surface area (1800 cm^2 in the present work) as compared to that with the flat sheet SLM (3.14 cm^2). Furthermore, it has been reported (127) previously that the selectivity of calix[4]arene-crown-6 ligands for Cs(I) ion from alkali metal ions such as Na^+ are $> 10^4$ which is amongst the highest known so far.

6.3.3 Hollow fiber supported liquid membrane (HFSLM) studies

After optimization of various conditions in the solvent extraction and subsequently, in a flat sheet supported liquid membrane (FSSLM), HFSLM studies were carried out with 300 mL solutions of both the feed and the receiver. In order to quantify the effect of feed acidity on the transport of Cs(I), experiments were performed from feed solutions of varying acidity (1-6 M HNO_3) which are already explained in Chapter 5. Results showed enhanced permeation rate of Cs(I) with increasing feed acidities.

6.3.4 Cs(I) Transport from SHLLW using a hollow fiber contactor

Since, HLLW contains significant concentration of Cs (~0.32 g/L), it was of interest to investigate its transport from SHLLW. ^{137}Cs tracer spiked SHLLW (feed) using a commercial hollow fiber contactor in the SLM mode and the results are given in **Figure 6.6.** Results suggest > 92% Cs(I) transport into the receiver phase in 6 h under simulated HLLW conditions. When the results were compared with the transport profile of Cs(I) containing 300 mg/L Cs, the transport under SHLLW conditions was higher, though both the feed solutions contained almost equal concentration of Cs. Higher transport rate in case of SHLLW was ascribed to the presence of large concentration of nitrate salts, which act as salting out agent and favor the forward equilibrium reaction.

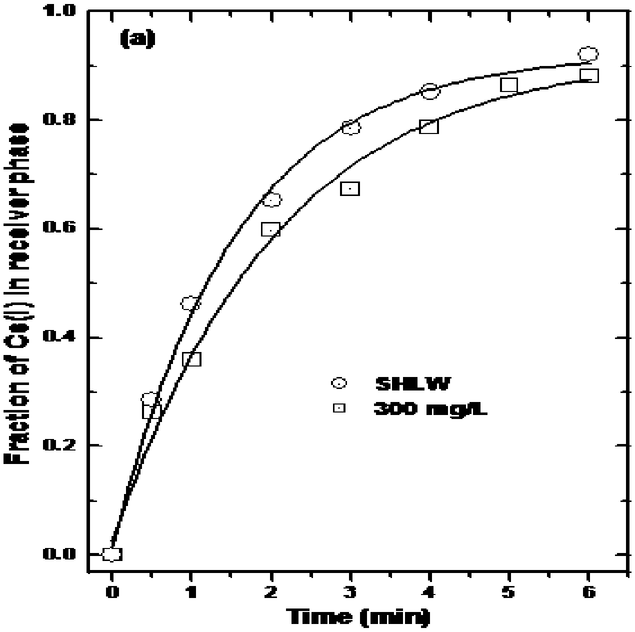


Figure 6.6: HFSLM transport profiles of Cs(I) from SHLLW and 300 mg/L Cs(NO_3) in the feed, Carrier: 1.0x10^{-2} M CMC in 40% iso-decanol/*n*-dodecane; Feed: 300 mg/L Cs(NO_3) at 4 M HNO_3 / SHLLW spiked with ^{137}Cs (300 mL); Receiver phase: distilled water (300 mL); Flow rate: 200 mL/min.

Transport data were used to plot Ln(C_t/C_o) as a function of time which are shown in **Figure 6.7.** The permeability coefficient values as obtained in Chapter 2 calculated for 300 mg/L feed and SHLLW were found to be 4.11x10^{-5} and 5.15x10^{-5} cm/s, respectively. Though only ~92% transport of Cs was observed in 6 h for SHLLW as the feed, the recovery and the efficiency of the process can be increased by increasing the surface area of the membrane by employing larger membrane contactors.

Above results clearly indicate the possible application of HFSLM method for the recovery of radio-cesium from actual HLLW.

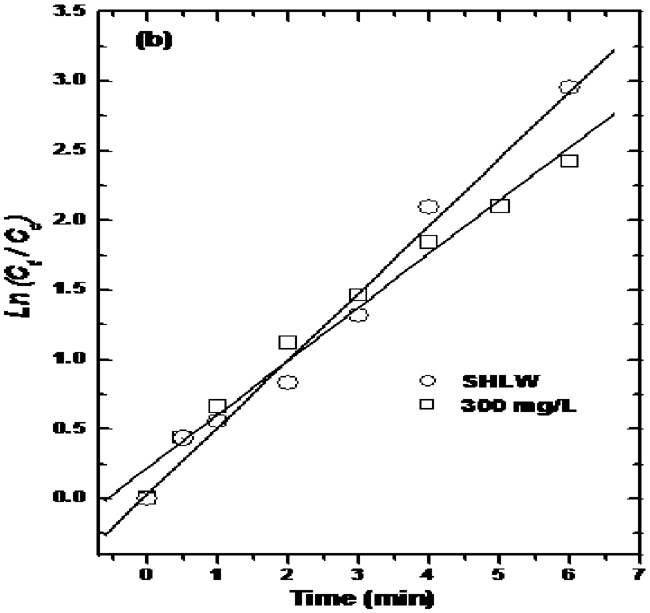


Figure 6.7: Plot of Ln(C_t/C_o) vs. *t* for calculation of permeability coefficient, Carrier: 1.0×10^{-2} M CMC in 40% iso-decanol/*n*-dodecane; Feed: 300 mg/L Cs(NO_3) at 4 M HNO_3 / SHLLW spiked with ^{137}Cs (300 mL); Receiver phase: distilled water (300 mL); Flow rate: 200 mL/min.

6.3.5 Studies using actual HLLW

In view of the highly encouraging results reported above, an attempt was made to recover radio-cesium from a diluted HLLW solution (100 times diluted actual HLLW where the acidity was kept close to 3 M). The photograph of the hollow fiber contactor assembly used in this study is given in **Figure 2.6** in Chapter 2. Though the studies involving SHLLW (vide supra) involved a commercial hollow fiber contactor with polypropylene (PP) fibers, the studies with actual diluted HLLW were carried out with a fabricated hollow fiber contactor made from polysulphone (PS) fibers details of which are also given in Chapter 2.

Apparently, there was no leakage observed during the operation and the mass balance was found to be within the experimental error limits of ±5%. As shown in **Table 6.7**, about 90% transport of radio-cesium was seen in 20 h which was quite encouraging under the circumstance that only 35 PS fibers were used in the fabricated contactor.

Table 6.7: Transport of ^{137}Cs using the PS fiber based hollow fiber contactor
Feed: 100 times diluted actual HLLW with Cs activity of 99.6 mCi/L for the first run 95.9 mCi/L for the repeat run; Volume: 100mL; Receiver: Distilled water (100 mL); Ligand: 0.01 M CMC in 40% iso-decanol + 60% *n*-dodecane.

Time (h)	**Strip solution (mCi/L)**	
	First run[a]	**Repeat run[a]**
1	0.88	0.79
2	2.80	2.67
3	5.20	4.89
4	12.9	11.3
5	20.7	18.8
6	34.9	32.7
10	--	58.9
12	67.2	
16	--	82.8
18	86.3	--
20	89.3 (89.7%)	87.5 (91.2%)

Note: [a]: The % transport data are given inside parenthesis

It was also observed that the transported radio-cesium was in its pure form as no other fission product nuclide was detected in the gamma ray spectra as shown in **Fig. 6.4.** This is in sharp contrast to the solvent extraction studies reported above where ^{106}Ru co-extraction was seen.

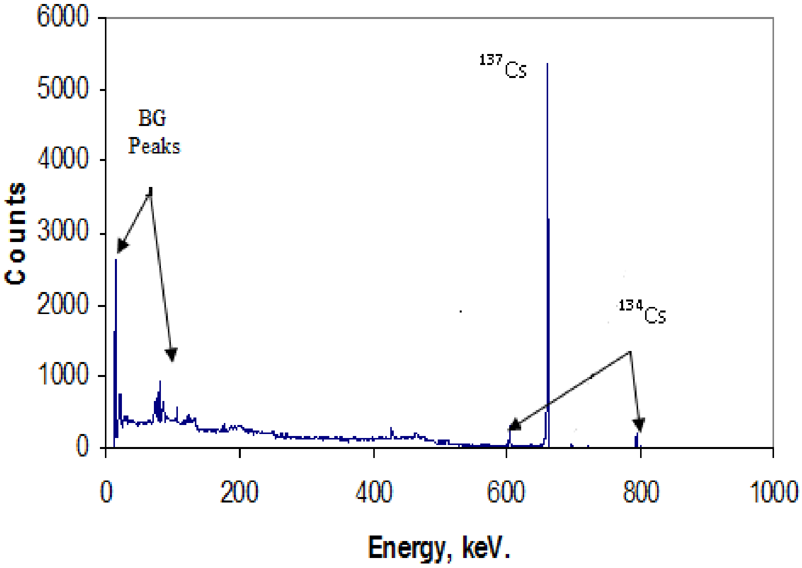


Figure 6.4: γ-Spectra of ^{137}Cs product separated using HFSLM

The major advantage of the hollow fiber contactor based separation method is that < 1 mL of the solvent was required to process 100 mL of the feed. Also, in view of the good stability of the SLM, it may be suggested that the same contactor could have been used for the processing of larger volumes of the radioactive feed. The major limitation of the scale up operation or to use undiluted HLLW was the unavailability of the hot cell facility for such purposes. One of the major limitations of polymeric membrane based separation methods applied to radioactive feed processing is the radiolytic stability of the fibers in long term usage. We have reported significant damage of PP hollow fibers in a previous study (128). However, our studies on radiolytic stability of polymeric fibers have indicated better stability of PS hollow fibers. In view of this, the hollow fiber contactor was kept in contact with the radioactive feed for about 50 days and another run was carried out. The results of the second run are also listed in **Table 6.7**. The transport data obtained in the two independent runs carried out under identical conditions were reproducible to a very large extent. Also, apart from obtaining a highly efficient separation of radio-cesium with very high decontamination from the other fission products, the hollow fiber contactor seems to be a viable option for radioactive waste processing in view of easy scale up option and very low solvent inventory.

In summary, the recovery of radio-cesium was carried out by a solvent extraction based separation method using 1.0×10^{-3} M CBC in PTMS in three different sets of experiments involving tracer spiked simulated HLLW, diluted actual HLLW and undiluted actual HLLW, respectively. The results of the extraction studies were highly encouraging as selective Cs(I) extraction was possible leaving behind the other radionuclides present in the HLLW. About 10 mCi of ^{137}Cs was separated in its purest state.

The hollow fiber contactor based SLM studies carried out using 0.01 M CMC in 40% iso-decanol + 60% *n*-dodecane were also highly promising in view of several factors; the most important being very low ligand as well as VOC inventory making it a green alternative to the conventional solvent extraction based separation methods. Furthermore, the hollow fibers were stable even after keeping in contact with the radioactive feed for about 50 days as indicated by almost reproducible transport results. It may be concluded that the hollow fiber SLM method can be scaled up, with more number of fibers, for the large scale processing of HLLW for radio-cesium recovery.

SUMMARY AND CONCLUSION

Recovery of radio-cesium from PUREX-HLLW is one of the most challenging tasks in the back end processes of nuclear fuel cycle and has been the sole objective of the present thesis work. This has been attempted in this study using solvent extraction and supported liquid membrane techniques using four calix-crown-6 ligands *viz.* calix[4]arene-bis-crown-6 (CC), calix[4]arene-bis-benzocrown-6 (CBC), calix[4]arene-bis-naphtho-crown-6 (CNC) and bis(octyloxy) calix[4]arene-mono-crown-6 (CMC) in different diluents. The first set of studies involved a fluorinated solvent *viz.* PTMS (phenyltrifluoromethylsulphone; also known as FS-13) with the calix-crown-6 ligands for the first time. On the other hand, a liquid membrane based separation methods employing all the four calix-crown-6 ligands in PTMS and also using a solution of CMC in a diluent mixture have also been investigated. Possible uses of the recovered radio-cesium include its potential to replace ^{60}Co to be used for blood irradiator due to the following reasons:

1. Reduced frequency of source replenishment
2. Less shielding requirement
3. Abundant source in HLLW

The separation of radio-cesium from HLLW is also important from waste management point of view. Due to its large heat output (0.42 W/g), its removal from HLLW will reduce the damages caused by deformation of glass matrix. Among the several reagents used, calix-crown-6 ligands are known for their high selectivity for Cs(I) extraction with respect to a host of metal ions present in the HLLW. Extensive solvent extraction studies involving Cs(I) have shown the order of extractability and separation efficiency CBC > CNC > CMC > CC under identical experimental conditions. Further studies using CBC and CMC have shown that these ligands can be used for selective recovery of Cs from uranium depleted HLLW. The summary of the results are presented below.

1. Very low concentration of any of the calix-crown-6 ligand (1×10^{-3} M) is required to extract Cs(I) (when ^{137}Cs tracer is used) from acidic feeds (1-3 M HNO_3). Though the extraction of Cs(I) is somewhat lower with PUREX-HLLW as the feed, quantitative recovery is possible in several contacts. Extraction kinetics is fast which show that a contact time of about 5 minutes is sufficient to attain extraction equilibrium. Distribution ratio of Cs(I) increases with increasing concentrations of the calix-crown-6 ligands and nitric acid (in a limited range) in the aqueous phase. Above 2 M D_{Cs} decreases due to the competition of hydrogen ion with the metal ion of interest. D_{Cs} decreases as concentration of Cs in the aqueous feed increases which can be attributed to the less availability of free ligand due to loading effects. Distribution ratio of Cs(I) is comparatively higher for CBC and CNC ligands. The extracted species are found to have metal nitrate to ligand mole ratio of 1:1 as established by slope analysis method. The extracted Cs can be stripped from the organic phase using distilled water and the stripping efficiency can be enhanced when 0.5% v/v Alamine 336 is added to the organic phase. Quantitative extraction and stripping of Cs(I) is achievable in 4 contacts. It is possible to achieve concentration factor of as high as 4 by increasing the aqueous to organic phase volume ratio.

2. The radiolytic stability of the ligands is studied extensively by irradiating the solvents containing thecalix-crown-6 ligands kept in contact with 3 M nitric acid (which is a simulation of the conditions involving solvent extraction studies involving HLLW) and

subsequently carrying out solvent extraction studies involving Cs(I) from acidic feeds. Irradiation of the calix-crown-6 ligands carried out up to 100 kGy does not show any significant change in the D_{Cs} values. Subsequently, the D_{Cs} values were found to decrease with increasing absorbed dose. CBC is comparatively higher resistant to the radiolytic degradation possibly due to the aromatic substituent. Instability Index (defined as the ratio of the D_{Cs} values obtained with the unirradiated to the irradiated ligands) data show that CBC is the most stable among the ligands studied. CBC shows reasonable D_{Cs} (~3) values even after irradiation to an absorbed dose of 1000 kGy. Degradation products are evaluated for all the calix-crown-6 ligands using GC-MS. Though distribution ratio of these ligands decreases with increasing absorbed dose, the metal ligand complex conforms to the mole ratio of 1:1 even after 1000 kGy exposure. Extraction of other metal ions from SHLLW was found to be negligible which indicates that selective extraction of Cs is possible from HLLW using calix–crown-6 ligands in the fluorinated diluent (PTMS).

3. Selective extraction of Cs(I) was achieved from diluted as well as actual HLLW by giving four contacts of the solutions of CBC in PTMS. A small contamination of ^{106}Ru in the organic phase, observed during the extraction involving actual HLLW, could be removed by scrubbing with 3 M HNO_3. No other fission products (present in the HLLW) were co-extracted along with the recovered radio-cesium. In both the cases, quantitative recovery of Cs was observed during the extraction and stripping stages. It is important to mention that no loss of radio-cesium was observed during the scrubbing step. The gamma

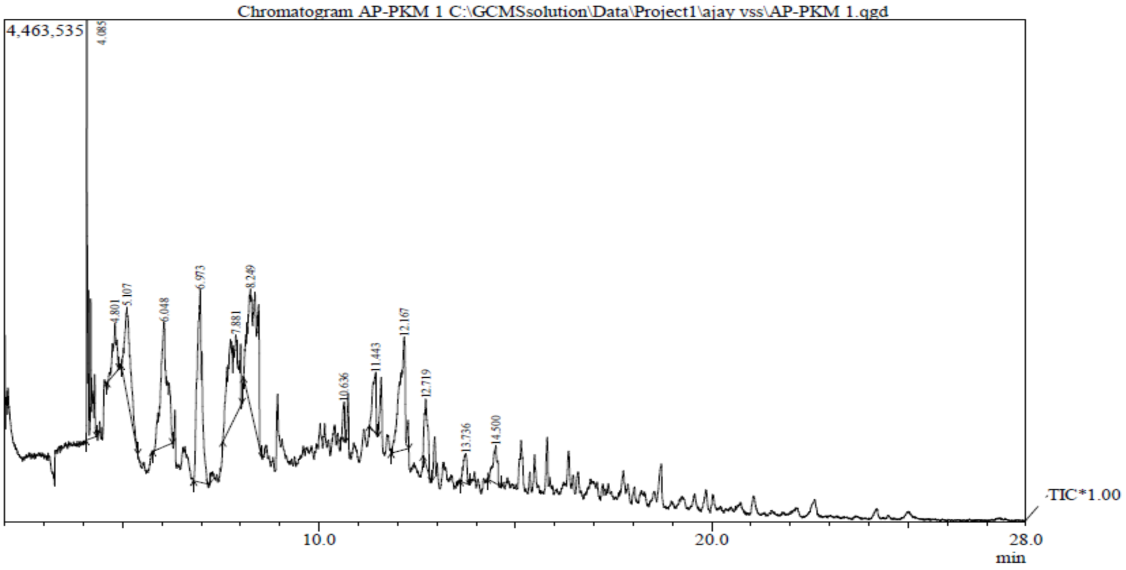
ray spectra clearly show the purity of the recovered radio-cesium. About 10 mCi of radio-cesium was extracted from HLLW using the solvent extraction method.

4. Though the solvent extraction data are found to be highly promising, studies were also carried out to develop supported liquid membrane (SLM) based separation methods using all the four calix-crown-6 ligands. The major advantages of the SLM based separation methods include simultaneous extraction and stripping and very low solvent inventory which has a direct bearing on the process cost as the calix-crown-6 ligands are highly expensive. Though the transport data using flat sheet SLMs were found to be highly promising with solvents containing calix-crown-6 ligands in PTMS as the diluent, the SLM stability was not satisfactory. In view of this, subsequent flat sheet SLM studies were carried out using a solvent containing 0.01 M CMC in 40% iso-decanol + 60% *n*-dodecane. In the later SLM system, not only the transport efficiency was quite good, but the stability of the SLM was also satisfactory. This was subsequently validated by the selective transport of Cs(I) from an aqueous feed containing 3 M HNO_3. Introduction of 0.5% v/v Alamine 336 into the solvents enhances the stripping capability for Cs(I) at the membrane - receiver interface. No other metal ion was detected in the receiver compartment during the transport studies from HLLW. Subsequently, the SLM studies were extended to the hollow fiber configuration. Transport rates are dependent on the no of capillaries available in the hollow fibre contactor (related to the active transport area) for Cs(I) mass transfer. Recovery of radio-cesium from the actual HLLW was carried out by a solvent extraction method using 1.0×10^{-3} M CBC in PTMS in three different sets of experiments involving tracer spiked simulated HLLW, diluted actual HLLW and

undiluted actual HLLW, respectively. The results of the extraction studies were highly encouraging as selective extraction of the radio-cesium was possible leaving behind all the other radionuclides present in the HLLW. The hollow fiber contactor based SLM studies carried out using 0.01 M CMC in 40% iso-decanol + 60% *n*-dodecane were also highly promising in view of several factors the most important being very low ligand as well as VOC inventory making it a green alternative to the conventional solvent extraction based separation methods. Furthermore, the hollow fibers were stable even after keeping in contact with the radioactive feed for about 50 days as indicated by almost reproducible transport results. It may be concluded that the hollow fiber SLM method can be scaled up, with more number of fibers, for possible large scale processing of HLLW for radio-cesium recovery.

Appendix

Appendix 1



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5	6.973	14938440	14.31	1716564	13.59
6	7.881	14064504	13.47	716763	5.67
7	8.249	19569043	18.74	1052423	8.33
8	10.636	1130432	1.08	336523	2.66
9	11.443	3251320	3.11	543218	4.30
10	12.167	10540105	10.09	1001639	7.93
11	12.719	3329518	3.19	582936	4.62
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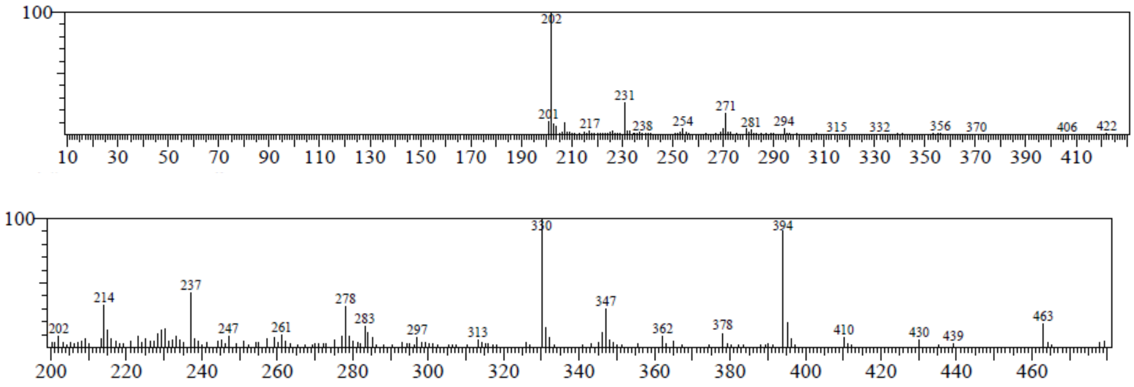
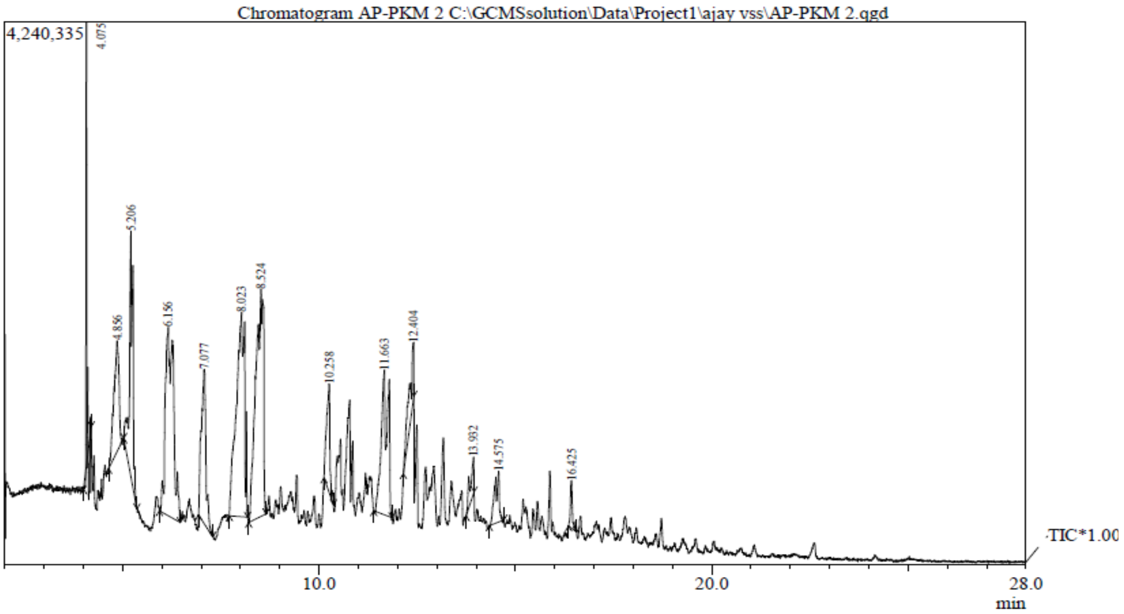
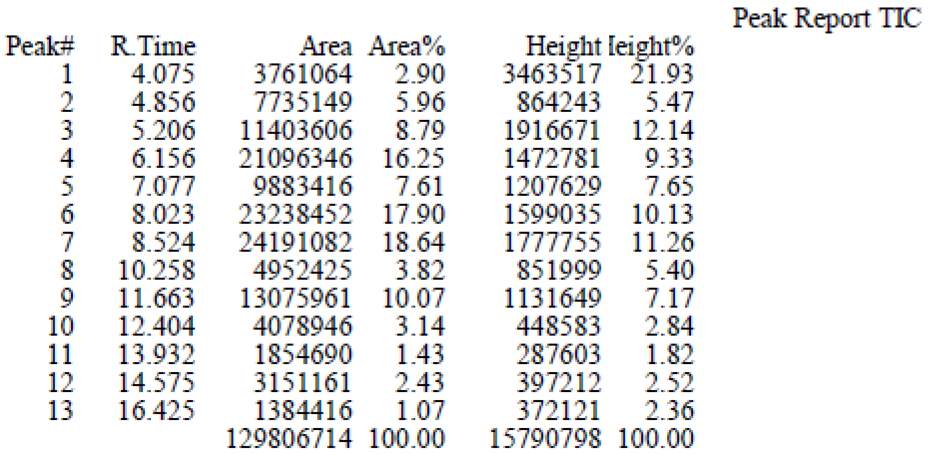


Fig.4.3: GC-MS chromatogram of CC

Appendix 2





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4	6.156	21096346	16.25	1472781	9.33
5	7.077	9883416	7.61	1207629	7.65
6	8.023	23238452	17.90	1599035	10.13
7	8.524	24191082	18.64	1777755	11.26
8	10.258	4952425	3.82	851999	5.40
9	11.663	13075961	10.07	1131649	7.17
10	12.404	4078946	3.14	448583	2.84
11	13.932	1854690	1.43	287603	1.82
12	14.575	3151161	2.43	397212	2.52
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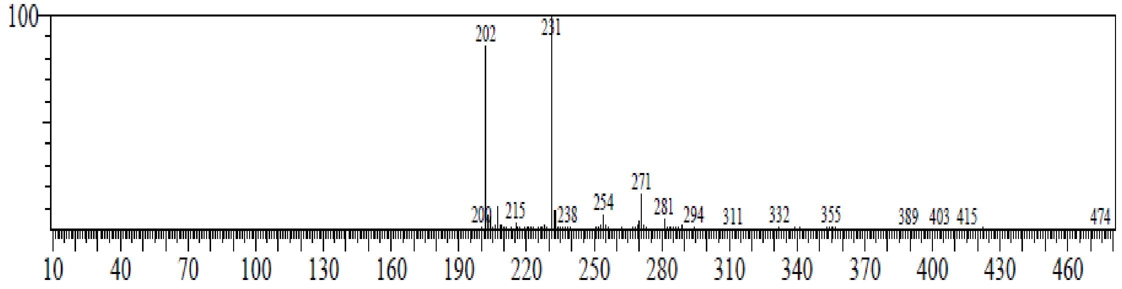
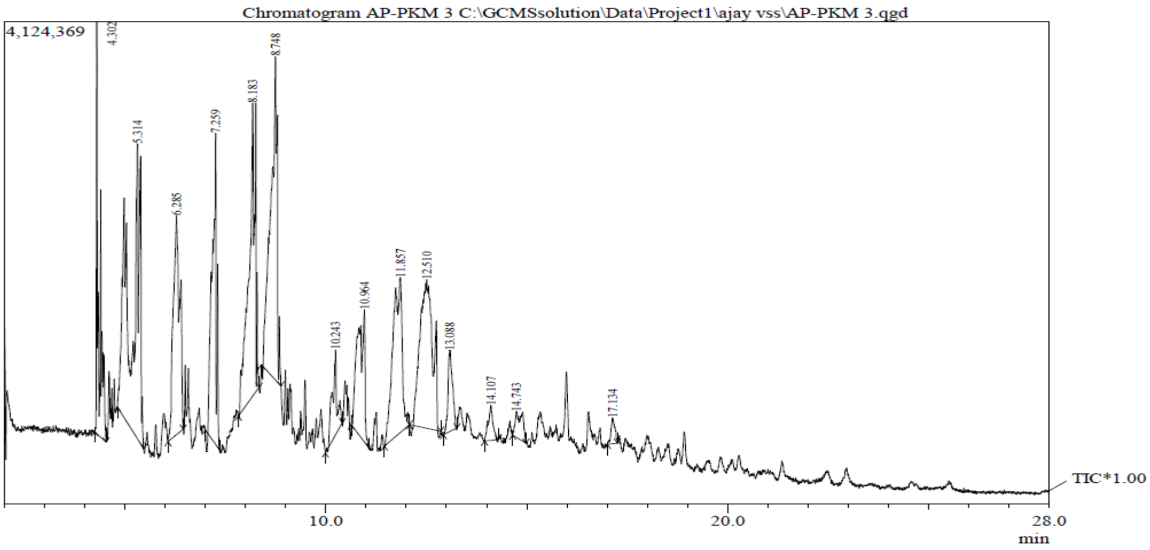


Fig. 4.4: GC-MS chromatogram of CBC

Appendix 3



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4	7.259	19186245	8.42	2661747	12.24
5	8.183	26154976	11.48	2506587	11.53
6	8.748	30147897	13.23	2766135	12.72
7	10.243	5743094	2.52	724058	3.33
8	10.964	13871492	6.09	1133049	5.21
9	11.857	21498976	9.43	1325099	6.10
10	12.510	27648592	12.13	1270868	5.85
11	13.088	5392271	2.37	688320	3.17
12	14.107	2383934	1.05	300485	1.38
13	14.743	2887134	1.27	223646	1.03
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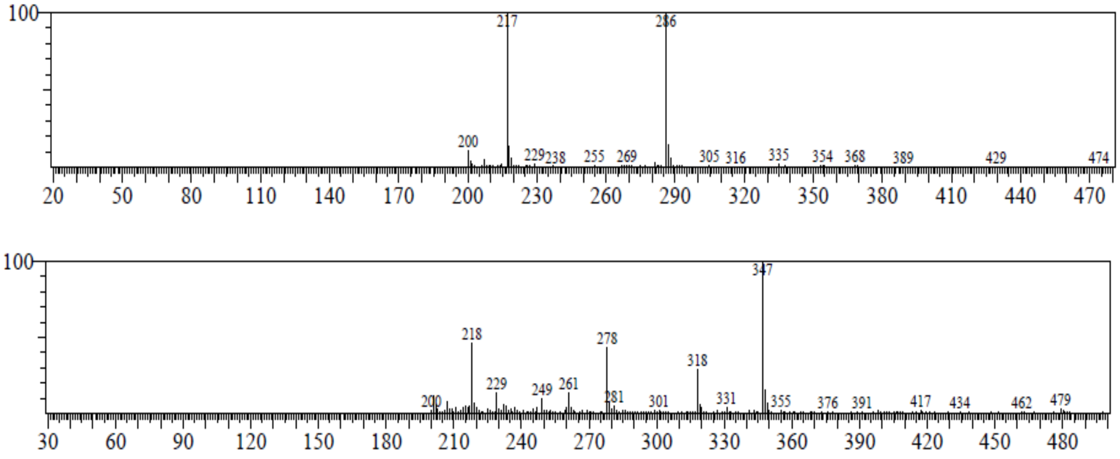
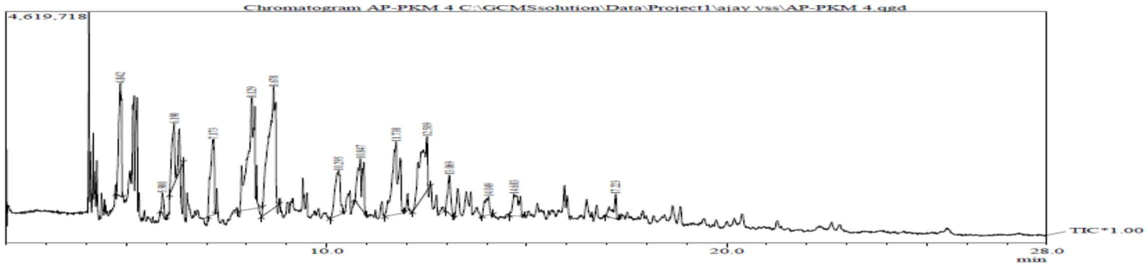


Fig. 4.5: GC- MS chromatogram of CNC

Appendix 4



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4	7.173	10199912	6.95	1511794	9.15
5	8.129	24930812	17.00	2218194	13.42
6	8.678	29415699	20.06	2421646	14.65
7	10.295	8380868	5.71	889637	5.38
8	10.847	9026383	6.15	983711	5.95
9	11.738	16889015	11.52	1451838	8.79
10	12.509	14477757	9.87	1084954	6.57
11	13.069	3999216	2.73	776454	4.70
12	14.049	2907840	1.98	368160	2.23
13	14.683	4961536	3.38	438380	2.65
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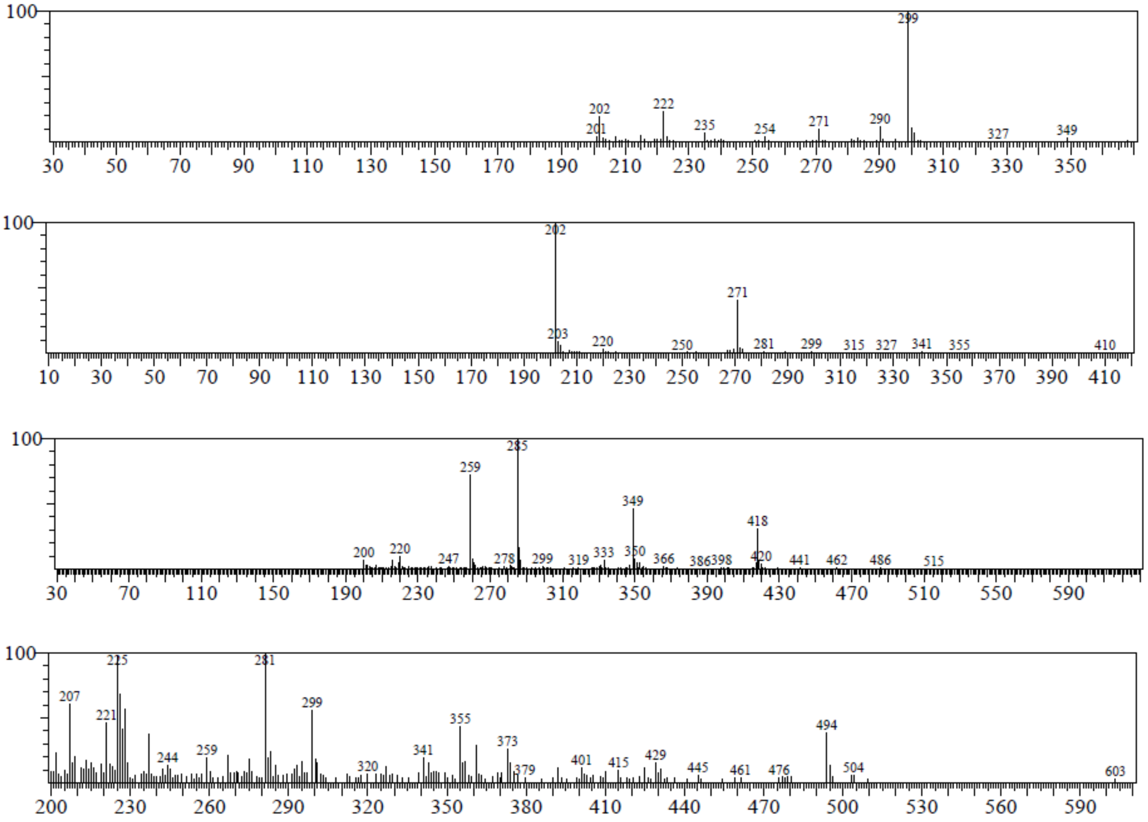

Fig. 4.6: GC-MS chromatogram of C

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