"Studies on the separation of Cesium and Strontium from acidic solutions using liquid membranes"

In view of increasing demand for energy in developing countries like India, the quest for new resources of energy is quite reasonable. Nuclear energy is considered to be one of the best alternatives to the conventional sources of energy. The discovery of nuclear fission by Otto Hahn (known as the father of nuclear chemistry) gave a new direction towards the fulfillment of increasing demands of energy. Nuclear fission of few grams of $^{235}\text{U}$ by thermal neutrons gives an energy equivalent to burning of tones of coal and since it produces significantly lower amount of pollutants, it can be considered to be ‘green technology’. In nuclear power plants, controlled nuclear fission is carried out in nuclear reactors and the nuclear energy is used for electricity production. It is estimated that about 15-20 % of the world’s electricity requirement is fulfilled by the 430 nuclear power plants installed all over the world [1].

In closed nuclear fuel cycle, U and Pu are recovered from the spent fuel by the well known PUREX process. After reprocessing of the spent fuel, the safe management of nuclear waste is a challenge for nuclear scientists. The nuclear waste contains heat emitting fission products like $^{137}\text{Cs}$, $^{90}\text{Sr}$, minor actinides ($^{241}\text{Am}$, $^{243}\text{Am}$, $^{245}\text{Cm}$ and $^{237}\text{Np}$) and unrecovered U and Pu. Along with this, structural elements like Fe, Cr, Zr etc., are also present in the waste. The fission products $^{137}\text{Cs}$ ($t_{1/2}=30.1$ y) and $^{90}\text{Sr}$ ($t_{1/2}=28.5$ y), due to their long half life and large heat output ($^{137}\text{Cs}$: 0.42 W/g and $^{90}\text{Sr}$: 0.90 W/g), may create deformation of the glass matrix and hence increase the risk of leaching out of the radionuclides from the vitrified blocks. Therefore, require regular surveillance of the disposal sites may be required leading to an increase in the overall expenditures of waste management. Also, leaching out of radionuclides from the repositories can be hazardous to the environment. Along with this, the chemical similarity of Sr with Ca and that of Cs with Na can lead to serious problem of interference of these nuclides in the biological system of human beings. Hence, on one hand, the separation of such radiotoxic nuclides reduces the waste volume in the vitrified blocks and hence will
minimize the MANREM problems while on the other, it will reduce the risk generated due to their toxicity to the biological system.

Long half life and high energy gamma rays 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, $\gamma = 1173$ keV and 1332 keV) for the sterilization of medical accessories, food preservation, sewage sludge treatment, etc. Similarly, $^{90}$Sr, due to its high heat output, has applications in various useful purposes like as heat source for thermo-electric and thermo-mechanical power generators (RTGs and RTMGs) in remote areas, military applications, etc [2,3,4].

Various reagents have been used for the separation of cesium and strontium from acidic as well as basic solutions. Precipitation of cesium has been carried out by using phosphotungstic acid, tetraphenyl borate anion, metal ferrocyanide / ferricyanide, etc. while lead sulfate as carrier was used for the precipitation of strontium from acidic solutions [4]. Ion-exchange methods have also been developed for the recovery of these metal ions. Inorganic ion-exchangers like zirconium phosphate, AMP etc., have been employed for the removal of cesium from solutions but the high cost and non-availability of these materials limit their use in larger scale. Recently, a new class of ion exchangers composed of combination of [(CH$_3$)$_2$NH]$_2^+$ and [Ga$_2$Sb$_2$S$_7$]$^{2-}$ ions have been found to be highly selective for cesium [5]. Zeolites and crystalline silicotitanate have also been found to be highly selective for cesium in the presence of large concentration of sodium and other alkali metals. Antimonic acid was used as ion-exchanger for strontium removal from wide range of acidity of aqueous solution. Simultaneous recovery of Cs and Sr has been carried out by adding PEG-400 with CCD in diluents like nitrobenzene / FS-13 [6, 7]. Recently, crown ethers and calix-crowns have drawn attention due to their high selectivity for a particular metal ion and ease of operation. Substituted 18 crown 6 ethers have been found to be selective extractants for Sr(II) from acidic solution [8]. These compounds are soluble in polar diluents like nitrobenzene, 1-octanol etc. However, the toxic nature of these diluents makes them less suitable for large scale processing.

Techniques like solvent extraction, ion-exchange, extraction chromatography and liquid membranes have been utilized for the recovery of metal ions from solutions. Out of
these, liquid membrane techniques are important in view of the fact that a very less amount of solvent is required for carrying out separation studies and simultaneous extraction and stripping is possible. Hence, expensive and exotic chemicals can be used in liquid membrane based separation methods. On the other hand, process modeling is an important aspect when we talk about large scale application of a process. Modeling of a process is important as a) it helps in better understanding of the process, b) optimization of process can be done with much less human efforts and, c) the scale up of the process can be achieved with less experimental trials. Various mathematical models are present in literature but the complexities of those models make their use very complicated [9].

In view of these, the main objectives of present work are to develop liquid membrane techniques (particularly hollow fibre supported liquid membrane, HFSLM) for the recovery of Cs and Sr from the acidic solution under the pressurized heavy water reactor-simulated high level waste (PHWR-SHLW) conditions. Various experimental conditions have been optimized by varying system compositions. It was also of interest to develop alternative diluent system to the toxic / corrosive diluents for the simultaneous recovery of Cs and Sr by the CCD and PEG mixture. Finally, it was also required to develop HFSLM technique for the separation of carrier free $^{90}$Y from a mixture of $^{90}$Sr-$^{90}$Y for its therapeutic uses. A mathematical model was developed for transport modeling of metal ion through HFSLMs to simulate the transport processes.

Chapter 1: General Introduction

This Chapter gives an overview of the nuclear fuel cycle and sources of radio-cesium and radio-strontium. Various types of nuclear wastes generated during the reprocessing and their impact on the environment have been elaborated. The Chapter also describes the various separation methods viz., solvent extraction, ion-exchange, precipitation and liquid membranes etc., for the recovery of Cs and Sr from different waste solutions. Various challenges for recovery of these metals and their important applications have also been described. The advantages associated with calix-crowns and crown ethers over other reagents and challenges in their use have been elaborated. The merits of liquid
membranes including hollow fibre supported liquid membrane over other conventional techniques have been summarized. A brief comparison has been made on the different transport models for the transport of Cs and Sr in liquid membrane. The well known UNEX (UNiversal solvent EXtraction) process for the simultaneous recovery of Cs, Sr and minor actinides have been discussed in the light of the available literature [6]. The recent developments in the direction of recovery of Cs and Sr from aqueous solutions have been elaborated. This Chapter also lists the aims and objectives of the present study.

**Chapter 2: Experimental**

A general outline about different experimental techniques and instrumentations, used throughout the work, has been elaborated in this Chapter. Distribution studies have been carried out by equilibrating known volumes of organic and aqueous phases in stoppered glass tubes at constant temperature in a thermostated bath. Flat-sheet supported liquid membrane studies are performed with two-component Pyrex glass transport cells. The details of hollow fibre supported liquid membrane and impregnation of carrier solvent in the pores of the hollow fibre have been described in this Chapter. The sources of different radiotracers used in the present work along with their assaying methods have also been discussed. The estimation of gamma-emitting radiotracers was carried out by gamma counting employing NaI(Tl) and HPGe detectors. The assay of beta-emitting isotopes was performed by liquid scintillation counter. The basic principle and working of these detectors have been elaborated in this Chapter. A detailed description of the mathematical model developed and used in the present work has also been described.

**Chapter 3: Recovery of Cs by calix[4]arene-bis-(2,3-naphtho)-crown-6**

This Chapter elaborates on the recovery of cesium from acidic feed solutions using the cesium selective calix[4]arene-bis-(2,3-naphtho)-crown-6 (CNC) as the carrier ligand in the supported liquid membrane. Various parameters for the efficient transport of Cs were optimized in batch solvent extraction studies. A concentration of 1 mM CNC in 80% NPOE + 20% n-dodecane was optimized as the best carrier composition. Flat Sheet
Supported Liquid Membrane (FSSLM) studies on 20 ml scale indicated that ~ 90% of cesium transport was possible in 24 hours from 3 M HNO₃ as the feed and distilled water as the strip solution. On the other hand, > 99.9% Cs transport could be achieved in 6 hours on 500 ml scale using Hollow Fibre Supported Liquid Membrane (HFSLM) under the optimized condition. Effect of feed acidity, ligand concentration and feed composition on the transport in HFSLM was studied and the results have been described in this Chapter. About 90% recovery of Cs was achieved from Pressurized Heavy-Water Reactor-Simulated High Level Waste (PHWR-SHLW) on 500 ml scale with excellent selectivity from the other metal ions present in the SHLW. The membrane stability was excellent and the results suggested possible application of the present technique for the recovery of Cs from nuclear waste solutions.

Chapter 4: Transport studies on Strontium by liquid membrane
This Chapter describes the transport behaviour of Sr by HFSLM containing di-tert-butylcyclohexano 18-crown-6 (DTBuCH18C6) as the selective carrier for strontium. The batch solvent extraction studies as well as literature data suggested 0.1 M DTBuCH18C6 in 80% NPOE + 20% n-dodecane as the suitable carrier solvent composition for polypropylene hollow fibre membrane. Various experiments were performed to see the effect of feed acidity, metal ion concentration and feed composition on the transport of Sr. The results suggested that ~ 94% recovery of Sr can be achieved in 3 hours from PHWR-SHLW under the optimized conditions. Quantitative transport of Sr was not possible and was ascribed to the significant amount of acid
transport from feed to strip phase solution. Due to higher acid transport to the strip side, the back transport of Sr was also observed. The back transport of Sr was prevented by neutralizing the strip phase acidity with NaOH at regular interval. Efforts were made to improve the transport efficiency of Sr using different strip solutions.

$^{90}$Y, a daughter product of $^{90}$Sr, is an important radiopharmaceutical isotope due to its short half life (64.1 hours) and suitable beta-energy. In literature, different techniques have been reported for the purification of $^{90}$Y from a mixture of $^{90}$Sr / $^{90}$Y at a relatively smaller scale (5-10 ml scale) [10]. HFSLM technique was successfully developed for the separation of carrier free $^{90}$Y from the mixture of $^{90}$Sr / $^{90}$Y at litres scale using bis(2-ethylhexyl) phosphonic acid (PC-88A) as the carrier. Solvent extraction studies indicated that Y(III) can be selectively extracted by PC-88A at 0.1 M HNO$_3$ with D.F. values with respect to Sr(II) > 1000. The extracted Y(III) could be back extracted with > 3 M HNO$_3$. With the optimized experimental parameters, the $^{90}$Y was selectively transported into the receiver phase by HFSLM, containing 20% (v/v) PC-88A, leaving behind the entire amount of $^{90}$Sr in the feed solution. The purity of $^{90}$Y was ascertained by various techniques and was found to be in the range of acceptable level. Hence, HFSLM technique can be used for the separation of carrier free $^{90}$Y at liters scale with the required purity.

Chapter 5: Mathematical modeling for mass transport in liquid membranes

This Chapter describes the mathematical models developed for the mass transport phenomena in FSSLM and HFSLM. The models have been developed based on different diffusional parameters of the transported chemical species. Various assumptions have been made for the simplification of transport process and the basic fundamental behind the process are discussed in detail. Many of the mass transfer models found in literature
are very complicated and hence it was required to develop a simple model to simulate the mass transport through liquid membranes. The Chapter describes the procedure to formulate the equations by using mass-balance in the liquid membrane phase. The mathematical model developed to predict the transport behaviour of different metal ions was successfully validated by the experimental data. The proposed model can be used to predict the transport behaviour of Cs and Sr by HFSLM technique from different waste solutions.

Chapter 6: Simultaneous recovery of Cs and Sr by CCD and PEG

There is a world wide interest in the simultaneous recovery of Cs and Sr from the HLW using CCD (chlorinated cobalt dicarbollide) and PEG (polyethylene glycol) as the extractants in nitrobenzene or FS-13 (Phenyl trifluoro methyl sulphone) as the diluent. However, the toxicity of nitrobenzene and corrosive nature of the fluorinated diluent (FS-13) pose serious limitations on their large scale applications. Now a days, due to strict environmental regulations, these toxic and corrosive diluents are not recommended for large scale uses. In this context, it was required to develop a new diluent for CCD and PEG, which can be an alternative to these toxic diluents. Mixtures of NPOE and n-dodecane were evaluated as the diluent systems and the results are discussed in this Chapter. With 0.01 M CCD as the carrier, different compositions of diluent (NPOE + n-dodecane) were studied and it was found that with the lowering of NPOE percentage in the diluent, the distribution ratio of cesium increases with a regular trend. This is probably due to the possible interaction of CCD with NPOE which will be affecting the free CCD concentration in the organic phase thereby decreasing the distribution ratio. Effect of acidity and ligand concentration on the distribution behaviour of cesium has also been studied. The ligand variation studies revealed the 1:1 stoichiometry of the extracted species. In addition, simultaneous recovery of Cs and Sr...
Sr was carried out by adding PEG with CCD. Addition of PEG increases the strontium extraction while cesium extraction was found to be decreasing. Based on these results, membrane transport studies were carried out taking 0.01 M CCD in 60% NPOE + 40% n-dodecane as the carrier solvent with 1 M HNO₃ as feed while 8 M HNO₃ was employed as the strip phase. It was found that > 97% recovery of cesium was possible in 24 hours of operation. Other studies regarding stability of the liquid membrane, effect of system composition, effect of CCD concentration and feed acidity have been discussed thoroughly. The results show the possible recovery of cesium and strontium in NPOE and n-dodecane mixture.

Chapter 7: Summary and conclusions

The present research work deals with the separation of cesium and strontium from nuclear waste solutions by supported liquid membrane techniques. CNC (calix[4]arene-bis-2,3-naphtho 18-crown-6) has been used as a selective extractant for cesium which shows 1000 times better selectivity for Cs as compared to other alkali metal ions such as Na, K etc. On the other hand, di-tert-butylcyclohexano 18-crown-6 (DTBuCH18C6) has been successfully employed as selective carrier ligand for strontium. The separation of Cs and Sr has been successfully demonstrated on 500 ml scale using of PHWR-SHLW by the HFSLM technique. A HFSLM method has also been developed for the carrier free separation of ⁹⁰Y from ⁹⁰Sr with the required purity of ⁹⁰Y. In an approach to recover Cs and Sr simultaneously, a new solvent system (NPOE + n-dodecane) has been developed for CCD and PEG as successfully demonstrated in solvent extraction as well as supported liquid membrane techniques. The major findings of the present research work are summarized in this Chapter along with the future perspectives.

References: