Review Paper

Membrane Assisted Liquid Extraction of Actinides and Remediation of Nuclear Waste: A Review

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GRAPHICAL ABSTRACT
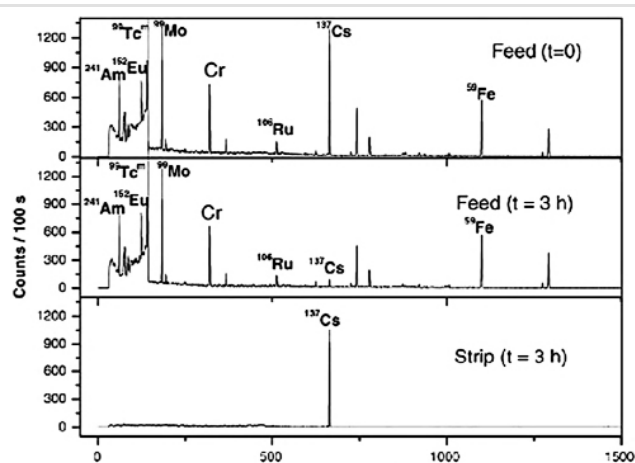
HIGHLIGHTS

- Membrane assisted liquid extraction (MALE) playing an important role as an extraction/separation technique for actinides
- Remediation of nuclear waste generated in reprocessing plant by hollow fiber supported liquid membrane
- Removal of trace level concentration of radionuclide and its application in analytical chemistry

ABSTRACT

Membrane assisted liquid extraction (MALE) technologies are gaining an important role as an extraction /separation technique for actinides and are being deployed as a promising tool for remediation of nuclear waste generated in the reprocessing plant and other radioactive wastes containing a trace level of radionuclides. The present contribution outlines the classification of membrane assisted liquid extraction techniques, its operating principle, associated transport mechanism and merits and demerits with respect to industrial applications. Finally, selected applications of MALE techniques (BLM, SLM and ELM) are presented for extraction/separation of actinides and other radiotoxic nuclides from different streams of low level and high level radioactive wastes.

1. Introduction

Steady growth of global fuel reprocessing activities (6000 ton heavy metal/annum) implies a vital role for the radiochemists, not only in developing efficient procedures for the separation and purification of actinides, but also in devising safe procedures for the management of nuclear waste arising at different stages of the PUREX process, universally used in fuel reprocessing. This large volumes of liquid waste generated in this

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process are referred to as low, intermediate and high level waste (HLW). The chemical engineering community is already paying significant attention to the quest for technologies that would lead us to the goal of technological sustainability. Thus, there is a need to develop procedures for the separation of long-lived isotopes of minor actinides and fission products from the HLW generated in PUREX process.

Solvent extraction, ion exchange, extraction chromatography, and precipitation are commonly used for separation and recovery of heavy nuclear metals from various sources [1–4]. All these processes have their own limitations and drawbacks such as solvent degradation, third phase formation, resin degradation and crud formation, etc. Due to the these demerits, membrane based separation technology has drawn maximum attention in last few years. Over the past three decades, this technology has come a long way from a simple laboratory curiosity to full fledged commercial environmentally friendly technology to answer the multifarious demands of industry. The growth of membrane science is largely due to the impressive developments in the field of membrane material science and the evolution of different membrane related equipments. The important advantages of membrane based techniques are: high efficiency, low power consumption and easy scale-up due to a compact design etc. A membrane is a semi-permeable barrier separating two phases of different composition and is often used in separation and purification schemes. Among the popular membrane process, LM is one of the important configurations which is further classified in to BLM, SLM and ELM. Due to industrial suitability for continuous processing, SLM with hollow fiber membrane is being deployed in chemical, environmental and nuclear applications [5-7]. In particular, substantial research is being carried out worldwide on optimizing the parameters for membrane processes for the removal of toxic or valuable metal ions from its lean sources [8-14]. In 1986, a recovery process for zinc from waste streams at a textile plant in Austria was developed as the first liquid membrane process on a commercial scale [15]. LMs are particularly important in instances where solute concentrations are extremely low and large volumes of solutions need to be processed [16]. The specific advantages of SLM based separation process are (a) high feed to strip volume ratio leading to a large enrichment factor of the transported species, (b) very low extractant (carrier) inventory, (c) no phase separation problem occurs as the organic and aqueous phases never mix, (d) negligible organic phase entrainment in the feed and strip aqueous solutions, (e) no moving parts and (f) simple to operate. Various neutral as well as acidic extractants and their synergistic combinations have been investigated as carrier in SLM for metal transport studies [6, 7].

Due to the stability issues of liquid membrane, membrane contactors are also introduced and proved to be efficient contacting devices, due to their high area per unit volume that may results in high mass transfer rates. They are not only compact but also eliminate several of the problems faced in conventional processes and in addition also satisfy the requirements for process intensification. In the field of analytical applications, these techniques exhibit high selectivity, and they concentrate analytes during the separation process. For this reason, these techniques have undergone significant development in the last decade and are used for analytical sample preparation, due to its advantages over conventional sample preparation techniques.

This paper presents an overview of MALE technologies and their applications in nuclear industries for extraction-permeation and separation of actinide and other radiotoxic nuclides. This also includes current scenario of these techniques applied worldwide. Authors also cover some of the results obtained in laboratory for treating waste generated by radioactive plants.

2. Classification and transport mechanism of different LMs

Before an in-depth consideration of advances in LM techniques, one should be familiar with the fundamentals of cation transport, which is more or less similar in all types of LM techniques.

The use of a liquid phase can enhance the solute flux owing to the higher diffusion coefficients in liquids than in solids. The addition of non-volatile complexing agent to a liquid membrane enhances permeability of solute by several orders of magnitude [7]. This organic carrier molecule can react selectively and reversibly with the solute. The selectivity and flux of metal ions are improved by this reversible reaction of the carrier and the solute. Facilitated transport is concerned with the reversible reaction between the solute and the carrier. It is not coupled to other components. This reaction normally takes place throughout the liquid membrane phase. Similarly, in the concept of coupled transport the reversible reaction takes place as an ion exchange reaction, and the solute flux is linked (coupled) to the flux of

another ion [7, 17]. The carrier (acidic extractant) is a cation exchanger reagent. The ion-exchange reaction normally occurs at a liquid-liquid interface since metal ions are not soluble in the organic membrane phase. Coupled transport is analogous to performing solvent extraction in a thin film. The majority of liquid membranes for metal ion separation involve a coupled transport mechanism.

In BLMs, two miscible aqueous liquids (feed and strip) are separated via a third immiscible organic liquid (carrier) (Figure 1). The mass transfer from one liquid (feed) to the other liquid (strip) takes place via the carrier. Because transport through the bulk takes place by convection, the unstirred boundary layer often forms the largest transport resistance. BLMs are frequently used to investigate novel carriers, carrier systems or transport mechanisms [7]. Their main action is optimise data for both SLMs and ELMs. The principal disadvantage of traditional BLMs has been the low interfacial surface areas and mass transfer rates as compared to SLMs and ELMs. Direct scale-up of this type of contactor is therefore very impractical.

In SLM configuration, an organic liquid containing an active complexing agent (carrier) in suitable diluent can be impregnated in the pores of a porous polymeric solid support by capillary action. This membrane solvent should not mix with water. The membrane is clamped between two cells which are filled with an aqueous source and receiving phase. The aqueous solutions are constantly stirred either mechanically or magnetically in order to achieve homogeneity and reduced thickness of the stagnant aqueous layers. This form is also designated as an immobilized liquid membrane in literature. An SLM technique not only has considerable significance for laboratory practice but is also of interest for a range of technological purposes because of the large phase boundaries which are attainable. SLM systems can be arranged in many ways [7, 18]. A planar or flat geometry is very useful for laboratory purposes. For industrial purposes, a planar geometry is not very effective since the ratio of surface area to volume is too low. Hollow fibre and spiral wound modules can be used to provide high surface area to volume ratio. Usually a set of some hundreds of hollow fibres are used in a standard module (Figure 1). The organic carrier solution is held within the pores of the membrane. The source and receiving phases are inside and outside the hollow fibers respectively or vice versa. In SLM process, the drawbacks are: solvent loss can occur by evaporation, dissolution in aqueous stream or large pressure difference forcing solvent out of the pore support structure. Carrier can also be endured to irreversible side reaction, solvent condensation, solubility and distribution of solvent to both sides of the membrane. Up to some extent these problems of membrane stability can be solved either by choosing highly hydrophobic diluent/carrier or reimpregnating the membrane during experimental runs [19]. In this review, more attention is paid to continuous processes such as HFSLMs under the heading "Supported liquid membranes".

ELMs which consist of a water-in-oil-in-water system are also known as double emulsions. Two immiscible phases are mixed with a surfactant to produce an emulsion. This emulsion is then dispersed in a continuous phase (Figure 1). 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 deemulsified into two immiscible phases after the extraction step of the process. This is achieved by heating, centrifugation or application of electric fields [8]. The LM phase containing the surfactant and carrier will be recycled to the emulsion preparation step while the internal phase of the emulsion will have the concentrated solute. The main problem associated with ELMs is emulsion breakage. The emulsion must be formulated to withstand the shear generated by mixing during the extraction but must be broken to remove the internal phase and reformulate the emulsion. An additional consideration in the ELM system is water transported along with the solute. This causes permeant dilution in the inner phase, welling and possible breakage of the emulsion globule. Attempts are being made to modify the surfactant structure in such a way that break-up of the emulsion is minimized, in order to improve the performance of the ELM process. More information on ELM can be referred in comprehensive review on ELM published by Fouad et al. [8, 20].

3. Applications of LM techniques

3.1. Separation of actinides and other radiotoxic radionuclides from various aqueous waste streams

Several researchers from Bhabha Atomic Research Centre (India) are working on this area and to scale up laboratory studies to pilot-scale ones. An ELM process was investigated by Kulkarni et al. [21], for the separation and

concentration of dilute uranyl ions from leach liquor using Alamine 336 and sodium carbonate. The use of 30% heavy paraffin in the composition of the membrane markedly improved the stability of the emulsion and the recovery of uranium. It was observed that uranium has the highest separation factor of 1462 over manganese from the given composition of leach liquor (Table 1). The selectivity of uranium over other metal ions was found to increase in the order Ca < Fe < Mg < Mn. Thus, a very high amount of separation factors can be achieved in a single stage of the ELM process. It was observed that the feed-phase pH plays a vital role among the other parameters studied. The experimental findings suggest that, in one step, nearly 7 times uranium and less than 0.2 times other metal ions were concentrated inside the strip phase. Selective permeation of uranium from various co-ions suggests potential applications of this method in the nuclear industries.
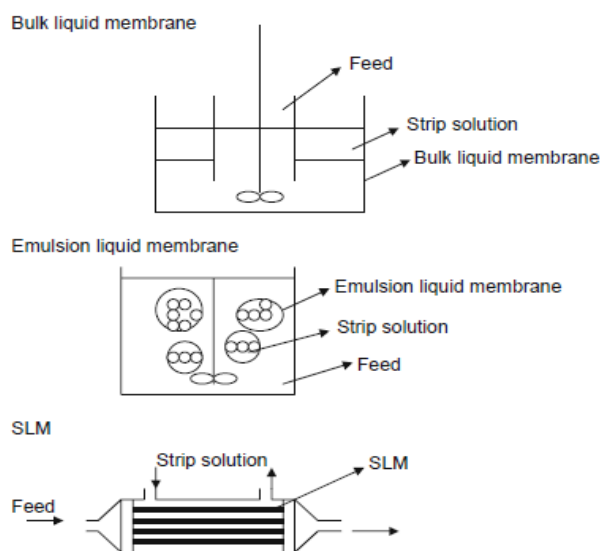

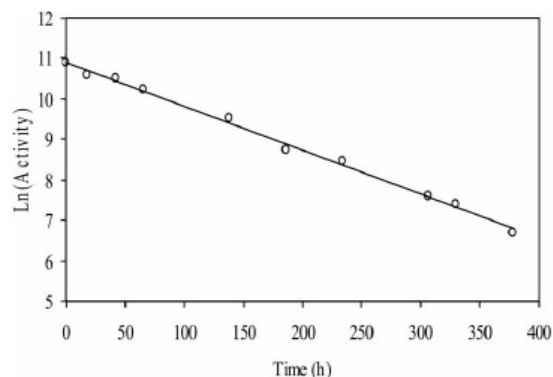Fig. 1. Schematic of various liquid membrane systems.

Fig. 3. Decay curve of carrier-free ^{90}Y produced from two stage SLM [20].

Table 1
ELM extraction of Uranium from the leach liquor of Jaduguda Ore [21].

initial metal ion concentration in leach liquor (g/L)	final metal ion concentration in stripping solution (g/L)	stripping or enrichment factor	selectivity with respect to uranium
U(VI)= 0.32	U(VI) = 2.2	6.9	-
Fe(III)= 0.47	Fe(III) = 0.025	0.05	129
Mg(II) = 0.45	Mg(II)= 0.004	0.009	781
Ca(II)= 0.062	Ca(II) = 0.01	0.16	43
Mn= 2.55	Mn= 0.012	0.005	1462

In another study, a two stage supported liquid membrane based separation technique employing KSM-17 as carrier in the first stage and CMPO in the second stage was found superior to the single stage SLM system developed earlier by Dhami et al. [22] in terms of quality, yield, and chemical form. The second stage acts as a barrier for ^{90}Sr in case it accompanies ^{90}Y in the intermediate compartment. For selective and faster transport of ^{90}Y, an alternative approach has also been worked out in which two single stage membrane cells are used sequentially (Figure 2). ^{90}Y is efficiently transported through KSM-17 based SLM in the first stage. The product ^{90}Y in the second stage is further transported through CMPO based SLM. The yield of the generator system is found to be 95±3% (n = 4) (Figure 3). Decay curve of carrier-free ^{90}Y produced from two stage SLM in about 9–10 hours was shown by authors. The product is free from radiochemical impurities and is suitable for use in bio-medical applications.
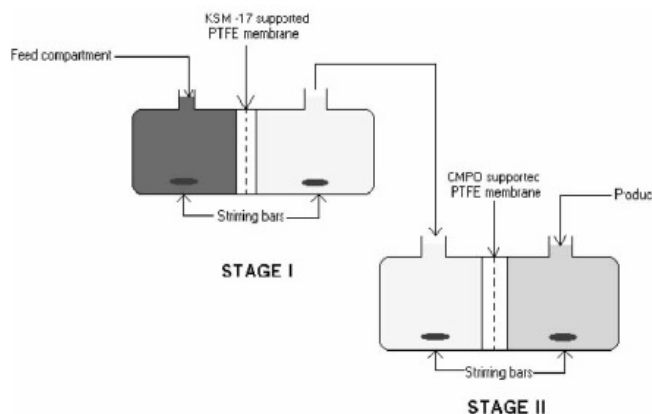

Fig. 2. Schematic diagram of a two stage membrane cell in sequential mode [20].

Panja et al. [23] have carried out extensive studies on the solvent extraction, extraction chromatographic, and membrane based separations of actinides using TODGA as the extractant [24, 25-27]. Out of all these separation methods, the supported liquid membrane based separation methods were found to be the most promising. While trivalent actinides such as Am^{3+} and Cm^{3+} are of particular relevance in "actinide partitioning", it is also required to understand the extraction of Pu and Np which are invariably present in the High Level Waste (HLW) stream. While Pu is mainly present as Pu^{4+}, it can also simultaneously be present in the +3 as well as +6 oxidation states. To understand the behaviour of Pu^{4+} (without any possible interference from Pu^{3+} and PuO_2^{2+}), Th^{4+}, in view of its non-variable oxidation state, was used as a model tetravalent actinide ion. Moreover, it is also of interest to recover Th from various effluent streams [including THOREX (THORium Extraction] process effluents) in nitric acid. This work deals with the transport behavior of Th^{4+} from HNO_3 medium under varying experimental conditions such as, nitric acid concentration, TODGA concentration, and Th concentration. PTFE flat sheets impregnated with 0.1M TODGA in n-dodecane have been used as the extractant while 0.1M oxalic acid has been used as the strippant solution. Authors claimed that the FSSLM method can be actually applied for plant application as an alternative to the solvent extraction technique. For solvent extraction methods, separate scrubbing stages are required for decontamination, which may not be possible with the FSSLM technique. However, it is possible with the HFNDX (hollow fiber non-dispersive extraction) technique which can have the advantage of both the solvent extraction (scrubbing is possible) as well as liquid membrane technique (low ligand inventory) [23]. Alternatively, extremely specific ligands can be designed so that very high decontamination is possible in a single extraction and stripping step as in the SLM based methods.

The work carried out by Mohamed et al. [28] was directed mainly to investigate the possible recovery of thorium from nitrate medium using LEM technique. Teramoto et al. [29] proposed a general mass transfer model for the extraction of weak bases and weak acids by LEM in which the diffusion in the W/O emulsion drops, the external mass transfer, and both the chemical and phase equilibria were taken into account. This study was carried out using HTTA as a carrier to extract thorium from an acidic solution based on the proposed mass transfer model of Teramoto [29] and the Chan and Lee model [30]. The permeation rate of thorium through the membrane can be quantitatively explained by the proposed model. Experiments were carried out

at various hydrogen ion concentrations with other conditions kept constant. As shown in Figure 4, the plot of ln y vs t gives straight lines and K_A's are calculated from their slopes. Figure 5 indicates that the plot of $1/K_A$ against H_1 also gives straight lines in accordance with following equation:

$$\frac{1}{K_A} = \frac{1}{k_A} + \frac{H_1}{k_f B_o} \qquad (1)$$

K_A, k_f, H_1 and B_o are overall mass transfer coefficient (cm/s), forward rate constant (cm/s), concentration of hydrogen ion, molar, in phase I (external aqueous phase) and partition coefficient respectively. The values of k_A (mass transfer coefficient of metal under investigation (cm/s)) and k_f can be calculated from their intercept and slope, respectively. It was impossible to determine k_B or k_C (mass transfer coefficients of carrier and complex through the oil layer around W/O emulsion drop, respectively, cm/s) in the W/O/W multiphase system, however, a rough estimate was made by the extraction experiment using an agitation vessel 7 cm and 14 cm height equipped with a magnetic stirrer. 200 cm³ of the aqueous thorium solution was first introduced into the vessel. Then 50 cm³ of the W/O emulsion phase was carefully poured over the aqueous phase so as not to disturb the interface. Stirring in the emulsion phase was started at 100 rpm and samples were taken from the aqueous phase for analysis. Under the condition that $A_{I,o}$ (concentration of metal ions, M) was sufficiently high and $H_{I,o}$ (concentration of hydrogen ion in external aqueous phase, M) was considerably low, the resistance of the aqueous stagnant diffusion film and the interfacial reaction could be neglected. It was anticipated that, the diffusion rate of the complex in the emulsion phase would be fast due to the convection caused by agitation.
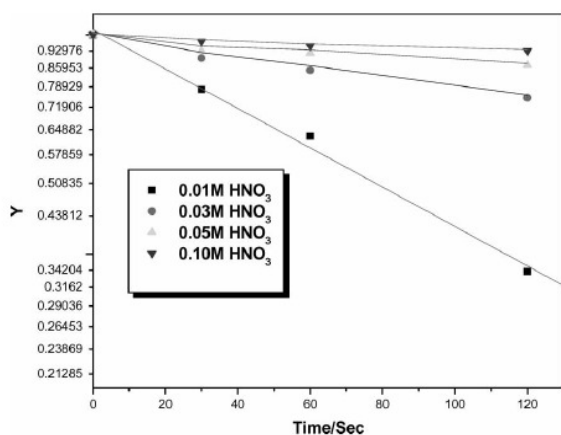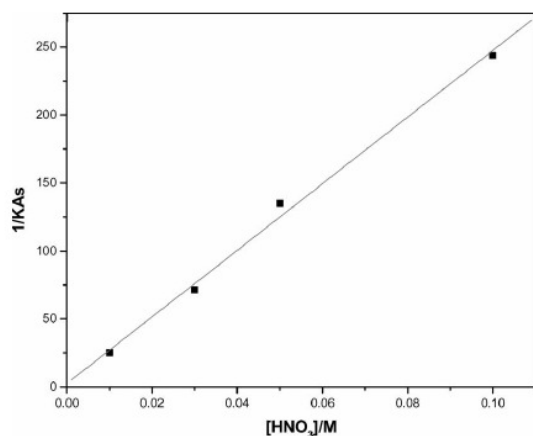
From the extraction data of U(VI) by TBP, it is indicated that the 30% TBP and aqueous feed in 3M nitric acid is quite suitable for DFSX by HFC [31]. This system can be successfully utilized for separation of both micro and macro concentration of U(VI) from aqueous acidic solutions. Due to high surface area to volume ratio of this technique, the feasibility of separation of uranium from nuclear waste in presence of oxalate ions using 30% TBP/n-dodecane as an extractant and 0.05M HNO₃ solution as strippant was clearly demonstrated. The extraction and stripping could be achieved simultaneously using two HFC and mass-transfer for stripping in this system could be enhanced by using the hydrophilic hollow fiber membrane. Presently, in conventional methods, uranium is recovered from treated oxalate supernatant by solvent extraction using Purex process. Hence, this will be an additional burden on recovery cycle. This step can be avoided if uranium is recovered on the spot (at the place of generation) by DFSX technique. Further, radiation stability of such polymer (polypropylene fiber) is well proven for 1M Rad which is far lesser than the limit required to damage the fibers.

After optimizing all the chemical parameters, dispersion-free solvent extraction (DFSX) technique was applied for the recovery of U(VI) from oxalate supernatant [31]. The composition of the waste is given in Table 2. Mass transfer coefficient for stripping are shown in Figure 6 and TBP concentration variation vs uranium extraction are shown in Figure 7. Experiments were performed with treated (oxalate ion destroyed by KMnO₄ and H₂O₂) and untreated (without oxalate decomposition) waste separately. As obvious from Figure 8, the recovery of uranium was well above 90% in case of untreated waste while in case of treated waste it was more than 99%. Both the experiments were run in counter-current recirculation mode with A/O ratio at 1. The decrease in uranium recovery in case of untreated waste was due to the neutral soluble oxalate complex of uranium having lower D_U value. Also the presence of plutonium in feed affected the overall recovery of uranium due to competitive extraction. The presence of important fission products such as ¹³⁷Cs and ¹⁰⁶Ru did not affect the recovery of uranium. This clearly indicated that present method could be successfully applied for the recovery of U(VI) from oxalate supernatant waste. The morphology of the membrane and structural stability is also a important factor and play an important role in HFSLM performance [31-35]. The radiation stability of polymeric support is separately discussed in section 3.2.

Fig. 4. Determination of K_A^s [28].

Fig. 5. Determination of K_A and K_f [30].

Table 2
Composition of the oxalate supernatant waste [31].

Component	Value	Unit
Uranium (U)	5	g dm⁻³
Plutonium (Pu)	25	mg dm⁻³
Ruthenium (¹⁰⁶Ru)	0.0032	mCi dm⁻³
Caesium (¹³⁷Cs)	0.003	mCi dm⁻³
Nitric acid	3	mol dm⁻³
H₂C₂O₄	0.1	mol dm⁻³

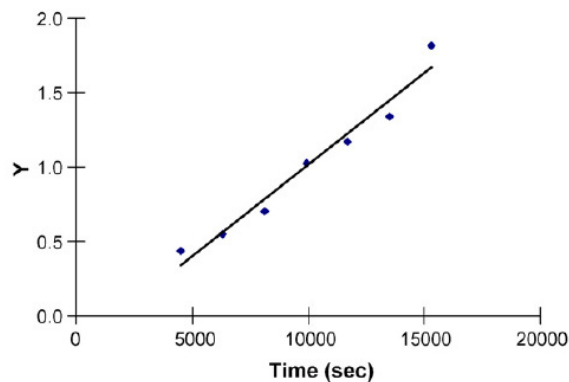**Fig. 6.** Mass transfer coefficients of uranium for stripping: conc. of organic 30%TBP in n-dodecane, strippant: 0.05M nitric acid, feed flow rate: 5.83 cm³ s⁻¹ and organic (pseudo-emulsion) flow rate: 1.53 cm³ s⁻¹ [31].
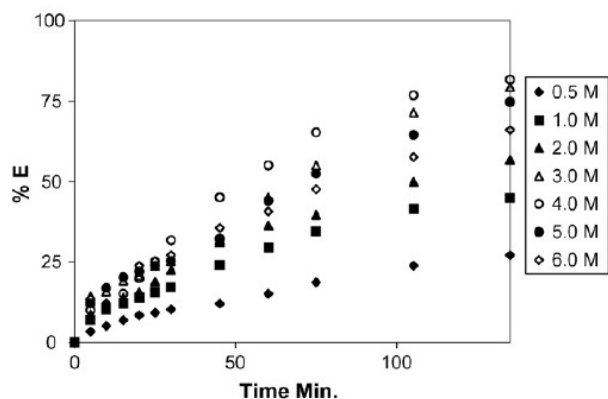
Fig. 7. Influence of organic concentration on U(VI) extraction: feed acidity: 3M HNO$_3$, conc. of U(VI): ~35gdm^{-3}, conc. of extractant (TBP in *n*-dodecane): variable, feed flow rate: 5.83 cm^3 s^{-1}, organic (pseudo-emulsion) flow rate: 1.53 cm^3 s^{-1} [31].

Unfortunately, there is very little information available in the literature on Cs separation from acidic wastes based on liquid membrane separation methods [37-39]. Mohapatra et al. have used crown ethers as the Cs(I) selective extractant in supported liquid membrane [38] and polymer inclusion membrane [39] studies for selective transport of radionuclides. However, the transport efficiency was not encouraging though excellent selectivity was observed. An attempt has been made by Mohapatra [36] to develop a membrane based method for the selective separation of ^{137}Cs from solutions of acidic origin (such as the HLW) using chlorinated cobalt dicabollide (CCD) in phenyl trifluoromethyl sulphone (PTMS) as the carrier solvent. The transport behaviour of Cs(I) was investigated from nitric acid medium using in phenyl trifluoromethyl sulphone (PTMS) as the carrier in microporous PTFE membranes. The transport rates were influenced by the feed acidity and an increase in the feed acidity resulted in a sharp decrease in the permeability coefficient value. Though, increasing the carrier concentration is expected to result in higher transport rates, an opposite trend was observed which was ascribed to poor stripping at the membrane–receiver interface. The selectivity studies have shown promise while the stability of the liquid membrane is of concern suggesting each time a fresh liquid membrane has to be used. Alternatively, diluent modification may be tried which may arrest the leaching of the extractants from the membrane pores. Strip dispersion technique can also be used for longer stability and hence reusability of this liquid membrane [40].
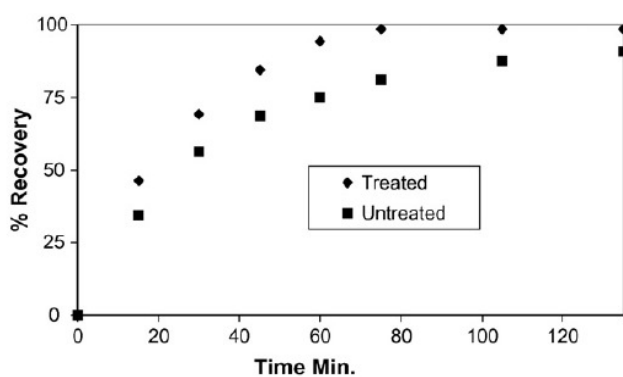

Fig. 8. Percentage recovery of U(VI) from oxalate supernatant waste: conc. of organic 30% TBP in *n*-dodecane, strippant: 0.05M nitric acid (composition of the oxalate supernatant waste is given in Table 2), feed flow rate: 5.83 cm^3 s^{-1} and organic (pseudo-emulsion) flow rate: 1.53 cm^3 s^{-1} [31].

Polymer inclusion membrane may also be evaluated for Cs recovery from acidic wastes. The problem of stability needs to be addressed to enable its application for large scale recovery of Cs from HLW solutions maintained at 1M HNO$_3$. Under the optimum conditions (1M HNO$_3$ as the feed and 8M HNO$_3$ as the receiver solutions), selectivity of Cs transport using CCD as the carrier extractant was examined. This was done by preparing a synthetic mixture of radionuclides such as ^{99}Mo, ^{99m}Tc, ^{106}Ru, ^{137}Cs, ^{152}Eu (some

representative fission products), ^{51}Cr, ^{59}Fe (some typical structural materials) and ^{241}Am in 1M HNO$_3$ and using it as the feed solution. The transport data after 3 h of operation is presented in Figure 9. This figure also includes the gamma ray spectrometry data of the feed data before the start of the experiment as well as after 3 hours of operation along with the strip phase data after 3 h. As indicated in the figure, excellent selectivity was observed with respect to the fission products, activation product and structural materials suggesting feasibility of the present method for selective recovery of Cs from HLW at 1M HNO$_3$. The decontamination factor (D.F., defined as the ratio of products to impurity in the product divided by that in the feed) values are listed in Table 3. Though ^{99m}Tc lines are indicated in the figure, the D.F. values with respect to this radioisotope was not included as decay product of ^{99}Mo also contributed to the total ^{99m}Tc quantity. As indicated, the D.F. values are >100 for all the radionuclides studied in the this work suggested that this separation method is effective and similar to the liquid membrane based separation methods reported earlier by Mohapatra et al. [38] using crown ethers. In another publication, selective separation of ^{137}Cs from solutions of acidic origin (such as the HLW) using DTBB18C6 as the carrier was investigated in detail using polymer inclusion membrane (PIM) based scheme [39]. Transport selectivity of the present PIM for Cs$^+$ with respect to other fission products was investigated by irradiating a natural uranium target (~2 mg) wrapped with Al foil at a thermal neutron flux of 1×10^{12} neutrons cm^{-2} s^{-1}. Subsequently, the irradiated target containing the fission products were dissolved in 6M HNO$_3$ and finally, the acidity was adjusted to 1M HNO$_3$ prior to transfer into the feed compartment for the transport experiments. The fission product mixture was spiked with ^{137}Cs tracer for the convenient monitoring of Cs. The plasticized polymeric membrane made from cellulose triacetate (CTA), di-*tert*-butylbenzo-18-crown-6 (DTBB18C6) and tri-*n* butylphosphate (TBP) was efficient in transporting Cs from acidic solutions suggesting the applicability of this method as a viable option for radioactive waste remediation. The optimum concentrations of the three components were 24.6 wt.% CTA, 15.3 wt.% DTBB18C6 and 60.1wt.% TBP. The stability of the membrane was good only for the feed at 1M HNO$_3$, suggesting application of this membrane can be done for pre-concentration of radio-caesium from waste solutions of low acidity. However, selective pre-concentration requires utilization of membranes made from NPOE as the plasticizer.
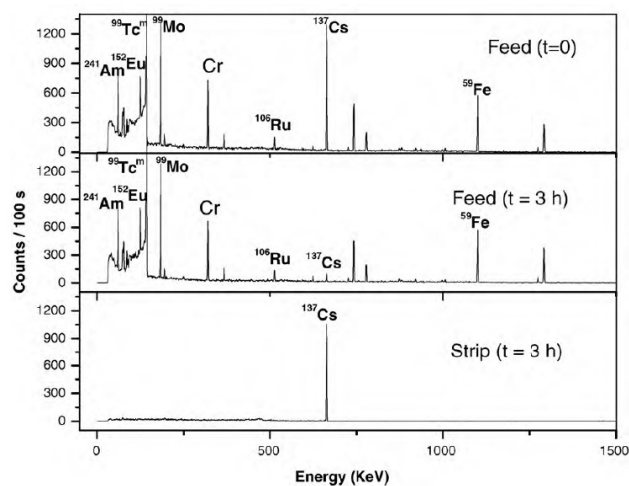

Fig. 9. Gamma spectrum of the radionuclides in the feed, strip and raffinate solutions showing the selective transport of ^{137}Cs through 0.45µm PTFE flat sheet supported liquid membrane after 3 h of operation; Carrier: 0.025M CCD in PTMS; Feed: 1M HNO$_3$; Strip: 8M HNO$_3$ [36].

Polymer inclusion membranes (PIMs) are a new and very promising type of visibly homogeneous extracting membranes. They are suitable for the separation of ions and small organic molecules which substantially reduces the hazard sassociated with SX-like techniques. PIMs entrap an extractant with in a polymer matrix, often with the addition of a plasticizer or modifier to improve their extraction characteristics. As the extractant is wholly encapsulated in the polymer, the exposure of workers to toxic extractants is minimized. The polymer replaces the organic diluent which removes the fire hazard associated with conventional SX. PIMs are mechanically strong and

stable, easy and safe to handle and reasonably simple to fabricate [7]. The possibility also exists for PIMs to be deployed for environmental remediation. Nghiem et al. [41] outlined their ability to selectively and completely extract heavy metals from aqueous solutions, even at trace concentrations, which makes them ideal candidates to clean up industrial waste water or as an emergency rehabilitation procedure. We envisage that insituations where mine discharges pose a pollution risk, PIM technologies may provide an effective clean up tool due to the ability to deploy pre-fabricated membrane modules insitu. Surprisingly, whilst the body of knowledge on the extraction of uranium is voluminous, there are only four reports on PIM systems for the separation of uranium. Bloch et al. [42] reported in 1967 that a PIM-like membrane coating consisting of tri-n-butyl phosphate (TBP) and poly(vinylchloride) (PVC) supported on Kraft paper was effective in separating uranyl nitrate from nitric acid solutions. However, it was noted that the thin supported membranes had short life times of only 1–2 days (at which point the flux of uranium had dropped to below 20% of its original value).

Table 3
Decontamination factors (D.F.) of 137Cs over fission products, activation products and structural materials. Carrier: 0.025MCCD in PTMS; Feed: 1MHNO3 containing the radiotracer mixture; Receiver: 8M HNO3 [36].

Radio tracer	D.F.	Radiotracer	D.F.
[51]Cr	389±15	[106]Ru	114±15
[59]Fe	312±12	[152]Eu	301±21
[99]Mo	329±13	[241]Am	232±18

Matsuoka et al. [43] reported on a PIM (which they termed a liquid membrane) consisting of cellulose triacetate (CTA) and TBP. Using this membrane, uphill transport of uranium was achieved by having a sufficiently high concentration of the counter-ion in the receiver phase. Again, this membrane suffered from poor stability due to the relatively high wáter solubility of TBP which led to leaking of this extractant from the membrane unless the aqueous phases contacting the membrane were saturated with TBP. More recently, Sodaye et al. [44] described a PIM for the pre- concentration of alpha emitting actinides for scintillation purposes. This PIM was fabricated from di-(2-ethylhexyl) phosphoric acid (D2EHPA) and CTA, in combination with a number of plasticizers and scintillants, and showed almost complete extraction of uranium from acidic nitrate solutions.

In another interesting study, PIM was examined by Kolev et al. [45] for the extraction and separation of uranium (UO_2^{2+}) from acidic sulfate solutions. Poly(vinylchloride) (PVC) based PIM s containing the following commercial extractants were screened for their ability to extract uranium: Alamine336, Cyanex 272, Aliquat336, di-(2-ethylhexyl) phosphoric acid (D2EHPA), and tri-n-butyl phosphate (TBP). The membrane containing 40% (m/m) D2EHPA is shown to be the most effective in the quantitative extraction and backextraction of uranium using sulfuric acid solutions. Facilitated transport of uranium across the membrane against its concentration gradient is demonstrated with uranium fluxes as high as 4.85×10^{-7} mol m^{-2} s^{-1}. A new method for determining the stoichiometry of extracted complexes in both membrane and solvent extraction systems has revealed the composition of the UO_2^{2+}–D2EHPA complex to be $UO_2 \cdot A_2 \cdot (HA)_2$ where HA and A$^-$ are D2EHPA and its conjugated base, respectively. Kinetics of membrane extraction of U(VI) Membrane extraction experiments were carried out using uranium solutions of three concentrations (10, 20 and 28 mgL^{-1}) at pH 1.0 and the corresponding transient solution U(VI) concentrations (Figure 10a) were found to follow first-order kinetics (Figure 10b). This fact can be explained on the basis of the following assumptions:

• The membrane is separated from the mechanically mixed bulk solution by a stagnant diffusion layer of thickness δ.

• The high excess of D2EHPA in the membrane results in negligibly low U(VI) concentration (Equation (2) at the solution side of the membrane/solution interface (x = δ).

$$[UO_2^{2+}]_{dll, \, x=\delta} = 0 \qquad (2)$$

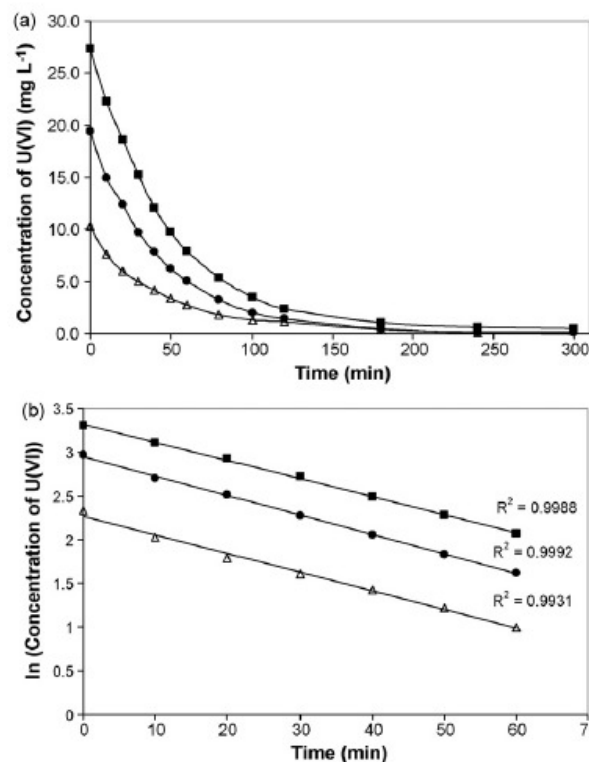where *x* is the axial distance and subscript *dl* refers to the stagnant diffusion layer.

Fig. 10. Extraction of uraniumfrom solutions of differentcon centrationinto 40% (m/m) D2EHPA PIMs: (a) transient U(VI) concentration curves from(■) 28 mgL^{-1}, (□) 20 mgL^{-1} and (Δ) 10 mgL^{-1}; (b) logarithm of the U(VI) concentration versus time (220±10 mg PIM segments in 200 mL of U(VI) solutions in 0.1M H$_2$SO$_4$) [45].

In order to improve PIM performance, Mohapatra et al. [46] have also evaluated the feasibility of PIM for transport behaviour of Am^{3+} across cellulose triacetate (CTA) based PIM containing Cyanex-301 (bis(2,4,4-trimethylpentyl)dithiophosphinic acid) as the carrier extractant and tri-n-butyl phosphate (TBP) or 2-nitrophenyloctylether (NPOE) as the plasticizer from different feed and strip conditions. The TBP plasticized membrane resulted back transport of Am when alpha-hydroxy iso-butyric acid was used as the complexing agent in the strip phase while no such effect was seen when ethylene diamine tetraacetic acid (EDTA) was used as the complexant. Long term reusability of the membrane was studied by measuring the permeability coefficient (*P*) after exposing the PIMs to a maximum gamma ray dose of ∼200 kGy. The surface morphology of the membranes was analyzed by atomic force microscopy and the roughness parameter was correlated to transport efficiency. In the series of novel extractants, a calix[4]arene appended with four diglycolamide moieties containing *n*-octyl groups (C4DGA) was evaluated for the transport of actinide ions such as UO$_2^{2+}$, Pu^{4+}, Pu^{3+}, and Am^{3+} from acidic feed solutions across PTFE flat sheet supported liquid membranes [47]. The supported liquid membrane (SLM) studies were carried out with C4DGA under varying feed acidities, carrier extractant concentrations, and membrane pore sizes. While low pH solutions resulted in no Am^{3+} transport, quantitative transport of the metal ion was observed when 0.01 M EDTA solution (pH 3.0) was used as the strippant in the receiver phase. The transport efficiency of the carrier solvent system was Pu^{4+} > Am^{3+} > Pu^{3+} ≫ UO$_2^{2+}$, which is not in line with those observed for diglycolamide extractants, where Am^{3+} was extracted to a much higher extent than other actinide ions. The results were compared with those reported earlier for TODGA (*N,N,N',N'*-tetra-*n*-octyldiglycolamide) and tripodal diglycolamide (T-DGA) under identical conditions. Eu^{3+} transport rates were found out to be significantly higher than those observed with Am^{3+}. The selectivity factors of the C4DGA extractant were compared with those of other DGA-based extractants reported earlier. The diffusion coefficient for the Am(III)–C4DGA complex was obtained experimentally using the lag time method. The stability studies indicated significant deterioration of the liquid membrane with time even after only 3 days of operation.

In continuation, a liquid surfactant membrane (LSM) technique was developed to remove Am(III) from aqueous nitrate solutions [48]. 2-

Ethylhexyl phosphonic acid mono-2-ethylhexyl ester (H_2A_2) was used as a carrier in LM phase, which is selective extractant for the quantitative extraction of actinide and lanthanide elements from their dilute solutions as established in earlier publication [49]. Span 80 (sorbitan monooleate), a commonly used surface-active agent is used as emulsion stabilizer. The recovery rates of Am(III) were investigated by changing pH in the external phase (EP) and concentration of H_2A_2 and Span 80 in the LM phase. The extraction of commonly associated fission product elements were also studied from EP adjusted at different pH. Removal and concentration of Am(III) was achieved from depleted uranium and plutonium (obtained in the nuclear fuel reprocessing operations by the process known as Plutonium Uranium Recovery by Extraction or PUREX) waste solution. The waste generated in the extraction process of Pu(IV) and U(VI) by 30% tributyl-phosphate in the fuel reprocessing operations is a rich source of fission product elements and trans- actinides. Partitioning of trans-actinides from fission products with the option of their transmutation is the process projected by several scientists for the safe disposal of high level waste [50-52]. For this study of LSM separation a PUREX waste solution (a diluted waste solution is used to maintain radiation exposure at an acceptable working level) spiked with extra amount of ^{241}Am was used. Table 4 presented the percentage removal of Am(III) from waste solution along with different coexisting fission product elements. In this process a concentrated solution of Am(III) was generated in the internal phase (IP) which can be treated for further purification. Along with Am(III), other trivalent and tetravalent fission product elements (Ce(III), Nb(III), Zr(IV) and Ru(III)) were also getting extracted by LSM. Extraction

efficiency for Ce(III), Nb(III) and Zr(IV) were almost similar to that of Am(III), whereas ≈40% of Ru(III) was transported to IP. A practically negligible extraction is noted for Cs(I) and Sr(II). Elimination of these two fission product elements reduces significant amount of beta and gamma activity in the concentrated Am(III) product solution and hence its handling for further processing becomes less hazardous. More than 10 times reduction in the alpha activity of waste solution was achieved in 30 min using single stage LSM separation process. The transport behaviour of Am^{3+} from $3MHNO_3$ as well as from a simulated high-level waste (SHLW) solution was examined conforming to the reprocessing of pressurized heavy water reactor (PHWR) spent fuel after 7000 MWD/T burn up [54]. The transport properties of other relevant elements present in the SHLW were also studied. As loading and radiation induced degradation of the organic extractants are the two important issues pertaining to radioactive waste management, such studies were also taken up by authors using 1 g/L Nd and TODGA irradiated up to a dose of 10 Mrad. In all the studies, di-n-hexyl octanamide (DHOA) was used as phase modifier and NPH was used as diluent. Hollow fiber-supported liquid membrane method containing TODGA as the carrier can be used effectively for the recovery of trivalent actinides and lanthanides from simulated high-level waste solution. About 10% co-transport of Sr, Mo and Cr was observed along with the rare earth elements which are transported quantitatively. The effect of radiation dose on the TODGA solvent system was negligible up to 10 MRad.

Table 4
Removal and concentration up gradation of fission by products from diluted PUREX waste solution. LSM: 2.5 mL containing 0.30 M H_2A_2 + 0.22 M Span 80 in dodecane + 0.50 M HNO_3. EP (feed): 50 mL waste solution adjusted to pH 3 ± 0.12 [48].

Element	Initial concentration (mCi L^{-1})[a]		Concentration after 30 min (mCi L^{-1})[a]	% Removal	Enrichment of metal ions (En) in the internal phase
	External phase		Internal phase	External phase	Internal phase
Am(III)	2.1 ± 0.1[b]	NIL	0.17 ± 0.01[b] 22 ± 1[b]	92 ± 2	11
Ce(III) _	(1.2 ± 0.1) x10^3 NIL		86 ± 2(13 ± 1) x 10^3	93 ± 2	10
Cs(I)	780 ± 12 NIL		780 ± 14 NIL	NIL	–
Nb(III)	54 ± 1 NIL		4.3 ± 0.15 52 ± 13	93 ± 2	10
Ru(III)	421 ± 10 NIL		257 ± 6 (1.8 ± 0.1) x 10^3	39 ± 1	4.4
Sr(II)	719 ± 16 NIL		719 ± 17 NIL	NIL	–
Zr(IV)	12 ± 1 NIL		0.72 ± 0.17 120 ± 2	94 ± 2	10

NIL, below detection limit (<10^{-3} mCi L^{-1} for alpha activity and <15 x 10^{-3} mCi L^{-1} for gamma activity).
[a] Concentration of fission products is given in terms of their gamma activity.
[b] Concentration of ^{241}Am is given in terms of its alpha activity.

Sportsman et al. [54] have shown that transport properties of mesoporous polycarbonate track-etched membranes (PCTE) which can be modified through surface engineering. As described by Hagen-Poisseuille's equation for laminar flow through a cylinder, reduction of pore diameter, via electroless gold plating, resulted in the decrease of diffusional flux across the membranes, with a similar order of magnitude reduction occurring for each of the metal ions studied, ^{137}Cs, ^{85}Sr, ^{241}Am, and ^{239}Pu. Following gold deposition on the PCTE substrate, a dodecanethiol self-assembled monolayer (SAM) was added. Although the SAM did not significantly reduce the pore diameter, the hydrophobic nature of the thiol significantly increased the transport resistance of the membrane, essentially preventing any of the metals from diffusing across the membrane. The final step in the surface modification was the addition of the di-(4-t-butylphenyl)-N,N,-diisobutylcarbamoylmethyl phosphine oxide [D(tBuF)D(ibu)CMPO] ligand to the PCTE/Au/SAM membranes. The monovalent and divalent cations were still unable to diffuse across the membranes, but the trivalent and tetravalent actinides were quantitatively extracted from the feed cell to the sink cell through a carrier-mediated, facilitated transport mechanism. Furthermore, the flux rates of the actinides across the membranes were much greater than the flux rates across the bare PCTE membranes or the PCTE/Au membranes. However, the desorption mechanism into the sink solution under the experimental conditions was imperfect, causing a loss of 20 to 25% of the total activity from the experiments. Additionally, by extending the time of the diffusion experiments, the conditions of the feed and sink cells, in particular nitrate anion concentrations, were allowed to change. As the nitrate concentration in the sink cell increased, Pu(IV) was sorbed from the sink into the membrane, resulting in a near total loss of activity. These results indicate

that the carrier-mediated, facilitated transport approach is a promising method of removing low levels of actinides from process streams, while not generating copious amounts of secondary wastes. Operationally, the transient change in nitrate anion concentration could be easily avoided by recirculating the contents in the sink cell, by removing HNO_3 from the sink to prevent accumulation, or by binding the Pu in the sink with oxalate or other complexants.

For the SLM, several polymeric supports can be used, such as Polypropylene (PP), Polyvinylidene Fluoride (PVDF), Polytetrafluoroethylene (PTFE), silicone, and Polysulfone (PSf), among others [55]. Homemade PSf membranes and commercial PVDF membranes have been used here for the design of the uranyl ion SLM separation system [56]. The BLM and SLM membrane systems used for separation (extraction/recovery) and pre-concentration have been shown to be effective for the transport of uranium ion using D2EHPA/Kerosene as carrier, and a mixture of phosphoric and citric acids in the stripping/ recovery phase, under different combinations of chemical conditions (Systems 1 and 2, details given in Table 5). The BLM and SLM systems are successful for the pre-concentration of trace Uranium (VI), which leads to an improvement in the quantification of trace metals, with recovery percentages above 57% and 89%, respectively. Comparing both systems, as it is well known, SLM can reduce the amount of liquid membrane, thus reducing consumption of carrier and solvent. Furthermore, SLM systems can be applied to actual samples with low concentrations of water containing uranyl ion, and thus a suitable quantification is possible, with low consumption of reagents. The permeability coefficient (P) values for each system were calculated from the slope of the graph obtained when using the natural logarithm of the uranyl ion

concentration ln $(C_{f,t}/C_{f,0})$ *vs.* time. The permeability coefficient values are presented in Table 5. When comparing the permeability coefficients of both chemical systems, the corresponding values are higher for System 1 than those obtained with System 2, for both supports (PVDF and PSf). In this sense, it seems that chemical conditions of concentrations carrier and recovery agents corresponding to System 1 favour the transport rate of uranyl ion through the membranes. As expected, permeability coefficients are higher when PVDF is used as the membrane support, compared to those obtained when using PSf, which confirms that the uranyl-carrier complex accumulates within the membrane phase in the latter case. This accumulation may be related to the more hydrophilic chemical structure of PSf (which interacts with the uranyl-carrier complex) and with the more dense morphological structure of PSf (which slows down the rate of transport through it), as can be seen in Figure 11. In all cases, pH gradient is shown to be the driving force of both liquid membrane systems (System 1 and System 2) for the uranyl ion transport. In the case of System 1 can obtain high extraction percentages (over 90%) and recovery of up to 75% in 5 h using PVDF as membrane, achieving maximum recovery in 24 h. In the case of System 2 has slower kinetics compared to the system 1, however, extraction and recovery yields achieved are above 90% in 24 h.

Table 5
Variation of permeability coefficient of Uranium (VI) (in cm/min) by using SLM, with PVDF and PSf supports. Chemical conditions used were those of System 1 and System 2 [56].

System 1	P (cm/min)	System 2	P (cm/min)
PSf_S1	4.10×10^{-3}	PSf_S2	5.75×10^{-4}
PVDF_S1	5.03×10^{-3}	PVDF_S2	1.88×10^{-3}

In view of the small concentration of minor actinides in analytical waste generated during Pu processing/HLW, it is of particular interest to evaluate hollow fiber based supported liquid membrane based separation method for the 'actinide partitioning' using TODGA as the carrier extractant [57]. For this, HFSLM technique was used involving DHOA and DHOA–TODGA cycles for the separation of Am from the waste. CMPO being one of the promising extractants for actinide partitioning [58] was employed for separation of Am from Ca(II). An attempt was made by authors to separate Am from waste consisting of complex matrix using HFSLM separation technique. A three step separation scheme was developed on the basis of constituents of the matrix wherein the first step involved separation of U from Am using 1 M DHOA while in the second step, Am was separated using 0.5 M DHOA + 0.1 M TODGA mixture from the other impurities.. The entire separation scheme was depicted in Figure 12. Ca(II) was removed from americium using CMPO column chromatographic extraction. The decontamination factor of uranium in DHOA cycle was found to be 162 while that of iron and sodium in TODGA–DHOA cycle were found to be 170 and 711 respectively. The decontamination factor of CMPO step was 30,000 for Ca(II). The overall recovery of americium in this separation scheme was found to be 77 %. HFSLM being a rapid, simple technique with less ligand inventory can be effectively employed for separation of americium from the assorted analytical waste. Dudwadkar et al. [59] have studied various parameters including the concentration of the carrier in the membrane phase, variation of acidity, macro concentration of uranium and concentration of salt and the concentration of the trivalent elements in the feed using ^{241}Am as tracer. Under optimised conditions the transport of the other radionuclides viz. ^{233}U, ^{239}Pu, $^{152-154}$Eu, ^{144}Ce etc. from nitric acid was studied. The studies have been further extended to the transport of americium from simulated HLW of pressurized heavy water reactor (PHWR) origin, and to the actual HLW solution originated from the reprocessing of spent fuel from the research reactor, to test the applicability of this technique for the separation of actinides. Results of the transport studies carried out from ^{241}Am spiked synthetic uranium depleted PHWR-HLW and actual HLW showed that 98 % of activity could be transported in 11 and 10 h respectively (Figure 13).

Ansari et al. [60] have investigated the transport behaviour of trivalent actinides and lanthanides from nitric acid solutions using HFSLM. In this HF membrane set-up carrier was impregnated into the membrane and feed and strip solution were pumped through lumen and shell side respectively. Its application was tested for the typical pressurised heavy water reactor high-level waste (PHWR-HLW) solution. The authors used TODGA (N,N,N´,N´-tetraoctyl-3-oxapentane-diamide) alone and a mixture of 0.1 M TODGA + 0.5 M DHOA (*N,N*-di-*n*-hexyl octanamide) dissolved in NPH was optimised as a suitable carrier for maximum transport of trivalent actinides and lanthanides.

The extraction of trivalent lanthanides (M^{3+}) from nitric acid medium by neutral extractant, TODGA was as follows [60]:

$$M^{3+}_{(aq)} + 3NO_3^-{}_{(aq)} + 3TODGA_{(org)} \leftrightarrow M(NO_3)_3 \cdot 3TODGA_{(org)}$$
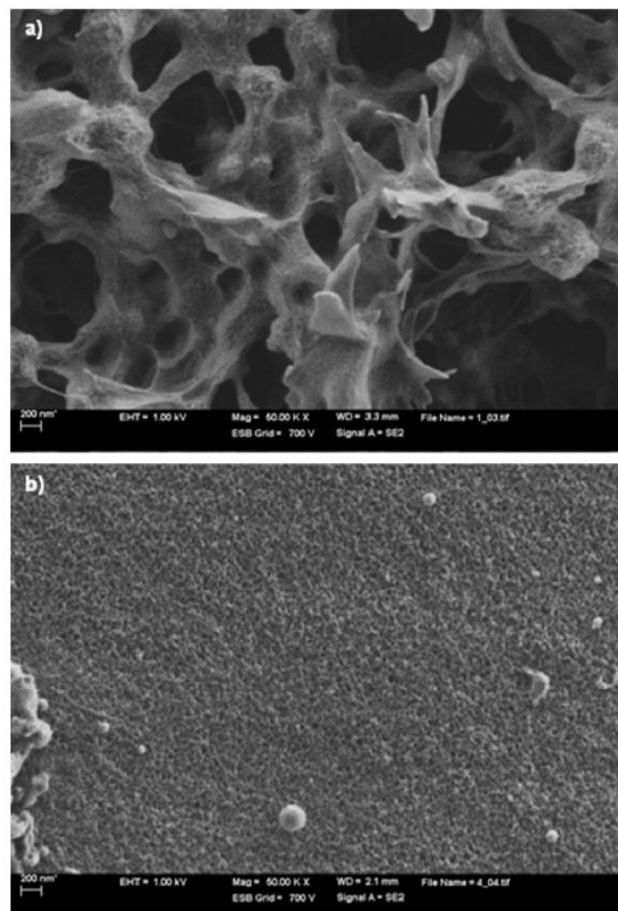

Fig. 11. Surface supported liquid membranes SEM images: (a) PVDF and (b) PSf. In both cases a magnification of 50.00 KX is used [56].

where (aq) and (org) represent the aqueous and the organic phases, respectively. The term $M(NO_3)_3 \cdot 3TODGA$ represents the extracted species in the organic phase. The addition of DHOA prevented possibility of aggregate formation of TODGA in the membrane pores [61], thereby enhancing the transport rate. Mass transfer coefficients were calculated on the basis of the described model, whose success was verified by excellent matching of the membrane diffusion coefficient values calculated by the model and the Wilke-Chang equation. The permeability of the lanthanides increased with the feed acidity. Quantitative transport of lanthanides and actinides was achieved within 45 min from a solution containing 1 g/L Nd at 3.5 M HNO$_3$ as well as from pressurised heavy water reactor simulated high-level waste (PHWR-SHLW) whose composition is given in Table 6. The stability of the HFSLM was found to be satisfactory in eight successive runs. The results suggest the possibility of using a TODGA-HFSLM system to recover minor actinides from nuclear waste. The separation of lanthanides(III) from actinides(III) (which is necessary for the transmutation of the actinides) was also successfully achieved by HFSLM using a different carrier. Efforts were made to couple the two HFSLM systems (one for total lanthanide/actinide separation and the other for lanthanide/actinide separation) to get pure lanthanide and trivalent actinide fractions separately. The main objective of the study was to recover actinides and lanthanides from a nuclear waste solution (high-level waste or HLW). To this end, Nd was taken as the representative element of lanthanides and the transport of Am(III) was investigated in the presence of 1 g/L Nd. The results are shown in Figure 14. The transport was also predicted theoretically from the permeability coefficient data. Authors should have planned experiments in non-dispersive extraction mode and comparison of these results with SLM mode would have

predicted operational stability for both the processes for longer run in continuous process.
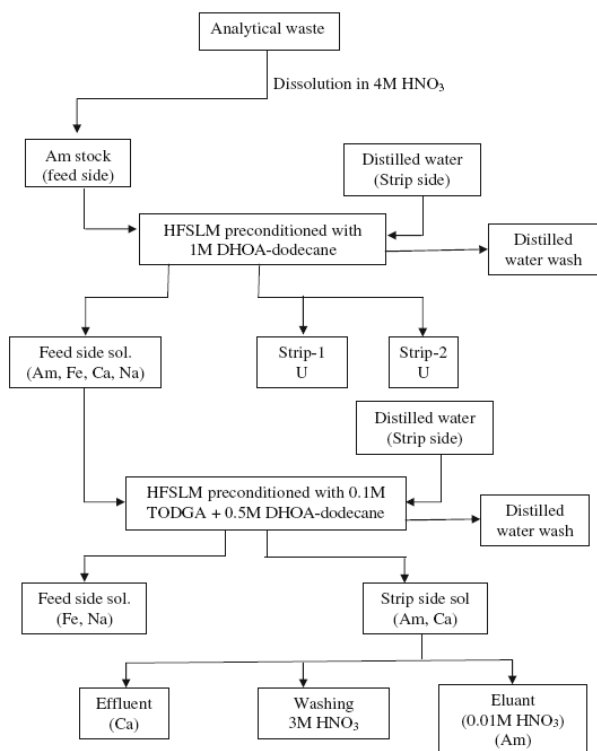

Fig. 12. Flow sheet of separation of americium from analytical waste [57].
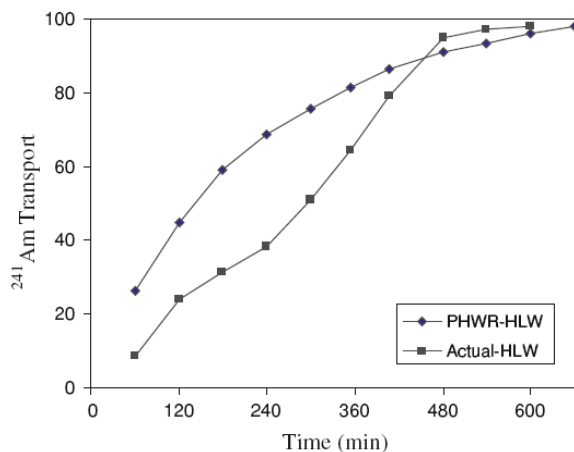

Fig. 13. Partitioning of alpha emitters from HLW [57].

In the same vein of continuous improvement, pseudo-emulsion-based hollow fibre strip dispersion (PEHFSD) techniques has been applied for the recovery of U(VI)/Pu(IV) from process effluent [62-64]. In used set-up, authors have performed extraction and stripping in a single HF module [62]. An aqueous strip solution is dispersed in an organic membrane solution containing an extractant or mixture of extractants. The pseudo emulsion is then pumped into a membrane module to contact with one side of a microporous support (which can be passed through the shell side of a microporous PP hollow fibre module). The aqueous feed solution containing the target species to be extracted is passed through the other side of the fibres on the other side of the support, i.e. the tube side. The continuous organic phase of the dispersion readily wets the pores of a hydrophobic microporous support (e.g. microporous PP hollow fibres in the module) and a stable LM (the organic phase) supported in the pores of the microporous support is

formed. A low pressure differential (0.2 bar) between the aqueous feed solution side (P_a) and the strip dispersion side (P_o) is applied to prevent the leakage of the organic solution for the strip dispersion into the aqueous side through the pores. The dispersed droplets have a typical size of 80-800 μm and the size of the pores of microporous PP support is 0.2 μm. Thus, these droplets are retained on the strip dispersion side and cannot pass through the pores and penetrate into the feed solution side [62]. For more details on the PEHFSD mechanism, see [62, 63].
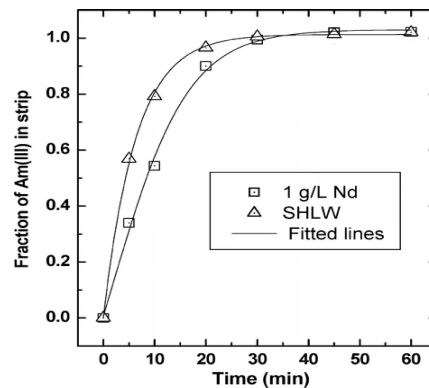

Fig. 14. Transport of Am(III) by TODGA-HFSLM. Carrier, 0.1 M TODGA+0.5 M DHOA in NPH; feed, 1 g L_1 Nd at 3.5 M HNO3 or PHWR-SHLW spiked with 241Am tracer (500 mL); receiver, distilled water (500 mL); flow rate, 200 mL min-1; temperature, 25 1C; Fitted lines represent the calculated values of transport data [60].

Plutonium (from PHWR fuel reprocessing) is recovered by first precipitating out plutonium nitrate as plutonium oxalate, and then extracting the oxalate supernatant, which contains milligram levels of plutonium. The typical composition of oxalate supernatant waste is 25 mg dm^{-3} of Pu, 5 gm dm^{-3} of U, 0.0032 mCi dm^{-3} of ^{106}Ru, 0.003 mCi dm^{-3} of ^{137}Cs, 3M of HNO$_3$, and 0.1 M of $H_2C_2O_4$. The separation of uranium and plutonium in the presence of fission products from this waste was investigated using 30% TBP/nph. The same PEHFSD setup was used for Pu(IV) extraction [63]. The extractant was TBP in nph. The transport proceeds through complexation at the feed phase-membrane interface and the formation of neutral solvated complex species (Pu(NO$_3$)$_4$.2TBP), which dissolve in the organic phase. Experiments were performed at concentrations ranging from 5% to 50% of TBP in nph. The extraction of Pu was observed to increase up to a TBP concentration of 30% and then decreased at concentrations above this value. The diffusion-limited flux increased linearly with the carrier concentration, but at higher carrier concentrations the viscosity of the membrane phase also increased. For fast stripping, hydrophilic modules can be used in place of hydrophobic modules. After the use of HF module, disposal plan for module has to be chalked out as solid waste. Similarly, non-dispersive solvent extraction studies were also carried by Gupta et al. for extraction of uranium and plutonium from acidic aqueous stream [64, 65].

An another important study, selectivity was studied in the SLM extraction of uranium(VI) from natural water by scanning the metal ions present in the sample prior to SLM extraction and in the extracts after extraction by inductively coupled plasma optical emission spectrometry [66]. The selectivity of the carrier towards uranyl ions was clearly demonstrated (Table 7). Most of the alkaline earth metal ions, despite having very high concentrations in the sample, were virtually not extracted.

The SLM technique could potentially be deployed for analytical applications and detailed review on this is published by Pabby et al. [67] and enrichment of trace quantities of radionuclides was studied in [68, 69].

In radiochemical laboratories, a significant quantity of analytical waste in a phosphoric acid medium is generated while analysing uranium (VI) using the Davies-Gray method [70]. The uranium should be recovered from this waste for safe disposal. Singh et al. [71] investigated the transport of uranium and fission products (produced during irradiation of natural uranium metallic fuel in nuclear research reactors) using 0.5M D2EHPA/n-dodecane SLM. The feed solution contains the actual radioanalytical waste generated after volumetric analysis of uranium by the Davis-Gray method. The results showed that 10% or less of major fission products were transported in 360 minutes. Similarly, around 60% of uranium was permeated through a 0.5M D2EHPA dodecane SLM in 1440 minutes. This may be attributed to the presence of other anions and cations in the analytical waste, which reduces

the permeation rate of uranium. However, it is significant that the concentration of uranium can be reduced substantially in feed by increasing the contact time. Figure 15 shows the concentration profile of the feed and receiving phase over time under optimum conditions. The authors should have used a bigger module to increase recovery in a shorter time.

Table 6
Composition of PHWR-SHLW Used in the Present Studies.
Acidity: 3 M HNO₃ [60].

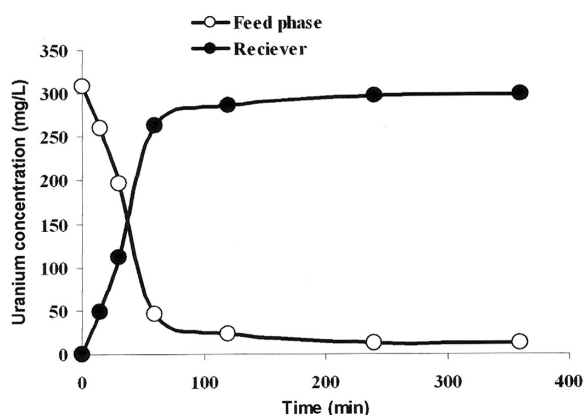| Element	Concentration (g/L)	Element	concentration (g/L)
Na	5.50	Mo	0.14
K	0.22	Cs	0.32
Cr	0.12	Ba	0.06
Mn	0.43	La	0.18
Fe	0.72	Ce	0.06
Ni	0.11	Pr	0.09
Sr	0.03	Nd	0.12
Y	0.06	Sm	0.086
Zr	0.004	U	6.34

Fig. 15. Concentration of uranium in feed and receiver side at condition given below. [Feed Acidity]: 0.001 M of H₃PO₄, [carrier]: 0.1 M D2EHPA¼n-dodecane, [strippant]: 0.5 M (NH₄)₂CO₃ [71].

Table 7
Concentrations of various metals in sample as found by ICP-OES before and after SLM extraction in the collected acceptor phase [67].

Element	Concentration of various elements in µg/l		
	Before SLM	After SLM extraction in collected	Extraction efficiency (%)
Li	1600	< 3	< 0.20
Mg	44330	36	0.08
K	88600	1400	1.60
Ca	21040	23	0.11
Sr	7800	< 5	< 0.06
P	68	15650	230
Ni	34	< 6	< 18
U	182	38	21

Although the Los Alamos National Laboratory has studied and used numerous traditional separation operations, it has long had an interest in the use of membranes to perform actinide extractions. Previous work in this area has included the characterisation of alumina membranes and their effect on cation transport [72, 73], the characterisation of steel membranes for possible use as a substrate [74], the nano engineering of a selective gate across the pore entrance of gold-sputtered alumina membranes [75], and the use of water-soluble polymers to floc the metal ions, thereby preventing transport across ultrafiltration membranes [76].

3.2 Evaluation of chemical and radiation stability of polymeric support

An attempt was made to evaluate radiation stability of several polymeric materials used as the support in supported liquid membrane studies for the transport of radionuclides from nuclear waste [77]. Flat sheets made from polytetrafluoroethylene, polysulfone, polyether sulfone, polyacrylonitrile and polyvinylidenefluoride were irradiated to varying extents using a ^{60}Co gamma ray source and subsequently, the transport efficiency of the irradiated flat sheets were evaluated. The membrane integrity was assessed from the transport rates of Am^{3+} from a feed containing 3 M HNO₃ into a receiving phase containing 0.01 M HNO₃ as the strippant while 0.1 M TODGA + 0.5 M DHOA in n-dodecane was used as the carrier extractant. The radiation stability of the membrane filters was evaluated after irradiating them up to 20 MRad absorbed dose in a gamma chamber. From the present studies it can be concluded that though membrane filters from polymeric materials like PTFE are not stable towards ionizing radiations, those made from polysulfone (PS) and polyethersulfone (PES), PAN and PVDF are stable up to an absorbed dose of 20 MRad. Though the diffusion of the metal–ligand complex in these membranes is rather slow in unirradiated membranes, they improve significantly after being exposed to the gamma radiation. This was reflected in the decrease in the metal ion hold up in the irradiated membrane filters. In another study conducted by Gupta et al. observed that physical integrity of fibers at radiation dose of 1M Rad was not affected as no topographical and physical changes occurred at this radiation level [30]. Radiation stability of polypropylene flat sheets are also examined and discussed by Kumar et al. [31-34]. Authors estimated that total dose absorbed by fibers would be far lesser than level of doses required injuring the propylene fibers while examining the viability of this technique.

Chemical stability of polypropylene support was checked with nitric acid (3-5M) [long term use of support in SLM experiments for 6 months] and found to be satisfactory as no flux decline was noted [78, 79]. More detailed surface morphology need be checked by SEM after long term use with nitric acid to analyse any possible damage on the surface of polymeric support.

4. Conclusions

This manuscript reviewed the main results from the literature on liquid membrane technology and membrane-based extraction and offers a perspective on the success of this research and its impact on membrane separations. Considerable progress has been made in a number of key areas, with some important and unanticipated developments. This type of technology assessment can play an important role in setting the directions for future research and development, both for individual scientists and engineers and for the broader membrane community. The following concluding remarks are listed point wise:

1. Transport of trivalent actinides and lanthanides was investigated from PHWR-SHLW using HFSLM technique. A mixture of 0.1 M TODGA + 0.5 M DHOA was optimized as a suitable carrier for maximum transport of metal ions. Quantitative transport of trivalent actinides and lanthanides was achieved within 30 minutes from PHWR-SHLW on laboratory scale. The present studies revealed that TODGA-HFSLM system offers a promising alternative approach for actinide partitioning. The basic phenomena governing the HFSLM process are similar to SLM and are sufficiently well understood to permit the scale-up of laboratory units.
2. The HFSLM technique was also applied on process scale for the recovery of radio-cesium, which revealed selective recovery of Cs(I) over other radiotracers with good decontamination factors. High decontamination factors as well as throughputs suggested possible application of the system for the recovery of radio-cesium from high level waste.
3. There is a need to develop the membranes which are compatible with the diluent/solvent mixture with respect to physical properties like surface tension, viscosity, etc. In addition, chemical/radiation environment of the feed/strip solution to which these membranes are subjected over long duration is an area of particular concern.

Abbreviations

DF	Decontamination factor
LM	Liquid membrane
SLM	Supported liquid membrane
BLM	Bulk liquid membrane
ELM	Emulsion liquid membrane
HDEHP	di-2-ethylhexylphosphoric acid
NDSX	Non-Dispersive Solvent Extraction
TOPO	Tri-*n*-octyl phosphineoxide
P&T	Partitioning & Transmutation
CMPO	Octyl-(phenyl)–*N,N*-diisobutyl carbamoyl methyl phosphine oxide
DGA	Diglycolamide
DHOA	N,N-dihexyl octanamide
DIAMEX	Diamide extraction
FSSLM	Flat sheet supported liquid membrane
HFSLM	Hollow fiber supported liquid membrane
HLW	High level waste
PHWR	Pressurized heavy water reactor
PUREX	Plutonium uranium extraction
SF	Separation factor
SHLW	Simulated high level waste
TBP	Tri-*n*-butyl phosphate
TODGA	*N,N,N',N'*-tetraoctyl diglycolamide
TRUEX	Transuranium extraction

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