SYNTHESIS AND EVALUATION OF SPECIFIC EXTRACTANTS FOR SEPARATION PROCESSES IN BACK-END OF FUEL CYCLE

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Recommendations of the Viva Voce Committee

As members of the Viva Voce Committee, we certify that we have read the dissertation prepared by Prithwish Sinharoy entitled "Synthesis and evaluation of specific extractants for separation processes in back-end of fuel cycle" and recommend that it may be accepted as fulfilling the thesis requirement for the award of Degree of Doctor of Philosophy.

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DECLARATION

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

Prithwish Sinharoy

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List of Publications arising from the thesis

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- 2. Prithwish Sinharoy, Dayamoy Banerjee, J. N. Sharma, C. P. Kaushik, J. G. Shah,K. Agarwal, Separation of Sr(II) from Eu(III) across a supported liquid membrane using TEHDGA and 18-crown-6, Journal of Radioanalytical and Nuclear chemistry, 317 (2018), 2,919–923.
- 3. Prithwish Sinharoy, Pasupati Nath Khan, Dayamoy Banerjee, J.N. Sharma, C.P. Kaushik. Extraction of technetium (HTcO₄) with N,N,N',N'-tetra(2-ethylhexyl) diglycolamide from simulated high level waste, Desalination and water treatment, 136 (2018) 268-272.
- 4. **Prithwish Sinharov**, Deepika P. Nair, J.N. Sharma, K. Banerjee, Effect of degradation products of TEHDGA on actinide partitioning Process, Separation and Purification Technology 161 (2016) 32–37.
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Dedicated to -My family

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7 Chapter 7: Conclusion and future work

Chapter 7 Conclusion and future work

7.1 Introduction

This chapter summarizes the results obtained from experimental studies carried out towards separation of metal ions from high level liquid waste using synthesized ligands. Separation of radionuclides from nuclear waste streams serves two purposes, firstly reducing radiological burden on environment and secondly the separated elements can be further used for betterment of mankind. It is noteworthy to mention that the radionuclides should have very high radio-chemical purity for deployment of further application. Among several separation methods, Solvent extraction technique results in higher separation factor between two metal ions and has been widely used worldwide for separation of elements from HLW. Extractants or ligands play the crucial role in any solvent extraction process. The present processes of separation of different elements from HLW and ligands involved in those processes has been discussed in detail in Chapter 1. Efforts were made under scope of the present thesis work to synthesize ligands in our laboratory and use them for development of better separation processes in back end of nuclear fuel cycle.

7.2 Results of present studies

Three ligands namely PDGA, BEHGA and TEHDGA has been synthesized and tested for separation of various radionuclides from simulated waste solutions. PDGA is tested for selective Pu extraction whereas TEHDGA was used for Sr/Am co-extraction followed by their mutual separation. In the subsequent studies, selective extraction of Am over Sr was tried by BEHGA.

Process parameters were optimized for better separation/extraction and finally developed process was tested with actual/simulated HLW solution. In the case of Ru extraction, Ru species were oxidized to RuO₄ and extracted using carbon tetrachloride. As RuO₄ is volatile, so the detailed physio-chemical properties of Ru volatilizations were evaluated. All the experimental results are summarized as follows.

PDGA was found to extract Pu preferentially over other metal ions from nitric acid medium. The purity of the compound was established using GCMS and FTIR. The ligand was found to be insoluble in industrial diluent system i.e. *n*-dodecane + iso-decyl alcohol commonly used in plant scale operation in back end of nuclear fuel cycle in India. Extraction properties of the ligand was first tested in nitro benzene molecular diluent system in which D_{Pu} was found to be 57 for a solvent composition of 0.2 M PDGA in NB at a feed acidity of 4 M nitric acid with Pu tracer concentration. The extracted Pu can be quantitatively stripped using oxalic acid or hydrazine solutions. Due to chemical toxicity and volatile nature of NB, as an alternative diluent system, RTIL's were studied and it was found that PDGA retains its selectivity for Pu in this diluent system also. The extraction kinetics was slow in RTIL which is attributed to higher viscosity and density of the same. Extraction mechanism is found to be different in the two diluent system. Solvation mechanism is the sole mechanism for Pu extraction in all nitric acid concentration for NB diluent system whereas it is a mixture of solvation and ionexchange for RTIL system. Pu forms a 1:1 complex with PDGA in NB diluent system and rest of the coordination are satisfied with nitrate ions. The organic phase can be regenerated after quantitative stripping and can be further used for extraction. The solvent retains its extraction-stripping efficiency at least for six cycle of operations.

Selective separation of Pu will result in lesser complication of process steps in the waste management practices adopted in India presently.

Glycolamides are well established ligands for Am extraction from HLW solution. But depending on the composition of organic phase (ligand/diluent/phase modifier concentration) it also co-extracts Sr along with Am. Such a solvent composition was optimsed to be 0.3 M TEHDGA in 5% IDA-n-Dodecane where DAm was more than 1000 and D_{Sr} was ~22. Further efforts were made to recover Sr from organic phase by using a Sr selective stripping agent. A water soluble Sr selective reagent namely 18-Crown-6 was chosen and is used in the study which selectively strips Sr from the loaded TEHDGA phase leaving Am in the organic phase. Different parameters were optimized and the process was tested with simulated HLW solution. It was observed that 0.05 M 18-Crown-6 dissolved in 4 M nitric acid is sufficient for complete stripping of Sr. Distribution of 18-corwn-6 is also studied between the organic and aqueous phase and negligible extraction of the compound is observed. To minimize the inventory of organic solvents, a new technique namely supported liquid membrane was tested using the same chemical principle. In this experiments feed and strip compartment was isolated by membrane loaded with TEHDGA. In the feed compartment, 18-Crown-6 was added to the feed solution to complex Sr ion and intern restricts its transport through the membrane. Eu ions in the feed are free and hence travels through the membrane to strip compartment leading to a separation between the two elements. High separation factor (>100) is obtained in this case. The Sr can be further recovered by precipitation method from the feed solution as SrCO₃. This method will reduce the requirement of new ligands for selective recovery of Sr from the waste as the process can be successfully used for separating ⁹⁰Sr from waste.

- ⁹⁹Tc is a long lived fission product from ²³⁵U fission and is found in substantial amount in nuclear waste solutions. It generally exists as HTcO₄ in the acidic waste. The long half-life, volatility at high temperature and high aqueous mobility of the ion imposes severe problem in its efficient management. It has been well reported in literature that it can form complexes with neutral ligands like DHOA, TBP and malonamides and can be extracted from nitric acid solution. A neutral ligand TEHDGA is used for trivalent actinide and lanthanide separation in India, was identified as a potential candidate for separation of Tc from nitric acid solution. It was found to have high D value (50) for Tc at low nitric acid (0.5) concentration. The extraction was found to decrease with increase in nitrate ion concentration indicating an exchange mechanism between the nitrate and pertechnetate ion in the organic phase. The extraction mechanism was described as HTcO₄ forms adduct with TEHDGA through H-bonding and gets extracted to the organic phase. Significant co-extraction of Mo was observed along with Tc at low nitric acid concentration. Tc can be quantitatively stripped using DM water from the loaded organic phase in three contacts. The results indicates quantitative separation of Tc can be done from HLW by adjusting the acid concentration to lower values.
- Separation of trivalent actinides/lanthanides from Sr was also attempted by synthesizing another ligand namely BEHGA. The ligand was synthesized and found have high purity as obtained from GCMS. BEHGA is found to extract Am (D_{Am}=10) over Sr (D_{Sr}=0.01) at a feed acidity of 4 M nitric acid. The –OH group at α-position of amide group makes the extraction feasible by forming a pre-organized five member ring with amide moiety

through intra-molecular H-bonding. No third phase formation was observed at high nitric acid concentration or high metal ion concentration. Mechanism of the extraction was also established by log-log plot. The extracted metal ions can be quantitatively stripped in three contacts.

Further the ligand was impregnated on XAD resins and separation studies were carried out. This was done in order to generate less volume of secondary waste. The Solvent impregnated resins were characterized and found to retain its selective extraction. The sorption is found to follow pseudo second order kinetics model and Langmuir isotherm adsorption model. The sorbent was finally tested in column mode and the maximum loading capacity was found to ~3 mg/g for Am. Based on all this results it was inferred that this ligand can be successfully used for effective separation of Sr and Eu from nitric acid solution.

Separation of Ru from nuclear waste stream is very difficult task owing to the complex aqueous chemistry of the metal ion. Its separation from waste solution is essential as Ru-106 can potentially be used in radiation sources for treatment of eye cancer. Till date no extractant is reported in literature which can quantitatively extracts Ru from acidic nuclear waste. Efforts were made to develop a process, involving oxidation of Ru species to RuO4 followed by extraction in chlorinated CCl4 and stripping in acidic hydrazine solution. The process was tested with actual waste solution and shows promising for the production of radiochemically pure ¹⁰⁶Ru from nuclear waste. It is confirmed that the recovered ¹⁰⁶Ru product is radiochemically pure and meets stringent quality requirements for the use in preparation of brachytherapy sources.

As the process involves conversion of Ru compounds to volatileRuO₄which can escape during studies, necessitates detailed study of the volatilization pattern. Detailed volatilization study was carried out using UV-Vis spectroscopy by quantifying RuO₄ at 385 nm. Results of the study established that UV-Vis spectroscopy can be used to monitor the progress of volatilization of RuO₄ form nitric acid medium. The volatilization of RuO₄ has been found to follow first order kinetic model with rate constant 5.6*10⁻⁴at 25 °C. It is evident that volatilization of RuO₄ is insignificant in room temperature. However, the rate of volatilization is increased significantly at higher temperature. This study gave better understanding in development of separation of processes for recovery of ¹⁰⁶Ru from high level waste by oxidation method. By using optimized process parameters loss of RuO₄ can be minimized and spreading of radioactive contamination can be controlled.

Extractant	Metal ion	Aim	Feed composition	Solvent composition	D _M	Stripping
PDGA	Pu(IV)	Selective extraction of Pu	4 M Nitric acid	0.2 M in Nitrobenzene	57.2	0.1 M oxalic acid (99%)
	Pu(IV)	Selective extraction of Pu	1 M Nitric acid	0.02 M in [C ₈ mim][NTF2]	11.4	
TEHDGA	Sr(II)	Separation of Sr from Am/Eu	4 M Nitric acid	0.3 M in 5%IDA + n- dodecane	23.0	0.05 M 18 Crown 6
BEHGA	Am/Eu	Separation of Am/Eu from Sr	4 M Nitric acid	0.3 M in n- dodecane	10.2	0.01 M HNO ₃
TEHDGA	Tc(VII)	Separation of Tc from waste	0.5 M Nitric acid	0.3 M in 5%IDA + n- dodecane	50.6	DM water
CCl ₄	Ru	Separation of Ru from waste	1 M Nitric acid	Chlorinated CCl ₄	3.2	Hydrazine sulphate

Table 7.1 : Summary table depicting extraction of metal ion using ligands

7.3 Future Work

In the present work, various aspects on separation of radionuclides like Pu, Am, Sr, Tc and Ru was discussed in detail. Each separation process has some or other benefits from the processes reported earlier in literature. But still scope of further improvements is still open which are as follows.

- PDGA was found to preferentially extract Pu over other metal ions but the specific reason for its preferential extraction is still a matter of research. Towards this computer simulation studies or some new spectroscopic technique can explain the extraction mechanism or selectivity. Apart from this as discussed earlier, the ligand is insoluble in IDA/n-dodecane diluent system which is commonly used in plant scale operation. Designing a new ligand with selectivity for Pu/U from acidic waste solution and also soluble in IDA/n-dodecane diluent system can be attempted.
- TEHDGA was found to co-extract Am/Ln's and Sr depending on the concentration of phase modifier i.e. iso-decyl alcohol. Such behaviour is unique and to gain further insight regarding effect of IDA on metal-ligand bonding requires further investigation. It was evident from the studies that Sr forms stronger complex with crown ether compared to TEHDGA. Experiments are planned for measurement of the binding constant between the metal ion and ligand and this will give better understanding of the chemistry.
- Development of new ligand for selective extraction of Ru and Tc is an open area of research. Separated Tc in pure form can be transmuted in ADS which will tremendously reduce the radiological burden. Whereas, separated Ru-106 in radiochemically pure form can be successfully used for treatment of eye cancer. Apart from this two, 125-Sb is found

in significant quantity in waste solution. Development of new solvents for separation of Sb-125 will ease the waste management practices.

Synopsis

Nuclear energy, one among the major non-renewable sources, has potential to meet the challenges of increasing energy demand in the world [1]. The success story of nuclear energy production partly due to efficient implementation of waste management programme in a comprehensive manner. In closed fuel cycle, lots of liquid waste are generated during fuel fabrication, reactor operation and spent fuel reprocessing. Among all the waste, most of the radioactivity (~99%) is contained in the high level liquid waste (HLLW) generated from spent fuel reprocessing of the spent fuel. The HLLW contains a large numbers of long-lived fission products and actinides, some of them are the major contributors for long term radio-toxicity [2]. The principle objective of nuclear waste management is to keep these hazardous radioelements in isolation from biosphere until their radio-toxicity level reduced to natural background level. It is needless to mention here that dedicated efforts have been made since the inception of the nuclear energy programme and are still being continued towards development of efficient processes for the management of waste. The outcome of the research brought out two major directives for the management of waste, such as (i) Immobilization of HLLW in suitable matrix followed by their burial in deep geological repositories and (ii) Partitioning of actinides and fission products followed by their immobilization or transmutation [3,4]. The conspicuous advantages of the partitioning process include significant reduction of the final waste volumes, reduction of radiotoxicity level (that can be obtained after successful implementation of transmutation or burning) and open up the possibility of using some radionuclides for beneficial use of mankind.

Partitioning of radionuclides implies selective separation of the radioelement from high level liquid waste followed by its recovery in a small volume. The recovered radioelement should be in radiochemically pure form, which is a prerequisite criterion for its use either in medical or industrial applications or preparation of target material for transmutation.

Towards selective separation and recovery of radio element from high level liquid waste which has an exotic radiolytic and hydrolytic environment, solvent extraction based processes have been emerged as most promising among all the other separation techniques. This is due to development of novel solvents which form very selective complexes with the targeted metal ions even in presence of higher concentration of other metal ions and well mature technology for plant scale adaptation of the solvent extraction process.

In Indian, a three stage solvent extraction based process has been deployed for effective partitioning of HLLW and recovery of valuable materials. In the first cycle, residual amount of U and Pu are separated using a conventional ligand tri-butyl phosphate (TBP). In the next step, 1,3 di-octyloxy Calix-[4]-arene crown 6 (CC6) is employed to separate Cesium ions from the waste. Separation of ¹³⁷Cs, which was the major gamma dose contributor, paves easier access for handling and processing of the remaining waste streams [5]. In third cycle, co-extraction of minor actinides and lanthanides from Cs lean HLLW is being carried out by using 2-ethylhexyldiglycolamide (TEHDGA)-isodecyl alcohol (IDA)-dodecane solvent system [6]. Further separation between minor actinides and lanthanides from TEHDGA strip product (dilute HNO₃) is being carried out by TALSPEAK process where D2HEPA is used for selective extraction of lanthanides leaving behind actinides in aqueous phase containing DTPA lactic acid buffer system. In this process, the recovered radionuclides like ¹³⁷Cs and ⁹⁰Sr (⁹⁰Y) are being used for various medical applications.

Results of the above processes show that further improvement of process performance, particularly with regard to product quality, is necessary for effective implementation of the partitioning process. This can be achieved by development of new solvents and new processes. Efforts have therefore been made as a part of the present dissertation towards synthesis of new ligands and development of new processes for separation of metal ions like Pu, ⁹⁰Sr ¹⁰⁶Ru, etc from acidic high level waste stream with a focus attention for their use in various societal

applications. Detailed deliberations including introduction, literature review and results of the study are documented in 7 chapters of the dissertation. A brief summary of the dissertation (chapter wise) is given below.

In Chapter 1, an overview of present waste management scenario highlighting the basic aspects like generation of waste, waste classification, waste management practices in India is presented. As indicated earlier, India is taking lead towards adoption of partitioning processes for the management of high level liquid waste. Detailed literature review on separation of metal ions from high active waste stream has been carried out to account the work carried out earlier in different laboratories. A summary report on literature review is prepared which includes a chronological evolution of extractants for separation of particular metal ion like Pu, Tc, Ru and Sr and the recent advancements on solvent development. Basic theory of solvent extraction, role of diluents and phase modifier was also discussed in brief and different parameters like distribution ratio, extraction efficiency, stripping efficiency and separation factor have been discussed.

In addition to solvent extraction based processes, feasibility of using processes like extraction chromatography (impregnating extractants in solid support) and supported liquid membrane (impregnating extractants in membranes) for separation of metal ions has been discussed.

Finally, scope of the present thesis work highlighting detailed lay-out of work plan including synthesis of new extractants and development of new processes for separation of radioelements from HLLW in radiochemically pure form is presented. Major scope of the work including the problem definition is discussed below.

Bulk scale separation of metal ions in back end of nuclear fuel cycle starts in PUREX process where TBP is used to co-extract U & Pu and thereafter the metal ions are separated during stripping. This same solvent system is also used for the separation of Pu from HLLW[7]. In recent literature, the use of ligands like BenzoDODA, Pyridine based diamides and Oxabridged tricycle di-carboxamide is reported for selective extraction Pu from nitric acid medium. Development of a ligand effective removal of Pu from HLLW is desirable for better management of nuclear waste. Efforts have therefore been made during the thesis work to design a ligand which can selectively extract Pu over other metal ions from nitric acid medium. With regards to the separation of minor actinides and lanthanides from nitric acid medium, extractants like Phosphine oxides, Carbamoyl methyl phosphine oxides (CMPO), malonamides and glycolamides have been known. In India, N,N,N',N'-tetra(2-ethylhexyl) diglycolamide (TEHDGA), is being used for co-extraction of lanthanides and actinides from HLLW [8]. It is noted that a significant amount of Sr(II) gets extracted by TEHDGA phase. Development of a process for separation of Sr(II), either from TEHDGA strip product or selective stripping of Sr(II) from TEHDGA phase will be useful for the production of radiochemically pure Sr(II) which eventually be used for generation of ⁹⁰Y for therapeutic applications [9]. An elaborative work on the development of processes for separation of Sr(II) in radiochemically pure form has been carried out as a part of present dissertation study.

The radioisotope, ¹⁰⁶Ru, which is present in substantial quantities in HLLW, has potential application as ophthalmic applicators for treatment of eye cancer [10]. Major emphasis placed during the thesis work includes development of processes for the separation of ¹⁰⁶Ru in radiochemically pure form.

Chapter 2 deals with experimental procedure for synthesis of extractants, their characterization and separation studies for metal ion. Synthesis of extractants is carried out mainly by reactions such as Condensation Reactions, Elimination Reactions and Acid-Base Neutralization Reactions. Detailed procedure (reaction conditions) for synthesis of each ligand and their purification are described. The purity of the product was evaluated using different techniques like GC-MS and FTIR. Brief description regarding various instrumental methods used during the thesis worknsuch as Gas chromatography hyphenated mass spectrometry (GC-

MS) and Fourier transform Infra-red spectroscopy (FTIR) is given in this Chapter. Once the purity is established, the extractants are employed for metal ion separation. Detailed procedure followed during solvent extraction experiments including preparation of feed solution, organic solutions, mixing and settling of phases, etc, have been discussed. Apart from solvent extraction, two other techniques namely extraction chromatography (impregnating extractants in solid support) or supported liquid membrane (impregnating extractants in membranes) has also been tested for separation experiments and the experimental procedure has been elaborately described in this chapter. The concentration of the metal ion was estimated by radiometric techniques. Brief discussion regarding the various radiometric counting systems employed in analysis is given in this chapter. The results of the studies are elaborately described in chapter 3 to 7 in thesis and have been summarized here.

Chapter 3 describes the results for separation of Pu from nitric acid solution using Pyridine N, N, N', N' tetra-isobutyl pyridine diglycolamide (PDGA). Structure of the ligand is shown in Figure 1. Synthesis, characterization and solvent extraction data for Pu separation from nitric acid medium of the ligand is discussed. In brief, the ligand is synthesized by nucleophilic substitution reactions. The purity of the product, evaluated by GC-MS and FTIR spectroscopy studies, was found to be >98%. The ligand was tested for Pu extraction in two different diluents namely (i) nitrobenzene (NB), a molecular diluent and (ii) 3-methyl-1-octyl immidazolium bis-[(trifluoromethyl)sulfonyl] imide, an Ionic Liquid (IL). The mechanism of Pu extraction as well as dependency of $D_{Pu(IV)}$ values with nitric acid concentration was found to be different for the two diluents. It is confirmed that solvation mechanism for NB whereas a combination of solvation and ion-exchange mechanism was followed for IL. The ligand in NB diluent has higher selectivity for tetravalent plutonium over minor actinides, alkali and alkaline earth metal ions, which are present in HLLW. Complete stripping Pu from loaded PDGA in NB as well as

 C_8 mimNTf₂ diluent system is established using 0.1M Oxalic acid and a reductive stripping mixture of 0.2M N₂H₄ in 0.3M HNO₃.



Figure 1: Chemical structure of Pyridine N, N, N', N' tetra-isobutyl pyridine diglycolamide (PDGA)

In **Chapter 4**, results of process development studies for the separation of Sr(II) is discussed. As an usual practice, the solvent extraction using TEHDGA (structure shown in Figure 2) in iso-decanol and dodecane is used for co-extraction Sr(II), Am(III) and the trivalent lanthanides from acidic HLLW and stripping is then carried out using dilute HNO₃. In this study, a process has been developed for selective sequential stripping of these elements from the loaded organic phase. The selective stripping of Sr(II) is accomplished by using a water soluble macro-cyclic poly-dentate ether, 18-crown-6. The selective binding affinity of the 18-crown-6 molecule for Sr(II) has been used in the present work to devise a procedure for the efficient recovery of Sr(II) from the bulk of trivalent lanthanides and Am(III) in the TEHDGA actinide partitioning process. In the first stage of stripping, the ligand 18-crown-6 is used in the aqueous phase to selectively strip Sr(II), leaving the other elements in the loaded organic phase. Subsequently, the loaded organic phase is stripped with nitric acidat pH 2 to recover the trivalent lanthanides and Am(III). Using this process, it is proposed that Sr(II) can be quantitatively recovered with a very high decontamination factor from High level Liquid Waste.

As an alternative, feasibility of using a supported liquid membrane (SLM) has been examined using N,N,N['],N[']-tetra(2-ethylhexyl) diglycolamide (TEHDGA) as a carrier for transport of Am(III) from HNO₃ medium and 18-crown-6 to selectively complex Sr(II) in feed solution to restrict Sr(II) transport. It is confirmed that under optimized conditions, about 99.6 % of Am(III) can selectively be transported over Sr(II) using 0.1 M 18-crown-6 in 4 M nitric acid containing Sr(II) and Am(III) as feed solution and 0.01 M nitric acid as stripant. Further, Sr(II) as SrSO₄ precipitate was separated leaving 18-crown-6 in the nitric acid solution using potassium sulphate.

Extraction of technetium (VII) from simulated high level waste using TEHDGA-isodecyl alcohol/n-dodecane has also been tested and reported in this chapter. The role of different process parameters affecting the extraction of technetium (VII) has been evaluated and used to arrive at optimum conditions for extraction of the metal ion. It is established that D_{Tc} of about 50 can be obtained from 0.5 M nitric acid using of 0.3 M TEHDGA in 5% isodecyl alcohol/n-dodecane system. Extraction from nitric acid medium and quantitative stripping of technetium using deionized water opens possibility of successful deployment of the process for technetium separation from actual high level waste.



Figure 2 : Chemical structure of TEHDGA (R=2-Ethyl Hexyl)

Further efforts were also made to separate trivalent actinides & lanthanides from Sr(II). Towards this an extractant, N, N-bis(2-ethyl hexyl)glycolamide (BEHGA), was synthesized and tested. The results of separation studies and characterization of the extractants are described in **Chapter 5**. BEHGA a neutral extractant, similar to TEHDGA, showed extraction for Am, lanthanides, Zr and Mo at higher acidities and negligible extraction for Sr. BEHGA exhibited bi-denticity through a pre-organized five member ring formed due to intramolecular hydrogen bonding between its α -OH and C=O groups. Extraction mechanism and

stoichiometry of the metal ligand complex was established from log-log plots. Same extractant was also tested in extraction chromatography mode after impregnating the ligand in XAD-7. The sorption of Am(III) in the SIR was observed to follow pseudo second order kinetics. The sorption capacity of Am(III) was found to increase with increasing HNO₃ concentration which is same trend observed in solvent extraction studies. Sorption of Am(III) was found to follow chemisorptions monolayer formation analyzed by isotherm models. The maximum sorption capacity of the SIR was found have the values of 3.27 mg/g in batch mode. Am(III) desorption and resin recycling can be performed using 0.2M Oxalic acid +0.2 M HNO₃ with sorption and desorption performance remaining undisturbed for at least six cycles of operation. The solvent impregnated resin (SIR) was found to have high separation factors for trivalent actinides over the fission products (Cs, Ru, Sr).



Figure 3: Chemical structure of N, N-bis(2*-ethyl hexyl*)*glycolamide (BEHGA) where (R=2-Ethyl Hexyl)*

Chapter 6 describes results obtained pertaining to separation of ¹⁰⁶Ru from High Level Waste (HLW). The separation and purification of the radio-isotopes is aimed towards fabrication of ¹⁰⁶Ru plaque ophthalmic applicators used for treatment of different kinds of cancer of the eye. Ruthenium present in aqueous waste stream was oxidised to volatile RuO₄ using potassium metaperiodate and selectively extracted to chlorinated carbon tetrachloride. Quantitative stripping of Ru(III) from organic phase was obtained using aqueous solution of hydrazine sulphate. The strip solution was free from other fission product or actinides contamination and was further used for fabrication of ¹⁰⁶Ru plaque. During process development study, major

focus was given on volatilization behavior of RuO₄ and towards this volatilization behavior of RuO₄ from nitric acid medium was studied using UV-Vis spectroscopy. Ru(III) solution was oxidized to Ru (VIII) using potassium metaperiodate and the absorption peak of RuO₄ at 385 nm was used to measure Ru(VIII) concentration in solution. The volatilization kinetics have been studied at different temperature and used to derive rate constant and activation energy values. Almost 82 % Ru(VIII) has been volatilized from nitric acid medium at 70 ^oC whereas it is only 15% at 25 ^oC. Effect of different parameters like temperature, potassium metaperiodate concentration and nitric acid concentration on volatilization has been studied in depth and reported in this chapter.

Chapter 7 gives the summary of the results from the above mentioned detailed investigations carried out on separation of radio-isotopes using different extractants. Future scope of the work with respect to further insight required for efficient separation and utilization of radio-isotopes are discussed in detail in this chapter.

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1 Chapter 1: Introduction

Chapter-1 Introduction

Nuclear energy is one of the viable options to meet the energy requirement in twenty first century. It is much cleaner form of energy when compared to energy derived from fossil fuel in terms of greenhouse gas emission. In a developing country like India, the demand per capita energy consumption is increasing and thus nuclear power plants are indispensable to meet the energy demand. As of March 2018, India has 22 nuclear reactors in operation, having a total installed capacity of 6,780 MW [1]. Though the present installed capacity is very small (~3% of total energy produced in India), Department of Atomic Energy (DAE) India has laid down an ambitious nuclear energy programme to produce ~10 % of total energy demand in the country by 2030. Successful realization of the nuclear energy programme is dependent on the safe and efficient management of the radioactive waste generated at the back end of nuclear fuel cycle [2]. In the following section, a brief overview on waste generations in nuclear fuel cycle and present waste management practices in presented. This was helped to identify the potential areas where innovations and improvements can be made. Motivations drawn from here are used to present problem definition and formulate the scope of the work.

1.1 Waste generation in nuclear fuel cycle

The story of power generation in nuclear reactor starts in uranium mines and ends in disposal of radioactive waste in deep geological repositories. In totality it is called nuclear fuel cycle as shown in **Figure 1.1**.



Figure 1-1: Schematic presentation of Indian option for closed fuel cycle.

The steps of nuclear fuel cycle are as follows: mining of Uranium, fabrication of fuel, reactor operation to generate electricity and separation of valuable elements from spent nuclear fuel for further use. Waste is generated in each step of fuel cycle and which can be solid, liquid or gaseous. The waste is unique in nature in each step with different chemical & radiochemical composition. Waste generated in front end of fuel cycle i.e. in mining of uranium and fuel fabrication; is much cleaner and contains mainly 'U' and its daughter products as radioactive elements[3, 4].The volume of this kind of liquid waste is huge and need high volume reduction factor during treatment. In the next step, uranium is burnt in nuclear reactor to generate power. Nucleus of Uranium and Plutonium atom splits when bombarded with neutron in a nuclear reactor and generates enormous energy (~200 MeV per fissionating atom) in a process called nuclear fission. Spitting the atom generates fission fragments along with energy. The distribution

of fission products are generally represented by fission 'M' curve. The thermal fission yield curve for different actinides is presented in **Figure 1.2** [5].



Figure 1-2:Fission yield curve for different actinides in thermal neutron spectrum(ref: Nuclear Safety in Light Water Reactors, Severe Accident Phenomenology,2012, Pages 425-517)

As we can see a large number of new elements are generated during fission and most of them are radioactive. During reactor operation all this radioactive element is contained in fuel rods. Apart from the fission products, several activation products like ⁵⁶Fe, ²⁴Na and ³H are also generated from structural materials or moderator due to high neutron flux in the reactor [6]. The coolant or moderator containing all the radioelements generated is a form of liquid waste and needs treatment. The spent fuel is taken out of reactor and cooled in a water pond. Actinides and fission products present in spent nuclear fuel is shown in **Table 1.1 and Table 1.2**.

Isotope	Half-life (years)
Uranium-235	7.1 x 10 ⁸
Uranium-238	4.5 x 10 ⁹
Plutonium-239	24,000
Plutonium-240	6,600
Plutonium-242	360,000
Neptunium-237	2,100,000
Americium-241	432
Americium-243	8,000
Curium-244	18

 Table 1-1: Actinides present in spent nuclear fuel

Table 1-2: Most significant (in terms of nuclear waste management) fission products present in
spent nuclear fuel

Fission products	Half-life (years)
Krypton-85	11
Strontium-90	29
Cesium-137	30
Cesium-135	2,300,000
Iodine-129	16,000,000
Tin-126	100,000
Technetium-99	210,000
Ruthenium-106	~1
Antimony-125	~1

Subsequently in the reprocessing step, actinides and fission products lying inside the fuel rod, are taken out by dissolving the spent fuel in nitric acid. Uranium and plutonium is recovered from the bulk of fission products and actinides using a process called "PUREX". In the first step of PUREX process, Uranium and plutonium is co-extracted using Tri-butyl phosphate (TBP) from dissolver solution. Thereafter, Plutonium is selectively stripped from the TBP phase to aqueous phase using reducing agents like ferrous sulfamate or U(IV) resulting into its separation from Uranium. The acidity of Plutonium product solution is further adjusted to 8 M nitric acid to convert all Pu species to anionic complexes and is further purified using Dowex 1x4 ion exchange resin columns. Uranium is stripped back from TBP phase using dilute nitric acid and converted to Uranium oxide. The recovered Uranium and Plutonium oxides are sent back to fuel fabrication facility for fast reactor [7,8]. During PUREX process, large volume of acidic waste is generated containing fission products and actinides. Waste generated in each step needs treatment to minimize burden on environment. But before treatment, proper classification of waste is required based on the radiochemical nature of waste.

1.2 Classification of nuclear waste

Nuclear waste generated at different steps of fuel cycle can be solid, liquid or gaseous and contains different radionuclides at different activity level depending on their generation route. In order to have a safe and economical storage and ease of treatment/management, they have been classified in different categories. Based on the activity content, radioactive liquid waste streams are commonly classified as exempt waste, Low Level Waste $(37-3.7\times10^{6}Bq/L)$, Intermediate Level Waste $(3.7\times10^{6}-3.7\times10^{11}Bq/L)$ and High Level Waste (above $3.7\times10^{11}Bq/L$). The general categorization of radioactive waste is presented in Table below [9].

Category	Activity level in Liquid (Bq/L)
Exempt waste	< 37
Low level waste	37-3.7×10 ⁶
Intermediate Level waste	3.7×10 ⁶ - 3.7×10 ¹¹
High level waste	>3.7×10 ¹¹

Table 1-3: Categorization of liquid waste based on radioactivity level

Low level waste contributes to <1% of total radioactivity generated in total fuel cycle whereas its volume contribution is very high and it is almost ~90% of total waste generated. In comparison, high level waste contributes ~95 % of radioactivity and ~3% of volume total generated in nuclear fuel cycle. Rest volume and activity is contained in intermediate level waste. Management of all three types of nuclear waste is equally important to reduce burden on environment.

1.3 Management of liquid Waste

Basic principle followed towards the management of radioactive liquid waste envisages separation of the radioactive elements in a small volume and the radioactivity lean large volume part can be discharged to environment. It is therefore desirable that the processes should have high volume reduction factor and high decontamination factor for treatment of nuclear waste streams. Separation of metal ions from nuclear wastes can be done by several methods like solvent extraction, ion exchange, precipitation, reverse osmosis or evaporation. Various techniques are used for treatment of low, intermediate and high level waste is discussed below [10,11].

1.3.1 Low level waste treatment

The major radioelements present in LLW (spent fuel reprocessing origin) are ¹³⁷Cs and ⁹⁰Sr. The pH of LLW is near neutral and contains ~5 g/l of total dissolved solid. Processes employed for treatment of low level waste in India are as follows: chemical treatment, ion-exchange, steam and solar evaporation and membrane based separation. In a chemical treatment process, the radionuclides are co-precipitated using chemicals like barium sulfate for ⁹⁰Sr and potassium copper hexa-cyanoferrate for ¹³⁷Cs. The radioactivity is concentrated in the precipitate whereas supernatant is devoid of radioactivity. The supernatant becomes exempted waste and can be disposed. The precipitate is immobilized in cement and disposed in near surface disposal facilities (NSDF). LLW generated in spent fuel storage pool are treated by conventional synthetic organic ion exchange resins. Materials like crystalline silicon titanate, mono sodium titanate, hydrous zirconium oxide, hydrous manganese oxide, zeolites and several materials are tested for removal of radionuclides from LLW. In recent years, potassium copper hexa-cyano impregnated zeolites and crystalline silicotitanate as composite material have also been found to be very effective decontamination of LLW streams. Apart from this two processes, membrane based processes like reverse osmosis and ultra-filtration has also been tried for treatment of LLW. In general, membrane based process, particularly, reverse osmosis, is very effective for decontamination of low active and lower salt containing waste. This process gives very high decontamination factor as well as high volume reduction factor. A solar evaporation technique has been adopted in nuclear power plants in Rajasthan. Volume reduction factor in this process is also very high [12,13, 14,15].

1.3.2 Intermediate level waste treatment

Intermediate level waste is generated from spent fuel reprocessing plants is made alkaline and stored in carbon steel tank. In alkaline ILW, the major radionuclides presents are ¹³⁷Cs, ⁹⁰Sr, ¹⁰⁶Ru and ¹²⁵Sb. Several ion exchange materials are used for treatment of alkaline ILW. Resorcinol-Formaldehyde poly-condensate resin (RFPR) is used from cesium removal whereas Imino di-acetic acid resin (IDAR) is used for removal of strontium [16,17]. After removal of these two major radionuclides, remaining waste is treated like low level waste as discussed above.

1.3.3 High level waste treatment

High level liquid waste is generated from reprocessing of the spent fuel and it contains host of radionuclides including fission products such as, rare earth elements, ¹³⁷Cs, ¹³⁵Cs, ⁹⁰Sr, ⁹⁹Tc, ¹⁰¹Ru, ⁹¹Zr, ⁹⁵Mo, and the minor actinides, ²⁴¹Am, ²⁴³Am, ²⁴⁵Cm, and ²³⁷Np. Concentration of each of the elements will depends on various factors like nature of the fuel, burn-up in the reactor, cooling period of the fuel and volume of the waste. As a reference, a typical composition of the HLLW of research reactor origin is shown in **Table 1.4**[12]. The inventory of a fission isotope thus can be arrived from the knowledge of fission yield, burn-up, cooling period and the volume of the generated waste. The HLW of power reactor origin will be of similar nature except higher concentration of radionuclides in it. The significant inventories of these long-lived radioisotopes demands efficient strategies for the management of HLW. On the other hand, is can be seen that HLW is a treasure-trove of radioisotopes which can be used in various medical and industrial radiation technology applications. A short list of radioisotopes and their potential area of applications are illustrated in **Table 1.5**. Considering the application potential of each of the useful radioisotope and inventory, it can be stated that HLLW is no longer a waste material.

Rather, it is an important resource material of national importance both in terms of revenue and benefits towards serving the mankind.

Sr No.	Properties	Values	
1	Molarity (M, Acidic)	1.5 -3.5	
2	Density (g/ml)	1.2 -1.3	
3	Total solids (g/l)	100 - 300	
4	Na(g/l)	30 - 40	
5	U(g/l)	20 - 25	
6	Fe(g/l)	6 -7	
7	Cr(g/l)	0.4 - 0.6	
8	Gross β , γ (Ci/l)	10 - 60	
9	Gross α (mCi/l)	4 - 6	

Table 1-4: Typical composition of HLLW of research reactor origin

Both these factors have been considered while formulation of strategies towards management of HLW. Broadly, two practices have been emerged worldwide which are (i) direct vitrification of waste in glass matrix and (ii) partitioning of waste followed by transmutation of long lived actinides. The separation of long lived actinides and fission products also opens up possibility of their application for betterment of mankind.

Radioisotopes	Half life	Radiation type	Energy (MeV)	Major area of Application
¹³⁷ Cs	30 y	Gamma	0.66	Blood irradiation Food Irradiation Sludge hygenation
⁹⁰ Sr/90Y	28 y	Beta	0.5 and 2.7	Power source
90Y	64 d	Beta	2.70	Bone pain pallation Radio-pharmaceutical
¹⁰⁶ Ru	365 d	Beta	3.54	Eye cancer (Brachytherapy)
²³⁸ Pu	24500y	Alpha	5.59	Power source
²⁴¹ Am	368y	Alpha	5.48	Smoke detector Power source

Table 1-5: A short list of valuable radionuclides present in the HLW

1.3.3.1 Vitrification:

As a management practice HLLW is vitrified in glass matrices utilizing either a joule heated ceramic melter or metallic melter. In vitrification process, high level liquid waste is immobilized in borosilicate glass matrices. The vitrified waste product is kept on interim storage to allow the decay of heat-dissipating nuclides such as ¹³⁷Cs and ⁹⁰Sr and later on they will be disposed in deep geological repositories. Glass matrix is chosen because of its high stability over billions of years and its capacity to accommodate high amount of waste. Though, composition of glass matrix depends on the nature of liquid waste, the leach rate of radionuclides lower than 1x10⁻⁶ g/cm²/d can be considered as acceptable glass. Beside all these advantages, vitrification has its own limitations. Vitrification is a high temperature process and hence volatilization of different fission products like Cs, Tc and Ru is a major concern. Not only this, noble metals like Ru, Pt, Rh and Pd has poor solubility in glass matrix and forms a separate phase in glass during vitrification [18,19,20,21,22].

1.3.3.2 Partitioning of high level liquid waste:

The process partitioning of high level waste implies separation of the major radiotoxic/long-lived fission products and actinides, followed by efficient management and safe disposal of each of streams. In this philosophy, alpha emitting radionuclides like Am and Cm will be separated from HLLW and then it can be transmuted in fast reactors or accelerator driven systems. Undoubtedly, effective implementation of the process will reduce the radiotoxicity of the waste and also decrease environmental hazards arising from the long lived actinides. Time required for attaining radio-toxicity to the level of natural uranium ore for normal HLLW and after partitioning of actinides are shown in following **Figure 1.3**.



Figure 1-3: Relative radioactive decay of spent nuclear fuel as a function of time [23]

The advantages of partitioning scheme are clearly reflected in the above figure. It can therefore be stated that selective separation of radionuclides from HLLW is the first step of the partitioning process. Among the separation techniques, Solvent extraction based processes have been widely used across the globe for partitioning of HLW. In this regards, a lot of focus has been given towards development of metal ion selective ligands.

In line with the objective of the thesis work, efforts have been made towards development of ligand/processes for recovery of radionuclides either for societal applications and or improvement in waste management practices. In the subsequent section therefore, basic aspect of solvent extraction and an overview of the existing processes towards separation of metal ions from HLLW is presented [24,25,26].

1.4 Solvent extractions for metal ion separation from nuclear waste

Transport of solute from one phase to another phase employing two immiscible phases is known as solvent extraction. Extractants are deployed for metal ion extraction in solvent extraction processes in different stages of nuclear fuel cycle.

1.4.1 Basic theory

Solvent extraction is a process where two immiscible liquid phases are contacted together and solute from one phase is transferred to another phase depending on the thermodynamic parameter. Solvent extraction is widely used in separation of metal ions from aqueous phase over the decades. This process has several advantages over the others such as ease of operation, convenience and rapidness. This technique of separation can be applied in trace quantity of metal ion to macro amount of metal ion. Reprocessing of spent fuel in nuclear industry and purification of uranium before fuel fabrication are generally done by solvent extraction processes.

In liquid-liquid extraction minimum number of components is 3 and there is 2 phases. Hence the degrees of freedom as calculated from phase rule (F=C-P+2) is 3. The total number of variables involved is 6. Hence at a fixed temp and pressure if we fix one concentration then rest of the three concentrations can be calculated from phase equilibrium. Effectiveness of extraction process is defined by *distribution ratio* as shown in equation 1:

where $[M]_{org}$ and $[M]_{aq}$ represents metal ion concentration in organic and aqueous phase respectively. The distribution ratio is derived from the classical **Nernst distribution law**. At equilibrium the ratio of metal ion concentration (solute) is constant at a particular temperature. One extractant can selectively extract one metal ion over another metal ion and this selectivity is stated in terms of separation factor. Separation factor is expressed in terms of ratio of distribution ratio for two metal ions as follows:

$$S.F. = \frac{D_1}{D_2}\dots\dots\dots\dots(2)$$

where D_1 and D_2 are the distribution ratio for two metal ions respectively. After extraction the metal ion is brought back to aqueous phase by a process called stripping. The efficacy of stripping is generally expressed in terms of stripping percentage as follows:

% stripping =
$$\frac{[M]_{strip solution}}{[M]_{loaded org}} X100$$

Where [M]_{strip solution} and [M]_{loaded org} represents metal ion concentration in strip solution and loaded organic phase respectively.

1.4.2 Extractants for metal ion separation from nuclear waste

Extractants or solvents play crucial role towards metal ion separation in solvent extraction processes. General criteria towards selection of suitable solvents can be summarized as follows:

- o High extraction capacity for desired metal ion
- o High loading capacity of desired metal ion
- Less prone to third phase formation
- Higher radiolytic and chemical stability
- Higher selectivity towards the desired metal ion over other metal ion present in solution
- o High boiling point
- o High flash point
- o Low viscosity to have better mass transfer
- o Low density
- Environment friendly
- o Ease of management of generated secondary waste
- Less harmful degradation products

Extractants are broadly classified based on their mechanism of extraction of metal ion as follows.

- Solvation: Metal ion forms an organic phase soluble complex with ligand and gets extracted to organic phase. Uranium extraction by TBP in Purex process is a classic example of solvation mechanism where U forms a complex with TBP as UO₂(TBP)₂(NO₃)₂ and gets soluble in organic phase.
- 2. **Ion exchange mechanism**: In this mode, metal ions (may be cationic or anionic) gets extracted to organic phase by exchanging with cationic (when metal ion is cation) or

anionic (when metal ion is anion) part of the ligand. Common examples of liquid cation exchangers are DEHPA, DNPPA, OPPA and TTA and liquid anion exchangers are aliquot 336 and alamine etc.

3. **Ion pair extraction**: In this mechanism, meal ions are extracted to organic phase by introducing an oppositely charged ion to the system. Extraction of americium by TBP at high nitrate concentration is an example of ion-pair extraction.

1.4.3 Composition of organic phase

In any solvent extraction experiments the organic phase is composed of two components namely, extractant and diluent. In certain cases during metal ion extraction at a definite acid or metal ion concentration third phase formation occurs. In third phase formation, organic phase splits in two phases one rich in diluent and another rich with metal ion-extractant complex. Generally third phase formation occurs for CHON based ligands at higher nitric acid concentration or else it can happen beyond a certain metal ion concentration in aqueous phase. The metal ion concentration beyond which third phase formation takes place is termed as "Limiting organic concentration (LOC)". To mitigate third phase formation phase in solvent extraction.

• Diluents:

Diluents have no role in extracting the metal ion from aqueous phase but they are indispensable in any solvent extraction. Generally extractants have high viscosity resulting in poor mass transfer during metal ion extraction. Hence extractants are diluted in diluents which decrease the viscosity resulting in increase in mass transfer. In modern practices in all stages of nuclear fuel cycle where solvent extraction is used as a tool for metal ion extraction, the common diluent used is n-dodecane or kerosene in plant scale. Apart from n-dodecane, nitro-benzene, FS-13, 1octanol, Nitro phenyl alkyl ether and aliphatic hydrocarbons can also be used as diluent. Diluents should have the following properties:

- Should be radiolytically and chemically stable
- o High boiling point
- o High flash point
- o Low viscosity to have high mass transfer
- o Low density
- Environment friendly
- o Ease of management of generated secondary waste

Another class of compounds i.e. room temperature ionic liquids (RTIL's) has also been tested in details in earlier studies and found to be superior compared to molecular diluents because of certain properties like negligible vapor pressures, non-flammability & wide electrochemical window and liquidous range. In certain cases metal ion extraction enhance dramatically when RTIL's are used as diluents in place of molecular diluents.

• Phase modifier:

Phase modifier acts a bridge between extractant and diluent. Phase modifier mitigates third phase formation. Phase modifiers have all chemical properties similar like diluent with increased dielectric constant. In Indian scenario, iso-decyl alcohol has often been used as a phase modifier.

1.4.4 Equipment for solvent extraction

In a chemical lab solvent extraction experiments are carried out at separating funnels. In industrial scale three type of equipment are used for solvent extraction.

- Pulse Column: organic and aqueous medium flows from opposite direction i.e., in counter current mode inside a column and mass transfer take place in each theoretical plate inside the column.
- Mixture Settler: Each unit in a mixture settler contains a mixing unit where to phases are mixed and a settling unit where two phases are separated under gravity. The organic flows in counter current mode.
- Centrifugal extractor: Mixing and separation of phases occur in a single unit. Both phases are mixed using a rotor and then get separated under centrifugal forces.

1.5 Other techniques for metal ion separation employing solvents

In solvent extraction experiments volume of the organic phase is too large. Their future management becomes very difficult after carrying out operation with radioactive nuclear waste. Besides, extractants sometime may be very costly. With this concern of protecting environment, various techniques have been evolved. Fundamental of this techniques is still the extractants whereas their quantity is much lesser and mostly operated in a single phase. Apart from this, all this techniques do not suffer from third phase formation issue.

1.5.1.1 Solvent Impregnated resins:

• Extractants are immobilized in inert matrices like XAD and operated in column mode. Generally breakthrough capacity of solvent impregnate resins is quite low when compared to conventional ion exchange materials. But this technique is very much useful for low volume of waste needs to be treated. The requirement of extractants is significantly low compared to solvent extraction experiments [27, 28, 29, 30, 31].

1.5.1.2. Supported liquid membranes:

 In this technique two solutions namely feed and stripant are separated by a membrane. The membrane is loaded with extractants. Metal ion gets extracted from feed to membrane and stripped to strip solution. Here also requirement of extractants is pretty low. This technique is very much useful when during separation of metal ions [32,33, 34, 35].

1.6 Separation of radionuclides from high level liquid waste: The present scenario

1.6.1 Separation of residual U and Pu from HLLW

Pu and U are found in trace quantity in the HLLW generated from spent fuel reprocessing. Long half-life and radiochemical toxicity has made plutonium extraction an interesting topic for research over the years whereas recovery and re-utilization of residual uranium is of high importance both in terms of cost effectiveness and radiological burden to environment. Plutonium (Pu) exhibits very complex redox behavior in aqueous nitric acid solution due to its ability of formation oxidation states typically from +3 to +6. The state can interchange depending upon acid concentration and presence of coordinating ligands [36].

As discussed earlier PUREX process uses extractant namely Tri-butyl Phosphate (TBP) for extraction of tetra- and hexa- valent cations like U and Pu from nitric acid medium [37, 38]. This ligand contains "Phosphorus" and because of this it forms sticky mass during incineration making secondary waste management very difficult. Quest for development of an environment friendly CHON based ligand resulted in development of a straight chain amide N,N-dihexyloctanamide (DHOA). This amide extracts U(VI), and Pu(IV) by forming complexes such as $UO_2(NO_3)_22DHOA$ and Pu(NO₃)₄.2DHOA, respectively at nitric acid concentration of 3.5M HNO₃. But at higher acidities (> 8M) ion pair formation happens as $[Pu(NO_3)_6^{2-}]$ [HDHOA⁺]₂ and Pu gets extracted to organic phase. The equilibrium constant values (log K_{ex}) for the formation of Pu(NO₃)₄ 2DHOA solvates were evaluated 3.55 ± 0.02 [39]. It was observed that DHOA preferentially extracts of Pu(IV) over U(VI) at higher acidities (≥3 M HNO3). Further insight on this extraction phenomenon was gained by quantum chemical calculations and small angle neutron scattering (SANS) measurements [40,41, 42,43].



Figure 1-4: Structure of TBP and DHOA used for Pu(IV) extraction

In recent years several amides has been designed, synthesized and tested for selective extraction of Pu at higher nitric acid concentration. Amide based ligands like O-phenoxydiamides, Oxabridged tricycle di-carboxamide (OTDA), Pyridine based diamides, Phenanthroline diamides and Picolinamides to name a few, were synthesized and tested for Pu selectivity.

The extraction performance of a series of novel O-phenoxydiamides showed selective Pu extraction over other metal ions like Zr, Am, U and Sr. Several ligands with different substituent group were tested and it was found that CycleDODA has maximum extraction efficiency for Pu and lowest being BenzoDODA. With same ligand D value for metal ion decrease in the order of $Pu(IV) \gg U(VI) > Zr(IV)$, Eu(III), Am(III) [44]. At 5 M HNO₃ concentration, the distribution

ratio for Pu is much higher compared to other metal ions for BenzoDODA/n-dodecane solvent system [45].

Conformationally constrained Oxa-bridged tricyclo-dicarboxamide (OTDA) ligands were tested for the selective extraction of Pu pertinent to the Plutonium Uranium Redox Extraction (PUREX) process. The nature of the extracted species was established to be [Pu(NO₃)4(OTDA)]. One of the OTDA ligands showed selective extraction of Pu(IV) and Np(IV) over other actinide species, *viz.*, U(VI), Np(V), Am(III), lanthanides and fission products contained in a nuclear waste from the PUREX process [46, 47].

Pyridine based diamides showed promising results for Pu^{4+} extraction in ionic liquid ([C8mim][NTf2]) diluent system. The D_{Pu} values are in the order of ~10 for Pu(IV). The extraction mechanism was solvation with formation of 1:1 complex with Pu. Extraction of other metal ions like Am^{3+} , Eu^{3+} , Sr^{2+} , UO_2^{2+} and Cs^+ was much lower than that of Pu^{4+} . Ionic liquid based solvent systems are reported to result in higher extraction efficiency compared to molecular diluent system but in case of this ligands D values are comparable both in molecular diluents and ionic liquids[48]. Apart from this several ligands containing amides donor group attached to N-containing aromatic groups are tested for selective extraction of actinides and reported in literature. The selectivity may arises from following reasons such as i) pre-organized geometry of the donor atoms to fulfill Pu coordination, ii) higher interaction between highly charged Pu ions (+4) and hard donor atoms of the ligand and iii) high degree of correspondence between the metal ion and ligands [49, 50, 51, 52]. Picolinamides are well known ligands usually used for minor actinides/lanthanides separation in pH medium though has also been found to extract Pu(IV) at high nitric acid concentration in highly polar diluents [53, 54, 55, 56].



BenzoDoda



Oxa-bridged tricycle di-carboxamide



Pyridine based diamide

Figure 1-5: Amide based ligands recently developed for Pu(IV) extraction



Figure 1-6: Picolinamide ligands developed for Pu(IV) extraction

Glycolamides are well studied ligand for extraction of trivalent minor actinides but has also been tested for Pu extraction. Glycolamides namely, TODGA (*N*,*N*,*N'*,*N'*-tetra-*n*-octyldiglycolamide), T-DGA (tripodal diglycolamide), and TREN-DGA (*N*-pivot tripodal diglycolamide) was constituted in diluent system such as 9:1 mixture of *n*-dodecane and iso-decanol and an ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C₄mim][Tf₂N]) were screened for Pu extraction studies Among them T-DGA has high extraction performance for Pu($D=3x \ 10^3$) as compared to D_{Pu} values of 4 and 17 obtained with TREN-DGA and TODGA [57, 58, 59, 60, 61].

1.6.2 Separation of Minor actinides from HLLW

Tri butyl phosphate (TBP), the work horse of nuclear fuel reprocessing, does not extract trivalent actinides from nitric acid medium. Hence search of new ligands started which can extract trivalent actinides from high level waste. Most of the investigations on nuclear waste management have focused on the separation of the long-lived radiotoxic minor actinides from this high level waste (HLW). It is noteworthy to mention that trivalent actinides have similar chemical properties to that of trivalent lanthanides because of same ionic radius and valence of

the two metal ions. Also the concentration of the lanthanides is much higher compared to Am in waste solutions. Selective separation of trivalent minor actinides over lanthanides directly from the waste solution is difficult. Hence both minor actinides and lanthanides are co-extracted from waste solution followed by their mutual separation in the consequent step before transmutation of Am in fast breeder reactors or ADS.

In this context, several extractants and processes have been developed for lanthanide-actinide coextraction from the HLLW in the past few decades, such as TRUEX, TRPO, DIDPA, and DIAMEX. The ligand used in each of the process is shown in Figure 1-7. A brief discussion on each of the processes along with the

TRUEX process

Trans uranyl extraction process (TRUEX) process has been developed in 1980 at Oakridge laboratory, USA for the separation of trivalent actinides and lanthanides from acidic feed. Octyl(phenyl)-N,N-di-isobutyl Carbamoyl Methyl Phosphine Oxide (CMPO)[62] is used as extractant in the TRUEX (Trans Uranium EXtraction) process. As the solvent forms third phase at higher nitric acid concentration, hence TBP is used in solvent phase to mitigate the third phase formation. For a solvent composition of O.2 M CMPO + 1.2 M TBP / n-dodecane, D_{Am} at 4 M HNO3 is found to be 22, whereas D_{Am} at 0.01M HNO3 is only0.01.[63] Later on the process was tested in several countries like Japan, India and Russian Federation. The process has been demonstrated with actual HLW and high decontamination factor is obtained for minor actinides. But use of the phosphorus based ligand and phase modifier makes the management of secondary waste difficult. Cleaning up of solvent after each use is another major drawback of this solvent system [64, 65, 66, 67].

TRPO process

Process based on TRi-alkyl PhOsphine (TRPO) [68] was developed in China for co-extraction of minor actinides and tested with actual high active waste. The 'R' alkyl group in the ligand can vary from hexyl to octyl hence it is a mixture of ligands which is used for the extraction. This ligand has high extraction performance in low nitric acid solution. The D_{Am} was found to be 3 at 0.5 M nitric acid for a solvent composition of 0.5 M TRPO in n-dodecane. Am is stripped from the loaded organic phase using high nitric acid concentration [69]. This ligand is also 'P' based hence management of the secondary waste is huge challenge. Apart from secondary waste management arising from organic solutions, further separation of the Am from lanthanides needs neutralization of nitric acid in strip solution resulting in high salt concentration in the product solution[70, 71, 72, 73, 74, 75].

DIDPA process

Process based on di-isodecylphosphoric acid (DIDPA)[76]was developed in Japan and tested for co-extraction of the minor actinides and lanthanides. Using DTPA as stripping agent, separation of the actinides(III)/Ln(III) elements is done by successive stripping from the loaded solvent. However, metal loading in the solvent and degradation of the solvent are the major disadvantages of the process [77].

DIAMEX process

Further efforts were made to develop new aqueous partitioning method based on organic compounds that contain only atoms of carbon, hydrogen, oxygen and nitrogen as extractants make the processes more environment friendly. Secondary waste generation is much less compared to TRUEX or TRPO as the solvent can completely be burned. DIAMEX (DIAMideEXtraction) process based on N,N'-dimethyl-N,N'-dibutyltetradecylmalonamide

(DMDBTDMA),N,N'-dimethyl-N,N'-dioctyl-2-hexylethoxy-malonamide (DMDOHEMA) solvents was developed by CEA France and tested for extraction. Solvent composition of 1 M DMDOHEMA/n-dodecane was found to have $D_{Am}15.5$ at 3 M HNO₃. Though it has high extraction performance for minor actinides but it suffers from co-extraction of other fission products like Pd and Ru [78, 79, 80, 81, 82, 83, 84].



Figure 1-7: Ligands used for trivalent minor actinides and lanthanide extraction from HLLW

Glycolamide based process

Recently, diglycolamide based extractants (Figure 1-9) such as N,N,N',N'tetraoctyldiglycolamide (TODGA) and N,N,N',N'-tetra-2-ethylhexyl diglycolamide (TEHDGA) have attracted considerable interest in the field of actinide partitioning due to their superior extraction properties than the earlier proposed extractants. For a solvent composition of 0.2 M TEHDGA + 30% Isodecyl alcohol / *n*-dodecane as Solvent, D_{Am} at 4 M HNO₃ is found to be 120 whereas at 0.01M HNO₃ it is only 0.01. And for solvent composition of 0.1 M TODGA + 0.5 M DHOA in *n*-dodecane, D_{Am} (4 M HNO₃)=289, (0.01M HNO₃) = 0.01 was observed. TODGA and TEHDGA is the most promising ligand with respect to high extraction performance. Glycolamides are CHON based ligand and generated secondary organic waste can be incinerated. Hence the volume of organic waste generation is very less. But major disadvantage of this process is co-extraction of Sr and Zr along with minor lanthanides which further complicates further management processes [85,86,87,88,89,90,91,92,93,94].



Figure 1-8:Glycolamides used for trivalent minor actinides and lanthanide extraction from HLLW

In India, a process flow sheet shown in Figure 1.9 is being followed for the recovery of the valuable radionuclides from HLLW. In first cycle, residual Uranium and Plutonium is recovered

using 30% TriButyl Phosphate (TBP) in n-dodecane solution. Uranium lean HLLW (raffinate of first cycle) is subjected to recovery of Cesium in second cycle. Details of Cesium extraction is discussed below. After separation of ¹³⁷Cs, the extraction of minor actinides and lanthanides has been carried out using TEHDGA-isodecyl solvent system.



Figure 1-9: Process flow diagram for the recovery of valuable radionuclides from high level waste of Indian reprocessing plant origin

1.6.3 Separation of ¹³⁷Cs

¹³⁷Cs is one of the major heat emitting radionuclides found in HLW and has potential application in fabrication of radiation sources to be used as irradiators for food, blood and sludge etc. in industry [95]. Several extractants have been developed and tested for selective extraction of Cs from both acidic waste solutions. Among them chlorinated cobalt di-carbolide (CCD) and calix crowns are widely used for their better selectivity and high extraction efficiency for Cs. CCD was developed at the Nuclear Research Institute in Czechoslovakia and successfully tested for Cs extraction by dissolving the extractant in polar diluent metanitro-benzo tri-fluoride [96]. On the other hand calix crown 6 compounds were first developed by Casnati et.al and established high selectivity of the compound for Cs over other alkali metal ions [97].



Figure 1-10: Structure of 1,3-alt-calix[4] arene with mono crown 6 and bis(crown-6) used for selective Cs extraction

These compounds are found to extract Cs selectively over other alkali metal ions both from acidic and alkaline nuclear waste solution [98]. Calix 4 arene bis(crown-6) dissolved in a mixture of fluorinated alcohol (phase modifier) and Isoper-L kerosene (diluent) was used for Cs extraction from highly alkaline HLW solution in ORNL [99]. Further developments were carried out by synthesizing new calix crown compound like calix[4]-arene-bis(o-benzocrwon-6) and calix[4]arene-bis(2,3 napthocrwon-6) for better Cesium extraction[100].

In Indian, selective separation of cesium from acidic HLW was carried out using 1,3dioctyloxycalix[4]arene-crown-6 (CC6)/*n*-dodecane modified with isodecyl alcohol. The process solvent was optimized as 0.03 M CC6 + 30% isodecyl alcohol/*n*-dodecane for efficient recovery of cesium [101]. The effectiveness of the process is well demonstrated with actual HLW of reprocessing origin having acidity of 3.5 M nitric acid and 1.8 Ci/l of ¹³⁷Cs. Almost 99.97 % Cs was extracted and was quantitatively stripped using 0.01 M nitric acid. Separation factor for Cs over Sr and Na was more than 50000. The separated Cs was vitrified in glass matrix and used as source in blood irradiators.

1.6.4 Separation of ⁹⁰Sr

⁹⁰Sr (half-life of 28.5 years) present in the HLW is another major contributor to the radio-toxicity of the waste.⁹⁰Sr is highly hazardous owing to its long physical and biological half-life. ⁹⁰Sr(II), a pure beta emitter is chemically similar to Ca(II) and has a tendency to accumulate in the bone tissues when introduced into the human body which makes it very dangerous as the high energy beta particles from its daughter nuclide ⁹⁰Y damage the bone marrow. It is present along with its daughter ⁹⁰Y and the high beta energy of the later makes it responsible for high heat generation in HLW. Consequently, it is highly desirable to separate this radionuclide from the HLW to prevent any accidental human exposure to ⁹⁰Sr present in the conditioned waste and also to benefit the geologic disposal of the waste. In fact, separation of ¹³⁷Cs and ⁹⁰Sr from HLW greatly reduces the human exposure to radiation while handling the radioactive waste. It also reduces the volume of the waste and the cooling time of the vitrified HLW before disposal in the geological repositories. Further, it reduces the risk of matrix deformation caused by the generated heat during the long term storage of the waste as vitrified mass and helps in the safe and less expensive disposal of HLW in shallow repositories [102,103,104].

On the other hand, there is a growing interest to use⁹⁰Sr as a compact power source i.e., as a fuel for thermoelectric and thermo-mechanical power generators and also as a source of radionuclide⁹⁰Y, which has radiopharmaceutical applications.

The separation of Sr(II) from nitric acid medium is achieved by several methods such as precipitation, ion exchange, and solvent extraction. Amongst these, solvent extraction is a widely accepted technique over other methods due to its continuous nature, convenience in combining with other processes, and ease of scale-up and operation. Over the years, various extractants such as bis(2-ethylhexyl) phosphoric acid, dicarbollides, and derivatives of crown ethers have been

studied for the selective extraction of Sr(II) from acidic waste solutions by the solvent extraction method. Based on these extractants, processes such as SREX (Strontium Extraction) [105,106] was developed.

In SREX,0.15 M 4,4',(5')-di-(t-butylcyclohexano)-18-crown-6 has been used as an extractant and 1.2 Mtributyl phosphate (TBP) as a phase modifier in Isopar L diluents. In, UNEX (Universal Extraction) [107,108,109] process, 0.08 M chlorinated cobalt dicarbollide, 0.5% polyethylene glycol-400, and 0.02 M diphenyl-N,N-dibutylcarbamoyl methyl phosphine oxide were used as extractants in phenyl tri-fluoromethylsulfone (FS-13) diluents.

FPEX (Fission Product Extraction) [110,111] based on simultaneous extraction of cesium and strontium from acidic waste solutions, by using a solvent containing combination of two extractants, 0.075 M 4,4',(5')-di-(t-butylcyclohexano)-18-crown-6 for strontium, and 0.007Mcalix[4]arene-bis-(tert-octylbenzo-crown-6) (BOBCalixC6) for cesium modified with 0.75 M1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol (Cs-7SB) and 0.003 M trioctylamine (TOA) in Isopar L diluent, have been developed.



Figure 1-11: 4,4',(5')-di-(t-butylcyclohexano)-18-crown-6 and PEG (slovafol-909) for SR extraction

It is reported that diglycolamides, N,N,N',N'-tetraoctyldiglycolamide (TODGA) and N,N,N',N'tetra(2-ethylhexyl) diglycolamide (TEHDGA), extractants investigated for the co-extraction of lanthanides and actinides from HLW for actinide partitioning also co-extract Sr(II). In fact, efforts have been made to devise strategies for the extraction and separation of Am(III) and Sr(II) using the above diglycolamide extractants, TODGA, and TEHDGA⁻ The use of diglycolamides for the extraction of Sr(II) offers several advantages over the other extractants and processes proposed for Sr(II). Both the dicarbollide and crown ether derivatives used as extractants for Sr(II) are unstable in aliphatic solvents, and experiments were performed using these in diluents such as nitrobenzene, phenyl tri-fluoromethylsulfone and Isopar L. These extractants are also tedious to synthesize and are expensive compared to the diglycolamides, which are more cost effective for plant scale operation.

1.6.5 Separation of 99 Tc

⁹⁹Tc, a beta emitting ($E_{\beta-max}$ =295.5 keV) radionuclide having half life of 2.11x10⁵ years, is produced with a high fission yield of 6.13% during fission of ²³⁵U in nuclear reactors. During reprocessing of spent fuel it mainly follows high level waste (HLW) route [112,113].Like minor actinides, partitioning studies are also being pursued for technetium in order to minimize longterm environmental hazard associated with it after geological disposal of HLW [114].The chemical form of technetium, TcO4⁻, in aqueous solution is highly mobile under environmental conditions and also its high volatility during vitrification necessitates the development a method for separation of technetium from HLW and to form a suitable matrix for its containment [115]. Speciation of technetium is simple and it primarily exists as HTcO4 or TcO4⁻ in highly oxidizing nitric acid medium and in alkaline solutions. After dissolution of spent fuel in nitric acid,

technetium comes into solution as pertechnetate ion and during TBP extraction process (PUREX)

mainly follows raffinate (HLW) route [116]. Thirst for more environments friendly CHON principle based ligands have been given and tested for technetium extraction from nitric acid medium. Effect of various parameters on the extraction of Tc(VII) with DHOA has been evaluated by Pathak et al. Picolinamides, cyclic amides, mixture of CMPO and TBP, tetraphenylarsonium,2,2'-(methylimino)bis(*N*,N-dioctylacetamide) and Aliquat-336/nitric acid system have also been tried for separation of Tc(VII) from nitric acid medium [117,118,119,120,121,122,123]. A summary of the different processes have been used for the separation of ⁹⁹Tc from acidic waste solution is highlighted in **Table 1.6** below.

Extractant	Conc of Extractant(M)	Diluent	Aqueous phase acidity (M)	D _{Tc(VII)}
TBP	1.1	n-dodecane	0.5 M	1.0
DHOA	1.5	n-dodecane	0.5 M	1.0
CyMe4–BTBP	0.01	cyclohexanone	1 M HNO ₃ +3 M NaNO ₃	14
Picolinamides	0.2	FS-13	0.6 M	1
TODGA	0.1	n-dodecane	2.9	1.5

Table 1-6: Processes developed for extraction of ⁹⁹Tc from HLLW

1.6.6 Separation of Ruthenium

Separation of ruthenium (¹⁰⁶Ru) from HLLW is a major challenge due to its complex aqueous chemistry [124, 125]. ¹⁰⁶Ru is produced in substantial quantity in fission of ²³⁵U in reactor and reports in HLLW streams generated during reprocessing of spent fuel. The radionuclide forms three-dimensional rutile type crystals during vitrification of HLLW and makes the process difficult.¹⁰⁶Ru has a half-life of about one year and decays down to ¹⁰⁶Rh which further decays

to ¹⁰⁶Pd with the emission of high energy beta particle of 3.54 MeV. Because of high energy beta particle of ¹⁰⁶Ru-¹⁰⁶Rh, it is used as ophthalmic brachytherapy source to treat uveal melanomas, retinoblastoma and choroid melanomas of the eye. Therefore, separation of ¹⁰⁶Ru from high level liquid waste will not only make vitrification process simpler but also opens up the possibility of utilizing the recovered radionuclide for treatment of patients suffering from eye cancer.

For the separation of ruthenium from HLLW, several processes like chemical precipitation with metal (Ni and Co) sulfides, solvent extraction with P-50 oxime & thio acid compounds, ion exchange materials, photo reduction with UV-Vis light, oxidation followed by distillation or solvent extraction and electrochemical methods have been reported[126,127,128,129,130,131, 132].

Among others, oxidation followed by distillation or solvent extraction has been successfully used to extract ruthenium quantitatively from HLLW. As the Ru(III) /Ru(VIII) redox couple has a reduction potential of 1.4 V, oxidizing agents having higher reduction potentials, like KMnO4, Ozone, H₅IO₆ and KIO₄ have been used for the oxidation of Ru(III) to Ru(VIII). The resultant oxidation product, ruthenium tetroxide (RuO₄), is a colorless liquid and has boiling point of around 40 °C. Despite its low boiling point, the high solubility of RuO₄ in water (2% w/v at 20 °C) keeps the generated RuO₄ in the solution. In order to drive out the RuO₄ from solution, an external driving force like increase of temperature is required. Many researchers have applied this technique, i.e., heating upto 101°C and then collected the volatile RuO₄ in suitable solution. Despite simplicity of the process, it is not promising for the recovery of the radioelement as substantial amount of the ruthenium was deposited onto surfaces of the process vessels. Alternatively, efforts have also been made to extract the RuO₄ by using chlorinated alkanes like chloroform and carbon tetrachloride. Blicharskaet.al reported a process flow sheet involving oxidation of ruthenium using potassium metaperiodate followed by its extraction in carbon tetrachloride. It can be noted that all RuO₄ volatilization data reported in literature was based on the measurement of Ru concentration in solution either by using ICP or radiometric analysis before and after experiments.

1.7 Summary of literature review on the present processes

Based on above comprehensive literature review and comparative evaluation of performances towards separation of various radionuclides, it can be stated that selective separation of radionuclides from HLW is evolving process. Further R&D is necessary towards development of new solvents/processes towards achieving selective recovery of radionuclides in small volumes and in radiochemically purest form. The radioelement is then can be converted in suitable form for utilization or transmutation. In the areas of separation of actinides and fission products, few areas have been identified as the potential areas for further research. A summary of the evaluation discussed below.

• **Pu separation from HLW:** Efficient separation of Plutonium and Uranium from HLW is necessary before partitioning of minor actinides and fission products. This is because of the fact that if the element is not separated by the ligand being used for actinides separation. After actinides separation, the traces of Pu will be the major contributor for long term radiotoxicity of the waste. Alternatively, it can be stated that without separation of Pu, the objective of actinides partitioning is lost.

For the separation of Pu, TBP-dodecane system is the only process have been tested in engineering scale. Other ligands such as di-alkyl amides, BenzoDODA, Oxa-bridged tricycle di-carboxamide and Picolinamides have been tested for Pu separation. Though these ligands are selective for Pu, the reported D_{Pu} values are in the order of ~10. Further research in this direction is necessary to develop suitable diluent system towards their deployment in plant scale operation.
• **Recovery of Strontium-90:** The utility of ⁹⁰Sr as heat source battery is well known. Further, pharmaceutical application of its daughter product ⁹⁰Y in recent times makes it a prominent candidate among others radionuclides present in waste.

Promising processes known for the separation of Sr includes solvent extraction involving bis(2-ethylhexyl) phosphoric acid, dicarbollides, and derivatives of crown ethers (4,4',(5')-di-(t-butylcyclohexano)-18-crown-6).

In India, TEHDGA has been used for extraction of minor actinides and lanthanides from HLW. As TEHDGA extracts substantial amounts of Sr, the generated strip solution will have Sr along with actinides and lanthanides. Process development for the separation of Sr either from loaded TEHDGA phase or from TEHDGA strip product will open up possibility for utilization of Sr.

- Separation of ⁹⁹Tc: In view of very long half-life and high mobility of ⁹⁹TcO₄⁻, removal of the radioisotope is important. The processes reported in literature for the separation of the radioelement is summarized in Table 1-6. Among others, the most promising process reported till date envisages separation of the radioelement from dissolver solution utilizing CMPO in UREX + process. To our view, a little work has been carried out towards the management of this long lived fission products and this problem is to be addressed in totality.
- Recovery ¹⁰⁶Ru: Ruthenium is the most troublesome radionuclide present in HLW. On the other hand, it is very useful as external radiation source for treatment of eye cancer. To use the ¹⁰⁶Ru as brachytherapy source, separation of the radioelement in radiochemically pure form followed by its conversion in suitable plaque form is necessary. It is seen that processes reported in literature is very scare. A dedicated

research is required towards utilization of the radioelement as radiation source for treatment of eye cancer.

1.8 Motivations of work:

Towards sustainable development of nuclear energy programme, partitioning of radionuclides will play pivotal role for the management of high level waste. Adaptation of this scheme will also open up the possibility towards utilization of the radionuclides in beneficial use of mankind. A number of potential radionuclides suitable for such application are listed in **Table 1-5**. In addition, it is quite obvious that adaptation of partitioning scheme has great advantages with respect to management of the high level waste. The separation of the long-lived actinides and

fission products will greatly reduce the radio toxicity of the waste.

In line with the Indian strategy for the management of high level through adaptation of partitioning scheme and comprehensive literature review on the subject topic, helped to identify few areas where intense research and development is required towards sustainable development of the programme. A short list of the programme is highlighted in section 1.7.

It can be seen that dedicated contribution on any of the topic listed above is important for our nuclear energy programme and it can also led realization towards implementation of processes for beneficial applications in our society. With this motivation, a detailed work plan, which are to be carried out during the course of the PhD work, has been formulated as discussed below.

1.9 Scope of the present thesis work

Based on the highlighted summary of literature review (section 1.7) and the motivation drawn for the development of solvent and processes for partitioning of radionuclides and also utilization of radioisotopes in beneficial use of mankind, a detailed work plan have been formulated, which are to be carried out during the course of the Thesis work. For successful execution of the work, in a time bound manner, detailed work plans have been formulated as discussed below.

A. Development of CHON based ligand for selective Pu extraction

Picolinamides are well known ligands usually used for minor actinides/lanthanides separation in pH medium though has also been found to extract Pu(IV) at high nitric acid concentration in highly polar diluents. Increase in donor sites in any ligand increases the coordination ability as observed in glycolamides compared to malonamides due to presence of etheric oxygen in glycolamides. Based on these inferences, it is planned that efforts will be made to incorporate one more oxygen atom in Picolinamides system. It can be expected that the new ligand will have in more chelation ability with metal ions thereby increasing the overall extractability. This would parallaly increase the ligand economy while retaining the selectivity.

As a part of the PhD work, synthesis of the ligand, Picolyldiglycolamide (PDGA), its characterization and detailed solvent extraction studies towards separation of Pu has been carried out. Results of the study are presented in **Chapter 3** of the thesis.

B. Separation of Sr from Am in TEHDGA cycle and distribution of Tc during actinide partitioning

• As indicated in Section 1.7, TEHDGA extracts a substantial amount of Sr during extraction of trivalent actinides and lanthanides from HLLW. In order to separate Sr from

actinides and lanthanides from the mixture, a detailed work plan has been executed as follows.

Initial efforts have been made to devise stripping process for the sequential separation of Am(III) from Sr(II) by stripping of these two elements from the loaded organic phase. Based on the relative stability of Sr complexes with different ligand, a water soluble macro cyclic polydentate ether, 18-crown-6, which is known to have very high selectivity for Sr(II), has been employed for the stripping study. After the recovery of Sr(II), the loaded organic phase is again stripped at pH 2 to obtain the trivalent lanthanides and Am(III). Results of the study are presented in the **Chapter 4** of the present dissertation. It is to be noted that Sr required for pharmaceutical application is in smaller quantities but should possess very high radiochemical purity. As an alternative approach, therefore, feasibility of using supported liquid membrane technique has been explored. The initial part of development work has been carried out with PTFE supported membrane loaded with TEHDGA-IDA/n-dodecane solvent system for transport of Eu(III)/Sr(II). Dilute nitric acid can be used as stripant. In view of the scarcity of Am source, process development work has been carried out with Eu as substitute for Am and ⁸⁵⁺⁸⁹Sr traces. While optimization of process, the role of 18-crown-6 towards mutual separation of Eu(III) and Sr(II) by allowing Am transport has been examined. To maximize the separation factor between Eu(III) and Sr(II), transport properties of both the radionuclides has been studied as a function of nitric acid concentration, 18-crown-6 concentration and physical properties of membrane are reported in this chapter.

• Since TEHDGA has been used in the actinide separation study mentioned above, it can be anticipated that ⁹⁹TcO₄⁻ can form adduct with TEHDGA through H –bonding and get extracted to organic phase. With this view, feasibility of using TEHDGA for the separation of ⁹⁹TcO₄⁻ has been examined. In this study, detailed investigation on distribution behavior of technetium has been carried out. All these study have been done with simulated HLLW with the TEHDGA solvent system. Different parameters like effect of acidity, effect of interfering metal ion, nitrate ion concentration and kinetics of extraction were optimized to develop a process for separation of technetium from HLW, and their results are also reported in this paper (Chapter 4).

C. BEHGA for selective extraction of minor actinides over Sr(II): Solvent extraction and solvent impregnated resin studies

Regarding separation of Sr from the mixture of Sr with Am/Eu, idea adopted earlier (chapter 3) include masking of Sr by selective complexation using a selective ligand (18Crown 6) and then actinides were separated by TEHDGA. As an alternative approach, efforts were made to identify a ligand which can selectively extract minor actinides/lanthanides over Sr(II)and can result in a better separation between the two metal ions. Based on the recent literature report, BEHGA has been identified for a promising ligand. Synthesis, characterization and detailed evaluation of the ligand have been carried out employing solvent extraction and chromatographic techniques. Results of the study have been presented in **Chapter 5** of the present thesis.

D Separation of Ru from HLLW and its utilization

As highlighted in section 1.7, separation of ¹⁰⁶Ru is important from its utilization point of view. The work on separation of ¹⁰⁶Ru was taken up with the objectives to use the recovered activity as a source for brachytherapy applications. It is needless to be mentioned here that the product ¹⁰⁶Ru should be radio chemically pure for the said application. Since ion exchange and solvent extraction based processes are bound to pick up some other radionuclides, at least to some extent, it was decided that oxidation of Ru to RuO₄ will be explored. Since RuO₄ is highly volatile, detailed study on volatilization behavior of RuO₄ from nitric acid and role of different process parameters, such as concentration of acid, oxidant, temperature and time was studied volatilization behaviour of RuO₄ has been studied initially. Further, efforts were made to devise a simple technique for real time monitoring of RuO₄ volatilization from aqueous solution. Results of the study presented in Chapter 6 are important towards adaptation of best practices for recovery of radio-ruthenium from nuclear waste solution.

In the second part of the work, process development for the recovery of Ru has been carried out. This was done by cconverting Ru species to RuO4and subsequently extracting them in an organic phase. The process developed during this study is useful for the production of radiochemically pure ¹⁰⁶Ru and has been successfully used in preparation of brachytherapy sources. Results of the study are also documented in the Chapter 6.

2 Chapter 2: Experimental

Chapter-2 Experimental

2.1 Introduction

The chapter covers the detailed experimental process adopted during the course of this thesis work. Synthesis procedures of different ligands and their characterization techniques have been discussed. Brief description of instruments used for characterization of ligands has also been discussed. Experimental Methodologies for metal ion separation by different technique is also incorporated in this chapter.

2.2 Synthesis of ligand

2.2.1 Synthesis of N, N, N', N' tetra-isobutyl pyridine diglycolamide (PDGA)

PDGA was synthesized from commercially available and tailor-made materials by the method as described in the literature and is shown in Figure 2.1. In a typical run a mixture of pyridine dimethanol (1mol), NaH (2.5 mol), α -chloro N, N di-isobutyl acetamide (2.1 mol) was refluxed in dry THF for 24 hours under nitrogen atmosphere. THF was evaporated and residue was dissolved in dichloro methane (DCM). The organic phase was washed with acid and subsequently washed with DM water to neutralize it. Then the organic phase was dried over MgSO4 and distilled off the DCM to get the product. The product was purified by passing through basic alumina column. The synthesized ligand was found to be pure >98% as characterized by GC-MS.



Figure 2-1: Synthesis scheme for PDGA

2.2.2 Synthesis TEHDGA (Tetra-2-ethylhexl-diglycolamide)

TEHDGA was synthesized by the reaction of di-glycolyl chloride with bis 2-ethyl hexylamine in the presence of a base tri-ethyl amine [Figure 2.2.]. One mole of bis 2-ethyl hexylamine was taken along with 1.03 mole of tri-ethylamine and 300 mL of xylene in a reaction flask and cooled to 0 °C under nitrogen atmosphere using dry ice. The addition of 0.5 mole of di-glycolyl chloride dissolved in xylene was done slowly over a period of 4 hour, maintaining the temperature at 0 to 5°C. The temperature of the reaction mixture was then slowly raised to 60 °C and maintained for another 4 h. After cooling to room temperature, the reaction mixture was washed with diluted HCl 5% v/v and with 5% w/v Na₂CO₃. The organic phase was washed finally with water to neutral pH. After drying over anhydrous sodium sulphate, the solvent was concentrated up to 140 ° C at 0.01 mm Hg pressure.



Figure 2-2: Synthesis scheme for TEHDGA

2.2.3 Synthesis BEHGA N, N-bis(2-ethyl hexyl)glycolamide

BEHGA was synthesized from commercially available and tailor-made materials in two step by the following method shown in Figure 2.3. In the first step, α -chloro N, N di-2-ethyl hexyl acetamide (2.1 mol) was reacted with sodium acetate. In the next step, the acetate substituted product was hydrolyzed using sodium hydroxide in methanol. Methanol was evaporated and residue was dissolved in dichloro methane (DCM). The organic phase was washed with acid and subsequently washed with DM water to neutralize it. Then the organic phase was dried over MgSO₄ and distilled off the DCM to get the product. The synthesized ligand was found to be pure >98.5 % as characterized by GC-MS.



Figure 2-3: Synthesis scheme for BEHGA

2.3 Instrumental techniques used for characterization of ligands

2.3.1 GC-MS

GC-MS is a hyphenated technique of GC and MS and can be effectively used to identify the purity of organic samples. It has been used to determine the purity of the ligands in the present study. GC-MS analysis was performed on Shimadzu GCMS QP ultra 2010 Plus instrument. Capillary column used in GC is made up of fused silica and has a dimension of 15 m x 0.25 m. The schematic diagram of GC instrument is shown in Figure 2.4. Samples are injected through injection port and get caught up in the column. High purity helium gas is used as a carrier gas. For detection of samples, a single quadrupole mass spectrometer at 70 eV was attached at the outlet of GC column. Temperature programming was used for elution of compounds from the column as follows: initial temperature was set to $60 \circ C$ and kept at this temperature for 2 min (this was basically solvent cut time for removal of low boiling solvents used for sample preparation), increased to $280 \circ C$ at $10 \circ C/min$ and held at $280 \circ C$ for another 120 min.

Sample injector port was kept at 280 \circ C whereas interface temperature and the ion source temperature were kept at 280 and 250 \circ C, respectively.



Figure 2-4: Schematic diagram of GC-MS

2.3.2 FTIR

Fourier transform infra red spectroscopy is a useful tool in organic chemistry to determine the functional group in a compound. FTIR technique used in the present study is briefly described below.

Dipole moment of any chemical bond changes during vibration. This results in absorption of infrared radiation. The absorption intensity depends on the nature of chemical bond and atoms involved in bonding. In modern instruments, the absorbance of particular bond is recorded in time domain and converted to frequency domain using Fourier transform. This helps also in increasing signal to noise ratio.

In the present study, infrared experiments were carried out using a FTIR spectrometer (Shimadzu IRAffinity-1S). This instrument is having a range of 500-4000 cm⁻¹ and with a resolution of 0.5 cm⁻¹. Source used for generation of IR radiation is a globar source (silicon carbide rod). KBr

single crystal is used as a beam splitter and deuteratedtriglycinesulphate (DTGS) as a detector. The liquid samples were placed between two KBr disks before putting in sample chamber for measurement whereas pallets were prepared for solid samples using KBr for analysis. The background of the sample was corrected from the spectra of KBr.

2.4 Radiometric analysis

Detection of alpha, beta and gamma rays is based on the principle of charge produced by the interaction of radiation with detector material. The principle mode of interaction of gamma rays with detector material utilized in detection is photoelectric effect. In this interaction, the whole energy of the gamma rays is transferred to the detector material and ejects energetic electron from one of the bound shell of the atom. Various detector systems are being employed to collect the charge and the intensity is used to quantity the radionuclide. A brief description of these two detector system is given below.

2.4.1 Alpha activity analysis

In the present study, assaying of Pu was done by alpha-liquid scintillation counting where a toluene based scintillator cocktail was used. The cocktail was procured from M/s Hidex and as it is a commercially available cocktail, the composition is not disclosed. In general, it is the mixture of solvent, scintillator and surfactant. Photons are generated when ionising particle passes through scintillation medium and these photons are detected and measured using a photo multiplier tube which in turn gives us the concentration of radioactivity. Generally voltage pulse generated during interactions between alpha particles and scintillation liquid, are counted during gross measurement of alpha particles. In this technique detector is calibrated using a standard

and later on alpha emitter can be assayed. This technique has several advantages like high efficiencies of detection, simple sample preparation and data processing.

2.4.2 β and γ activity analysis

2.4.2.1 Scintillation detector

Inorganic scintillation material Sodium Iodide (NaI) activated with thalium (Tl) based detector is used in the present study for measurement of γ -activity in samples. Energetic electrons are produced due to interaction of gamma rays with NaI through photoelectric effect. This electron during passing through the medium elevates large number of electrons from valence band to conduction band. And during de-excitation of electrons, photons are generated in the visible region which detected and measured by photomultiplier tube. Tldoping in NaI crystals actually shifts the wavelength of the emission light to visible region. During this the photons are converted to electrons and multiplied and later on counted. A NaI(Tl) detector with 3x3 inch circular geometry have a detection efficiency of 3.6% for ¹³⁷Cs enegy.

2.4.2.2 High purity HPGe detector

High purity germanium detector is used for gamma ray spectroscopy in the present study. Under ambient condition, 42 electron-hole pair is generated because of intrinsic property of the germanium crystal. To prevent this, the detector is generally kept under liquid nitrogen temperatures. Reverse biasing of the n-p junction is made to produce detector depletion region. Gamma rays interact with the detector materials via photoelectric effect, Compton scattering and pair production route. As a result of these interactions, charge is produced which is further processed with the use of advanced electronics. Detector efficiency is much less when compared with scintillation detector but peak resolution is high which makes it a suitable candidate for γ - ray spectroscopy.The energy line used for the evaluation of ²⁴¹Am, ^{152,154}Eu, ¹³⁷Cs, ⁸⁵⁺⁸⁹Sr, ¹⁰⁶ Ru and ¹²⁵Sb were 59.8, 121/242, 661, 514, 511/621,428 KeV respectively.

2.5 Materials and methods for Separation of metal ion using ligands

2.5.1 Plutonium extraction using PDGA

Ionic Liquids (Cn mim+.NTf2-, and Cnmim+.Cl-, where n = 4, 6, 8} were procured from Io-Li-Tec, Germany and used as received. Pu stock solution were available in the laboratory. During extraction studies, the valency of Pu was maintained as Pu(IV). In addition to the elements present in our HLLW solution, ²⁴¹Am tracer was added from outside along with Nd, Na and Fe as inactive components. The acidity of the diluted HLLW was maintained at three different acidities, viz., 0.3M, 1M and 7M HNO3.Titration against standard NaOH was used to determine the nitric acid concentration. PDGA solutions of desired concentrations were prepared in NB and Cn mim⁺.NTf2⁻. Equal volume of the organic phase and aqueous phase (2 mL each) was equilibrated in a rotary thermo stated water bath for desired time interval at ambient temperature (25.0 \pm 0.1 °C) followed by centrifugation for phase separation. After phase separation, suitable aliquots were taken from both the phases for radiometric assay. All the experiments were carried out in triplicate and the results were within \pm 5%.

2.5.2 Separation of Sr(II) from Am(III) during actinide partitioning using TEHDGA

18-crown-6 (1,4,7,10,13,16-Hexaoxacyclooctadecane, >99%)was obtained from Sigma Aldrich and used as such. Isodecyl alcohol (>99%), and *n*-dodecane (>99%) were obtained locally and used as received. Radioactive tracer ^{85,89}Sr was obtained from Board of Radiation and Isotope Technology (BRIT), Mumbai whereas ²⁴¹Am was obtained from Waste Immobilization Plant, Bhabha Atomic Research Centre (BARC), Trombay, India. Tracer solutions of ^{85,89}Sr at an approximate concentration of 10⁻⁷ M in 1 M nitric acid, and ²⁴¹Am at an approximate concentration of 10⁻⁸ M in 0.1 M nitric acid were used as stock solutions for extraction studies.

For the determination of distribution ratio (DM) of the metal ions, the organic phase composed of TEHDGA, isodecyl alcohol, and n-dodecane was equilibrated with equal volume of the corresponding aqueous acidic solution containing the requisite quantity of the metal ions for 30 min in a glass vial. After extraction, the phases were separated by centrifugation, and the organic and aqueous phases were analyzed for the metal ion concentration. All the extraction experiments were carried out in a thermostated waterbath maintained at temperature of 25 ± 1 ^oC.All the distribution ratio measurements were performed in duplicates. All the extraction and stripping studies were carried out for organic to aqueous ratio (O/A) of 1:1 except for studies carried out to determine the maximum stripping capacity of the aqueous phase containing 18-crown-6 where the volume of the organic phase containing Sr(II) was increased to give O/A ratio of 2:1, 3:1, 4:1, etc., till the maximum Sr(II) stripping was attained.

The percentage stripping of Sr(II) was calculated as follows:

% Sr(II) Stripped =
$$\frac{[Sr(II)]_{\text{strip solution}}}{[Sr(II)]_{\text{loaded organic}}} X 100$$

Where[Sr(II)]loaded organic is the concentration of Sr(II) extracted to the organic phase, and [Sr(II)]strip solution is the concentration of Sr(II) stripped from this loaded organic phase.

In order to investigate the solubility of 18-crown-6 in the organic phase chosen for our experiments, five different standard solutions of 18-crown-6 of concentrations, 0.01 M, 0.05 M, 0.1 M, 0.15 M, and 0.2 M, were prepared in 5% isodecyl alcohol/n-dodecane. To each solution, a fixed concentration of 0.02 M tri-n-butyl phosphate (TBP) was added as an internal standard.

The internal standard was added to the sample, so that the response from the desired 18-crown-6 peak in the chromatogram could be compared to the internal standard, which would correct for minor variations in the injection volume. All the standard solutions were analyzed using GC-MS. The peak areas corresponding to both TBP and 18-crown-6 were determined from the respective chromatograms obtained for each concentration of 18-crown-6. A calibration curve was plotted between the ratio of the peak areas of TBP and 18-crown-6 and the ratio of their respective concentrations.

To estimate the distribution of 18-crown-6 between the organic and aqueous phase during stripping studies, a solution of 0.1 M 18-crown-6 in 4 M HNO3 was equilibrated with an equal volume of 0.3 M TEHDGA – 5% isodecyl alcohol/n-dodecane phase for 30 minutes. After equilibration, the two phases were separated and the organic phase was analyzed using GC-MS after the addition of 0.02 M of the internal standard TBP. From the chromatogram, the peak areas corresponding to 18-crown-6 and TBP were obtained and from the ratio of the peak areas and the known concentration of TBP, the concentration of 18-crown-6 was calculated from the calibration plot.

2.5.3 BEHGA for selective extraction of minor actinides over Sr(II): Solvent extraction and solvent impregnated resin studies

BEHGA solutions were prepared in industrial diluent system regularly used in plant scale operations in back end fuel cycle where n-dodecane is used as the diluent and iso-decyl alcohol is phase modifier. Radioactive tracer ^{85,89}Sr was obtained from Board of Radiation and Isotope Technology (BRIT), Mumbai whereas ²⁴¹Am was obtained from Waste Immobilization Plant, Bhabha Atomic Research Centre (BARC), Trombay, India. Tracer solutions of ^{85,89}Sr at an approximate concentration of 10⁻⁷ M in 1 M nitric acid, and ²⁴¹Am at an approximate

concentration of 10^{-8} M in 0.1 M nitric acid were used as stock solutions for extraction studies. For the determination of distribution ratios ($D_{\rm M}$) of the metal ions, 2 mL of the organic solvent was contacted with an equal volume of aqueous nitric acid solution containing the metal ion at room temperature for 15 min. After phase separation by centrifugation, the organic and aqueous phases were separated and analysed for the metal ion concentration, and the $D_{\rm M}$ was calculated as the ratio of the concentration (or radioactivity) of the metal ion in the organic phase to the concentration of the metal ion in the aqueous phase. The estimation of Am(III) and Eu(III) in the organic and aqueous phases were carried out by analysing both the phases for the corresponding gamma activity using NaI(Tl) detector or HPGe semiconductor detector coupled with 8 K MCA.

2.5.4 Separation of Ru from HLLW and its utilization

RuCl₃ and potassium metaperiodate was obtained from Sigma-Aldrich and BDH chemical pvt. Itd respectively. AR grade nitric acid was procured from local market. UV-Vis spectrum was recorded using a JASCO UV-Vis spectrophotometer and nitric acid concentration was estimated using a Metrohm auto-titrator.

The actual HLW of research reactor origin was initially subjected to separation of ¹³⁷Cs by 1, 3 di-octyloxy Calix[4]-arene crown 6, followed by co-extraction of minor actinides and Sr by TEHDGA. The resulting activity lean solution is used as the feed in the reported study. Purification of ¹⁰⁶Ru in radio chemically pure form was carried out. Initial process optimization study was carried out with 25 mL simulated waste spiked with ¹⁰⁶Ru radiotracer. The conversion of Ru nitrosyl nitrate to RuO₄ was carried out by addition of KIO₄. Further optimization with regard to extraction of RuO₄ in CCl₄ has been carried out by conducting a series of experiments, by varying phase ratio (organic and aqueous), using different concentration of HNO3 in waste feed, extraction time, etc. On the other hand, a great deal of efforts has been made to finalize the stripping conditions. The use of different stripant in different combination was tried to make a simplified process flowsheet. The feasibility of reusing the CCl₄ in multiple extraction cycle was studied. Finally the optimized process has been testes, with actual waste and purity of extracted ¹⁰⁶Ru solution was analysed in details.

In a typical experiment, Ru(III) was dissolved in nitric acid solution and oxidized using KIO₄ and UV-Vis spectrum were recorded at different time interval. The stock solutions with Ru(III) concentration ranging from 0.25 to 0.75 mM were prepared by dissolving RuCl₃ in 1 M nitric acid. To a 5 mL of this solution 0.1 gm KIO₄ was added and shaken for 2 minutes. The sample was transferred quickly(~1min) to a cuvette of path length 1 cm and UV-Vis spectrum was recorded at different time interval to understand the kinetics of volatilization. The cuvette was kept at temperature controlled sample holder to maintain fixed temperature of the solutions. Magnitude of volatilization was evaluated as a function of temperature by keeping the solution at different temperature. Volatilization experiments were carried out with different initial Ru concentration to understand the effect of initial Ru concentration on volatilization. Amount of KIO₄ was optimized by adding different of KIO₄ (0.5 -3.0 wt %) to 5 mL of 1 mM Ru(III) solution. Similarly feed nitric acid concentration was varied from 1 M to 4 M nitric acid to realize the effect of nitric concentration.

3 Chapter 3: Pyridine di-glycolamide: A ligand for plutonium extraction from nitric acid medium

Chapter 3 Pyridine di-glycolamide: A ligand for plutonium extraction from nitric acid medium

3.1 Introduction

High level liquid waste originating from spent fuel reprocessing contains trace amount of actinides such as U and Pu. Separation of these elements from HLLW is essential to minimize the radiological burden on environment. This aspect has been as elaborately discussed in chapter 1. Towards this efforts were made to synthesize a ligand which can extract preferentially Pu over other metal ions from the waste solution. Our aim of separating the target radionuclide was achieved by designing a novel ligand where two di-glycolamide moieties were attached to a pyridine ring. The rigid structure of the ligand and availability of four oxygen donor atoms in near vicinity at a perfect position for coordination makes this ligand a suitable candidate for Pu extraction. The synthesis procedure has been discussed in the experimental section. This chapter deals with detailed characterization of the ligand and solvent extraction studies carried out employing the solvent Pyridine di-glycolamide (PDGA). The purity of the synthesized product was established using techniques namely GC-MS and FTIR spectroscopy and has been discussed in the first part of this chapter. Once the purity of the ligand is established, the solvent extraction studies were carried out.

The detailed solvent extraction data of various radionuclides present in the high level liquid waste has been presented in the second part of the chapter. Two diluent system namely a molecular diluent Nitro benzene and another room temperature ionic liquid was tested for better Pu extraction from nitric acid medium. The kinetics and mechanism of extraction was elucidated and reported in this chapter. The selective extraction of Pu over other elements was tested and viability of using this ligand in separating Pu from high level waste was also screened.

3.2 Synthesis of the Pyridine di-glycolamide (PDGA)

Detailed synthesis process of PDGA and its purification has been discussed in section 2.2.1 of chapter 2. In brief, the PDGA was synthesized from the by reacting pyridine di-methanol with α -chloro N, N di-isobutyl acetamide using NaH as base in dry THF for 24 hours under nitrogen atmosphere. Molecular structure of the final product is presented in **Figure 3.1.** The final product obtained after purification is used in characterization studies as discussed below.



Figure 3-1: Molecular structure of PDGA

3.3 Characterization

3.3.1 GC-MS

GC-MS has been used as a characterization tool to quantify the purity of the sample by identifying and quantifying the impurities present. Details of the GC-MS setup including instrumental parameters used in the present study has been discussed in section 2.3.1 of Chapter 2. The experimentally determined GC-MS data of the synthesized PDGA is shown in Table 3.1. Further the GC and MS spectrum of the sample is shown in Fig 3.2. From the data it can be inferred that the purity of the product is >98%.

Retention Time	Composition (%)	Component	EI-MS
22.9	> 98%	Pyridine Di-glycolamide	57, 72, 86, 107 (bp), 128,150,
			292,307,321,349,420,459,476(M+)

Table 3-1: GC-MS data of PDGA

bp= base peak and M+ = molecular ion peak



Figure 3-2: (a) Gas chromatogram and (b) Mass spectrum of PDGA

3.3.2 FTIR spectroscopy

FTIR spectroscopy has been utilized to identify the functional groups present in the compound which in turn provides deep insight about the purity of the compound. The FTIR spectrum of PDGA is shown in Figure 3.3. The peaks major peaks at 1220 and 1650 cm⁻¹ indicate presence of C-N and C=O groups, respectively. The C-C and C-H bond stretching frequencies are reflected from the peak at 1110 and 2900 cm⁻¹, respectively. The major peaks seen in the spectrum are collated in Table 3.2 for ready reference.



Figure 3-3: FTIR Spectrum of PDGA

Table 3-	2: FTIR	data of	PDGA
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Peak (cm-1)	Functional Group
1220	C-N
1110	C-C
1650	Amide C=O
2900	С-Н

3.4 Solvent Extraction Studies for Extraction of Pu

3.4.1 Selection of diluent

Diluent plays an important role in extraction of metal ions. Most common diluent used in Nuclear Fuel Cycle is *n*-dodecane. However, poor solubility of most the recently developed novel extractants in n-dodecane calls for development of new diluents. The synthesized ligand of present study, PDGA, has poor solubility in *n*-dodecane. Hence, solubility tests employing different diluents have been carried out. It was found that PDGA is completely solubilized in nitrobenzene. Hence, initial solvent extraction studies of PDGA were carried out using nitrobenzene as diluent. As Nitro benzene is not environmental friendly diluent for plant scale application because of its chemical toxicity, we look forward to search another diluent system which is environment friendly. During this study, the Ionic Liquid, "3-methyl-1-octyl immidazolium bis-(tri-fluoromethanesulphonyl) imide, was selected and used as diluent for extraction of Pu(IV).

3.4.2 Kinetics of extraction

The rate at which the metal ions transfers from aqueous phase to organic phase i.e. rate of metal ion extraction plays crucial role in any solvent extraction studies. Before proceeding further with solvent extraction experiments, we carried out the kinetic of Pu extraction in both the diluents. The extraction kinetics profile is shown in Figure 3.4. The extraction rate is faster in NB (15 minutes) compared to ionic liquid (60 minutes) which may be attributed to the higher viscosity and density of the ionic liquids. In general, viscosity affects the kinetics of extraction. Once equilibrium is reached viscosity does not play any role in metal ion extraction.



Figure 3-4: Kinetics of Pu(IV) extraction by PDGA in Nitrobenzene as well as C₈mimNTf₂ as diluent; Conditions: a) Nitrobenzene- Feed acidity- 4M HNO₃, [PDGA]- 0.2M b) C₈mimNTf₂- Feed acidity- 0.3M HNO₃, [PDGA]- 0.02 M

3.4.3 Effect of nitric acid concentration

PDGA being a neutral molecule, feed nitric acid concentration may have an important role in the extraction of Pu(IV). To verify the fact, the role of nitric acid in the extraction of Pu(IV) by PDGA as extractant, distribution ratio of Pu(IV) were determined in the HNO₃ concentration

range of 0.1M to 6M for 0.2M PDGA in NB and 0.1M to 7M for 0.02M PDGA in C₈mimNTf₂. The values are shown in **Figure 3.5**.



Figure 3-5: Distribution ratio of Pu(IV) in presence of varying concentration of HNO₃ in the feed solution using PDGA in NB and IL as extractant; [PDGA]- 0.2M in NB and 0.02M in $C_8mimNTf_2$

For NB as diluent, there was continuous increase in $D_{Pu(IV)}$ values for PDGA reaching a maximum value at 6M HNO₃. The behavior was found to be completely different for IL as diluent. In IL diluent, $D_{Pu(IV)}$ values were found to increase initially with the increased of HNO₃ concentration from 0.1M to 0.3M. Thereafter, an inverted trend to $D_{(Pu)}$ was observed with further

increase of HNO₃ concentration up to 3M. Further increase in HNO₃ concentration from 3 to 6M HNO₃ led to another increasing trend for D_{Pu(IV)} values.

The contrast in the pattern of Pu(IV) extraction behavior for NB and IL is quite understandable and can be explained as follows:

In molecular diluent like NB, the mechanism of Pu(IV) extraction by PDGA can be represented as nitrate ion assisted complex formation:

 $Pu^{4+} + xNO_3^- + y(PDGA)_{org}$ [Pu (NO₃)_x.y PDGA]_{org}.....(3-1)

Where species without subscript refers to aqueous phase and species with subscript org refers to organic phase.

In contrast the mechanism of extraction for metal ions in presence of IL as diluents is still a matter of research and different mechanisms have been proposed for different systems. There are reports for cation exchange, anion exchange or solvation or even multiple mechanisms for the extraction of metal ions and based on the mechanism of extraction the trend for D_M with HNO₃ concentration varies. The trend can be initial increase up to a certain acidity followed by a decrease or it can be continuous increase with increasing feed HNO₃ concentration or even it can be continuous decrease with increasing HNO₃ concentration. The trend observed for PDGA in IL is quite unique and to the best of our knowledge only one literature report on the extraction of Eu(III) by CMPO-TBP extractants in IL is available which also showed an increasing trend in $D_{Eu(III)}$ values initially with increasing HNO₃ concentration followed by subsequent decrease. The reason behind such behavior has not been discussed by the authors. Even for BenzoDODA-C4mimNTf₂ system, the trend was initial decrease with increasing HNO₃ concentration followed

by an increase with further increase. In order to understand the trend, detailed investigations on mechanism of extraction were carried out and the results are reported below.

3.4.4 Mechanism of Pu extraction using PDGA in molecular diluent (NB)

For NB as diluent, the mechanism of extraction for Pu(IV) by PDGA has been given by Equation 3.1. To determine the value of y, log-log plot of PDGA concentration $vsD_{Pu(IV)}$ values were plotted which is shown in Figure 3.6.



Figure 3-6: Slope analysis of PDGA for Pu(IV) in presence of NB; Feed acidity- 4M HNO3

From the **Figure 3.6**, slope of the plot obtained was around 1 which corresponds the value of y in equation 3.1 is 1. Now to determine the values of 'x', D(Pu) values were evaluated by conducting batch tests as a function of NO₃ concentration, keeping total nitrate concentration constant at 4 M. This was done by using varying concentration of sodium nitrate in 1 M HNO₃ acidity. Results of the study are presented in **Figure 3.7** in form of log [NO₃⁻] against log [D_{Pu(IV)}].

As earlier, slope of the curve was determined and the value is found to be 4. Therefore, equation 3.1 can be written as:

$$Pu^{4+} + 4NO_3^- + (PDGA)_{org}$$
 (3-2)



Figure 3-7: Plot of log D_{Pu}vs log [NO₃]⁻ for 0.2M PDGA in NB

But for IL as diluent, the mechanism is different as can be seen from the HNO_3 concentration variation studies. As mentioned above, there was no discussion on the mechanism for Eu(III) extraction by CMPO-TBP in bmimNTf₂ as diluent by the authors where the trend for distribution ratio with varying HNO_3 concentration was found to be similar to the trend observed in our studies.

3.4.5 Mechanism of Pu extraction using PDGA in ionic liquid diluent system

To identify the mechanism of Pu extraction PDGA involving IL as diluent, effect of alkyl chain length of the IL cation moiety on extraction of a Pu was studied. In this study, $D_{(Pu)}$ was evaluated as a function of HNO₃ concentration ranging from 0.1M to 7M using 0.02M PDGA in three different IL moiety with varying chain length of the cationic moiety (C4,C6 and C8). Results of this study are shown in **Figure 3.8**.



Figure 3-8: Effect of alkyl chain length of C_nmimNTf₂ on the extractability of Pu(IV) using 0.02 M PDGA as extractant in presence of varying HNO₃ concentration

It can be seen from Figure 3.8 that there are three different regions in the curve. The first region is from 0.1M to 0.3M HNO₃ where the effect of alkyl chain length of the IL cationic moiety is insignificant and there is an increasing trend for $D_{Pu(IV)}$ values with increasing

HNO₃concentration for all the three IL's studied. This type of behavior indicates solvation mechanism is followed for Pu(IV) extraction by PDGA in the acid range 0.1M to 0.3M HNO₃. In the second region, between 0.3M to 3M HNO₃, D(Pu) decreases with the increase of acid concentration. In this region, carbon chain length of the alkyl group played significant role. The decrease of D(Pu) values were found to more significant for C8, i.e., with increase of carbon chain length of the alkyl group. This type of behavior signifies cation exchange mechanism.

In order to prove the mechanism further, we determined distribution ratio for Pu(IV) at 0.3M and 1M HNO₃ employing varying concentrations of water soluble C₈mimCl in the aqueous phase employing 0.02M PDGA in C₈mimNTf₂ as extractant. If the ion-exchange mechanism is valid, $D_{Pu(IV)}$ values will decrease with increasing C₈mim⁺ ion concentration in the aqueous phase which is based on equilibrium shift. But for solvation mechanism $D_{Pu(IV)}$ values should be independent of C₈mim⁺ ion concentration in the aqueous phase. The result of the experiment is shown in **Figure 3.9.** The results were found to be in-line with our assumptions. There was no change in $D_{Pu(IV)}$ values with increasing C₈mim⁺ concentration at 0.3M HNO₃ suggesting that the mechanism of Pu(IV) extraction in this acid range is by solvation. But at 1M HNO₃, the behavior was opposite with increasing C₈mim⁺ concentration in the aqueous phase leading to decrease in $D_{Pu(IV)}$ values suggesting the extraction is by ion-exchange mechanism.



Figure 3-9: Effect of C₈mimCl concentration in the aqueous phase on the extraction of Pu(IV) by 0.02M PDGA in C₈mimNTf₂

The third region of the **Figure 3.8**, i.e., 3M to 7M HNO₃ concentration range, increasing trend for $D_{Pu(IV)}$ values suggest either solvation mechanism or an anion-exchange mechanism. Pu(IV) is known to form anionic complexes at higher nitric acid concentrations. As reported earlier C₄mimNTf₂ itself shows significant extraction of Pu(IV) from higher concentration of HNO₃ signifying the presence of anion-exchange mechanism. We also carried out extraction of Pu(IV) at different acidities using C₈mimNTf₂ itself and observed similar extraction behavior to that of C₄mimNTf₂ with significant extraction from 4M HNO₃ and higher. This indicates possibility of an anion exchange mechanism as mentioned in previous literature reports. The effect of alkyl chain length is insignificant for D_{Pu(IV)} from 4M and higher acidity. In order to prove the mechanism further, we carried out extraction studies of Pu(IV) using 0.02M PDGA in $C_8mimNTf_2$ in presence of varying aqueous phase concentrations of NTf_2^- employing LiNTf_2. Three different acid concentrations viz., 0.3M, 1M and 7M HNO₃ was chosen for the experiments. Results of the study are presented in Figure 3.10 in form of $D_{Pu(IV)}$ values against varying initial aqueous concentrations of NTf_2^- . The trend for 0.3M and 1M HNO₃ was identical with no change in $D_{Pu(IV)}$ values with increasing NTf_2^- concentration. But at 7M HNO₃, a continuous decrease in $D_{Pu(IV)}$ values with increasing NTf_2^- concentration was observed. This can be explained with the anion-exchange mechanism based on equilibrium shift. This indicates that Pu(IV) gets exchanged with NTf_2^- ion of the ionic liquid as $[Pu(NO_3)_6]^{2-}$.



Figure 3-10: Distribution ratios of Pu(IV) using 0.02 M PDGA in $C_8mimNTf_2$ in presence of varying concentrations of NTf_2^- in the aqueous phase in presence of different HNO₃ concentrations in feed

Based on the study, the mechanism of extraction for Pu(IV) by PDGA can be proposed as follows:



The values for number of PDGA molecules attached with Pu(IV) have been determined from log-log plot of $D_{Pu(IV)}$ against PDGA concentration at 0.3M and 1M HNO₃ (Figure 3.11).



Figure 3-11: Slope analysis of PDGA for Pu(IV) in presence of C₈mimNTf₂ at 0.3M and 1M HNO₃

3.4.6 Selectivity study

The selectivity of an extractant has been reported to be dependent on the diluent system employed. BenzoDODA was found to be highly selective for Pu(IV) compared to other elements present in HLLW in presence of n-dodecane as diluent but the selectivity was lost in presence of C4mimNTf2 which was reported to be due to mechanism of extraction. To study the selectivity of PDGA system for Pu(IV) over other elements in the HLLW solution, we carried out extraction studies of HLLW using 0.2M PDGA in NB as well as 0.02M PDGA in C8mimNTf2 for all the three acid range. The results are given in Table 3.3. As evident from the Table, in presence of NB, PDGA exhibits excellent selectivity over various other elements expected to be present in HLLW solution. But in presence of C8mim NTf2, the trend is different. Here the selectivity can be seen to be dependent on the acidity of the solution. PDGA showed excellent selectivity at 0.3M and 7M acidities when the mechanism of extraction was solvation and anion-exchange whereas at 1M acidity for cation-exchange mechanism, the selectivity decreased quite drastically. The experimentally observed trend for the uptake of different metal ion by PDGA can be represented as:

$M(IV) >> M(III) > M(II) \sim M(I)$

From our study, the mechanism of Pu extraction is inferred to be solvation at higher acidity and ion exchange for lower acidity (Fig 3.8). For ion exchange mechanism, possibly higher charge of metal ion is responsible for the higher uptake. In case of solvation mechanism, reasons for the very high Pu uptake can be attributed to the formation of Pu-PDGA bidentate complex through the carbonyl and the N of the pyridinic ring as predicted by G. Williams et al.
	0.2M PDGA in NB		0.02M PDGA in C8mimNTf2						
	4M I	4M HNO ₃		0.3M HNO ₃		1M HNO ₃		7M HNO ₃	
Elements	D _M	S.F	D _M	S.F	D _M	S.F	D _M	S.F	
Pu(IV)	57	-	71.34	-	11.42	-	14.23	-	
U(VI)	0.42	135	0.45	158	9.88	1.15	0.37	38.4	
Am(III)	0.31	185	0.33	216	8.58	1.33	0.26	54.7	
Nd(III)	0.27	210	0.29	246	7.96	1.43	0.24	59.2	
Ce(III)	0.26	219	0.24	297	8.01	1.42	0.25	56.9	
Eu(III)	0.28	203	0.24	297	8.11	1.41	0.26	54.7	
Ru	0.17	335	0.15	475	0.15	76.13	0.12	118.5	
Cs(I)	0.06	950	0.07	1019	0.04	285.5	0.05	284.6	
Sr(II)	0.05	1140	0.06	1189	0.05	228.4	0.04	355.7	
Na(I)	0.002	28500	0.002	35670	0.003	3806	0.002	7115	
Fe(III)	<0.1	>570	<0.1	>710	0.08	142.7	0.05	284.6	

Table 3-3: Extraction of various elements from diluted HLLW solution at different acidity using 0.2M PDGA in NB and 0.02M PDGA in C₈mimTf₂N

3.4.7 Stripping and reusability studies

Stripping of an extracted metal ion from organic phase as well as its reusability is an important parameter for process applications. In this connection, stripping studies of Pu from loaded PDGA in presence of NB as well as C₈mimNTf₂were carried out using 0.1 M Oxalic acid and a reductive stripping mixture of 0.2M N₂H₄ in 0.3M HNO₃. Table 3.4 gives the percentage stripping of Pu in two contacts for both the diluents. It can be seen that the Pu can be quantitatively stripped from

loaded organic phase using both the stripping solution. It can be further noted that both the stripping mixtures were equally effective as stripant for NB as well as C₈mimNTf₂ as diluent.

	Cumulative Stripping					
No. of	0.2M PD0	GA in NB	0.02M PDGA in C8mimNTf2			
Contacts	0.1M Oxalic	0.2M N ₂ H ₄ +	0.1M Oxalic	0.2M N ₂ H ₄ +		
	Acid	0.3M HNO ₃	Acid	0.3M HNO ₃		
1	90.12	87.12	89.61	80.12		
2	99.89	95.48	99.84	94.11		

Table 3-4: Stripping of Pu(IV) from PDGA in NB and C8mimNTf2

After optimization of stripping conditions, reusability of the lean organic solution in Pu extraction was studied. It has been found that 0.2 M PDGA in NB diluent can retain its extraction performance for six cycles of operations. In ionic liquid diluent system, at a feed acidity of 0.3 M, performance of the ligand is also intact for six cycle of operation whereas at higher nitric acid concentration, it needs a C8mimC1 treatment before next extraction cycle to retain its performance. The detailed data has been shown in Table 3.5. Good stripping properties and its reusability makes this ligand an efficient candidate for larger scale applications.

No. of Contact S	0.2M PDGA in NB (4M Feed acidity)	0.02M PDGA in C ₈ mimNTf ₂ (0.3M Feed acidity)	0.02M PDGA in C ₈ mimNTf ₂ (1M Feed acidity, without C ₈ mimCl treatment)	0.02M PDGA in C ₈ mimNTf ₂ (1M Feed acidity, with C ₈ mimCl treatment)
1	57.11	71.34	11.42	11.42
2	56.12	69.67	8.12	10.11
3	56.42	68.11	5.02	10.67
4	56.01	65.21	3.24	11.01
5	55.12 63.11		1.21	9.97

Table 3-5: Reusability studies of PDGA in presence of NB as well as C8mimNTf2

3.5 Summary of the results

- 1. Ligand PDGA was successfully synthesized, purified, characterized and tested for metal ion extraction. The ligand is found to preferentially extract Pu (D_{Pu} 57) from nitric acid medium over other metal ions ($D_M < 0.5$).
- 2. Extraction was studied both in molecular diluent nitro benzene and also in one room temperature ionic liquid. Pu is extracted by PDGA by Solvation mechanism in nitro benzene diluent system at all nitric acid concentration studied whereas extraction mechanism in ionic liquid is found to be a mixture of both ion exchange and solvation. The mechanism was understood by carrying several experiments by varying the feed composition.

- 3. The stoichiometry of the complex formed in nitro benzene and ionic liquid diluents are found to be different. PDGA forms a 1:1 complex with Pu in nitro benzene whereas it forms a 1:2 complex with Pu in ionic liquid diluents.
- 4. Kinetics of extraction is fast in molecular diluents compared to ionic liquid owing to the high viscosity and density of the ionic liquids.
- 5. The extracted Pu can be stripped from loaded organic phase using oxalic acid and the lean organic phase can be potentially be used further for extraction. The solvent phase is found to retain its extraction performance at least for six cycle of operation.
- The extraction and stripping properties of PDGA makes it a suitable candidate for its commercial application for separation of the radionuclides from high level liquid waste for further use.

4 Chapter 4: Separation of Sr and Tc from HLLW using TEHDGA

Chapter 4 Separation of Sr and Tc from HLLW using TEHDGA solvent system

4.1 Introduction

As discussed in Chapter 1, glycolamides (TODGA/ TEHDGA) are found to be the best suited ligand for separation of minor actinides from the HLLW. In India, TEHDGA (0.2 M) - 30% isodecyl alcohol/*n*-dodecane has been used at an engineering scale for the separation of minor actinides from actual HLLW. It is observed that TEHDGA extracts some amount of Sr along with minor actinides.

During the course of this PhD work, detailed investigations have been carried out to map the extractions behavior of minor actinides and Sr. Results of this study is used to devise process conditions for selective separation of Sr from trivalent actinides and lanthanides. The separated Sr in radio chemically pure form is suitable for further pharmaceutical applications. Results of the study have been discussed in the first part of the chapter.

The second part of the chapter describes studies pertaining to separation of Tc from simulated waste solution by further tuning the TEHDGA solvent composition. Separation of ⁹⁹Tc from HLLW is important from waste management point of view owing to its long half-life and high chemical mobility in the aqueous environment. Experimental parameters have been optimized towards extraction of Tc and with minimum extraction of other radionuclides. The extraction performance of this solvent system is evaluated for the first time for separation of Tc from simulated HLLW conditions. The result of the study is discussed in details in this chapter.

4.2 Separation of Sr using TEHDGA- Solvent extraction studies

Solvent composition of TEHDGA was optimized for quantitative extraction of both Am and Sr from nitric acid solution. Thereafter, a water soluble complexing agent, 18-crown-6, was used for selective stripping of Sr from the TEHDGA organic phase. To minimize the organic solvent requirement, the same process was tried in supported liquid membrane mode. The results obtained both in solvent extraction and SLM studies are described below.

4.2.1 Co-extraction of Minor actinides and Sr

In the actinide partitioning demonstration facility at Tarapur, India, it has been demonstrated that 0.2 M TEHDGA - 30% isodecyl alcohol/*n*-dodecane can selectively extract trivalent 'f' group elements from the HLLW leaving all other fission elements including strontium in the raffinate. At this extractant composition and feed acidity of 4 M HNO₃, the distribution co-efficient for Am(III) and Sr(II) have been reported as 70 and 0.2 respectively. In the above studies, isodecyl alcohol was used as a phase modifier to prevent third phase formation.

It is known that the addition of polar phase modifiers tend to suppress metal ion uptake with increasing modifier concentration. Hence, at lower concentrations of isodecyl alcohol, the uptake of both Sr(II) and Am(III) by TEHDGA will increase. Based on this, Sr(II) from the raffinate of the TEHDGA-actinide partitioning process was extracted using 0.3 M TEHDGA – 5% isodecyl alcohol/*n*-dodecane, in which the isodecyl concentration was optimized to 5% (v/v) to obtain maximum extraction of Sr(II) without third phase formation. D_{Sr} at aqueous nitric acid concentration of 3.5 M for 0.3 M TEHDGA – 5% isodecyl alcohol/*n*-dodecane was reported to be 23.

We investigated the above concentration of 0.3 M TEHDGA – 5% isodecyl alcohol/*n*-dodecane for the co-extraction of Am(III) and Sr(II) from aqueous nitric acid solutions. It was observed that while D_{Sr} is 22, the uptake of Am(III) at 4 M HNO₃ by 0.3 M TEHDGA – 5% isodecyl alcohol/*n*-dodecane is very high with D_{Am} >1000. However, it was also observed that the high *D*value of Am(III) did not pose problems during its stripping and Am(III) could be recovered quantitatively from the loaded organic phase using 0.01M HNO₃ after the complete removal of Sr(II) first from the loaded organic phase. For a concentration of 0.4 M TEHDGA – 5% isodecyl alcohol/*n*-dodecane, $D_{Am(III)}$ >1000 and D_{Sr} = 40 were observed respectively at 4 M HNO₃. However, the stripping of Am(III) was found to be difficult from this composition of the loaded organic phase. Hence, in view of the above observations of good extraction for Am(III) and Sr(II), quantitative stripping of both the elements individually and no third phase formation, 0.3 M TEHDGA – 5% isodecyl alcohol/*n*-dodecane was optimized as the concentration for the coextraction of Am(III) and Sr(II) from high level liquid wastes.

Using 0.3 M TEHDGA – 5% isodecyl alcohol/*n*-dodecane, Sr(II) and Am(III) were co-extracted from an aqueous nitric acid solution of 4 M. The two elements were then stripped separately from the loaded organic phase. First, Sr(II) was stripped from the loaded organic phase using water soluble 18-crown-6 in the aqueous phase ensuring that Am(III) does not stripped along with Sr(II). The Sr(II) removed organic phase was then stripped using 0.01 M HNO₃ to recover Am(III) quantitatively.

4.2.2 Role of nitric acid concentration on Sr stripping

In the actinide partitioning process involving TEHDGA as solvent, quantitative stripping of the loaded trivalent lanthanides and Am(III) is achieved using 0.01 M HNO₃. In this method, stripping of Sr(II) alone using 18-crown-6 in aqueous phase cannot be achieved at a low or

negligible acidity of the aqueous phase. Under those conditions, Am(III) and other co-extracted lanthanides will also get stripped. Hence, 18-crown-6 is taken in an acidic aqueous phase for the exclusive stripping of Sr(II) from the loaded organic phase without any recovery of loaded trivalent lanthanides and Am(III).

Figure 4.1 shows the effect of initial aqueous phase acidity on the stripping of Sr(II) from loaded 0.3 M TEHDGA – 5% isodecyl alcohol/*n*-dodecane phase using 18-crown-6. It can be seen from the figure that with increase in aqueous phase acidity, stripping of Sr(II) by 18-crown-6 decreases. This phenomenon can be attributed to the increase protonation of the 18-crown-6 molecules at higher aqueous acidity, thereby rendering their binding sites unavailable towards binding with Sr(II), and consequently decreasing the Sr(II) stripped from the organic phase. It was also observed that when stripping of Sr(II) by 18-crown-6 was performed at an aqueous acidity of 3.5 M, about 2-3% Am(III) was stripped along with Sr(II).



Figure 4-1: Stripping of Sr(II) using 18-crown-6 as a function of initial aqueous phase nitric acid concentration

The stripping of Am(III) further increased as the acidity of the aqueous phase was decreased. Less than 1% stripping of Am(III) was observed when the nitric acid concentration in the strip solution was greater than 4 M. At 4 M nitric acid, almost 69.7 % Sr(II) was stripped in a single contact using 0.05 M 18-crown-6, whereas only 40% Sr(II) was recovered at 6 M nitric acid concentration for the same concentration of 18-crown-6. Hence, in view of the above observations, stripping of Sr(II) using 18-crown-6 from loaded organic phase was carried out at an initial nitric acid concentration of 4 M.

4.2.3 Kinetics of Sr stripping

The kinetics of stripping is an important factor which affects the stripping efficiency. Studies were carried out to investigate the kinetics of the stripping of Sr(II) from loaded 0.3 M TEHDGA – 5% isodecyl alcohol/*n*-dodecane phase by 0.05 M 18-crown-6 in 4 M HNO₃. The percentage of Sr(II) stripped was determined as a function of time as shown in **Figure 4.2**. It was observed that the stripping equilibrium was obtained in 25 minutes and the stripping percentage remained constant thereafter. Therefore, all equilibration experiments were carried out for a contact time of 30 minutes to ensure that the equilibrium was attained in each case.



Figure 4-2: Kinetics of Sr(II) stripping using 18-crown-6 in 4 M HNO₃

4.2.4 Effects of 18-crown-6 concentration on Sr Stripping

The effect of concentration of 18-crown-6 in 4 M nitric acid aqueous phase on the stripping of Sr(II) and Am(III) from loaded 0.3 M TEHDGA – 5% isodecyl alcohol/*n*-dodecane phase was also studied. For this purpose, four different concentrations, 0.005 M, 0.01 M, 0.05 M, and 0.1 M of 18-crown-6 in 4 M HNO₃ were investigated. The results obtained are shown in **Figure 4.3**. It was observed that with the increase in the concentration of 18-crown-6, the percentage of Sr(II) stripped from the organic phase increased from 19 % for 0.005 M [18-crown-6] to 83 % for 0.1 M [18-crown-6]. It was also observed that at 4 M HNO₃, though the stripping of Am(III) slightly increased with increasing concentration of 18-crown-6 in the aqueous phase, it was still less than 1% at all the aqueous concentrations of 18-crown-6 in 4 M HNO₃for Am(III) and Sr(II) separation.



Figure 4-3: Stripping of Sr(II) and Am(III) as a function of 18-crown-6 concentration 4.2.5 *Mechanism of Sr stripping*

It is known that 18-crown-6 is a neutral water soluble polydentate macro cyclic ether which binds through the oxygen atoms to the metal ion. It forms a stable complex with Sr(II) ion which fits well into the cavity of the 18-crown-6 polyether ring. Consequently, in the present extraction and stripping studies, 18-crown-6 forms a strong complex with the Sr(II) ion present in the loaded organic phase, and selectively strips it to the aqueous phase. The mechanism for the complexation and stripping of Sr(II) from loaded TEHDGA organic phase may be proposed as follows:

Sr(NO₃)₂.(TEHDGA)₂.(HNO₃)_{2(org.)}+m18-crown-6_(aq.) ← →

 $Sr(NO_3)_2.m18$ -crown- $6_{(aq.)}$ + 2HNO_{3(aq.)}+ 2TEHDGA_(org.)(4-1)

The stoichiometry of the Sr(II) complex formed with TEHDGA in the organic phase has been reported. An attempt was made by us to investigate the stoichiometry of the stripped Sr(II)-18-

crown-6 complex from TEHDGA organic phase, or, the value of 'm' in **Equation 4.1**. The equilibrium constant for the above reaction, K_{eq} , may be written as:

$$K_{eq.} = \frac{[Sr(NO_3)_2. m18-crown-6]_{(aq.)} [TEHDGA]^2_{(org.)} [HNO_3]^2_{(aq.)}}{[Sr(NO_3)_2. (TEHDGA)_2 (HNO_3)_2]_{(org.)} [18-crown-6]^m_{(aq.)}} ...(4-2)$$

The distribution co-efficient for Sr(II), D_{Sr} , can be defined as:

$$D_{\rm Sr} = \frac{[{\rm Sr}^{2+}]_{({\rm org.})}}{[{\rm Sr}^{2+}]_{({\rm aq.})}} = \frac{[{\rm Sr}({\rm NO}_3)_2.({\rm TEHDGA})_2({\rm HNO}_3)_2]_{({\rm org.})}}{[{\rm Sr}({\rm NO}_3)_2. \ {\rm m18-crown-6}]_{({\rm aq.})}} \dots (4-3)$$

Substituting Equation 4.3 in Equation 4.2, and rearranging the equation, we get the following:

$$D_{\rm Sr} = \frac{[{\rm TEHDGA}]^2_{(\rm org.)} [{\rm HNO}_3]^2_{(\rm aq.)}}{[{\rm 18-crown-6}]^m_{(\rm aq.)} K_{\rm eq.}} \dots (4-4)$$

Taking log of Equation 4.4 and rearranging the equation, we get the following:

$$logD_{Sr} = -m.log[18-crown-6]_{(aq.)} - (log K_{eq.} - 2 log [TEHDGA]_{(org.)} - 2 log [HNO_3]_{(aq.)})$$
....(4-5)

In order to determine the value of 'm' from equation 4.5, $D_{Sr(II)}$ was estimated at different concentrations of 18-crown-6 taken in 4 M HNO₃ and a logarithmic plot of $D_{Sr(II)}$ as a function of [18-crown-6] was plotted as shown in **Figure 4.4**.



Figure 4-4: Logarithmic Plot of *D*_{Sr(II)} versus [18-crown-6] to understand stoichiometry of complex

The slope of the log-log plot of $D_{Sr(II)}$ and [18-crown-6] gives the value of 'm' as deduced in Equation 4.5. From the plot, a slope of 0.98 was obtained. Therefore, 'm' is approximately equal to 1, which indicates the formation of a 1:1 complex between Sr(II) and the 18-crown-6 molecule

4.2.6 Determination of maximum stripping capacity

Studies were carried out to determine the maximum stripping capacity of the 18-crown-6 aqueous solution. For this purpose, the organic to aqueous ratio was gradually increased so that the Sr(II) concentration in the 0.3 M TEHDGA – 5% isodecyl alcohol/*n*-dodecane phase gradually increased from 900 ppm to 5400 ppm. This concentration range was so chosen to avoid the formation of third phase by the organic phase at high metal ion loading and high aqueous acidity. The loaded Sr(II) was then stripped using 0.005 M 18-crown-6 in 4 M HNO₃. The results obtained are shown in **Figure 4.5.** It was observed that initially the amount of Sr(II) stripped increases with increasing concentration of Sr(II) in the organic phase, and then becomes constant.

The maximum Sr(II) stripped by 0.005 M 18-crown-6 in 4 M HNO₃ is observed to be 450 ppm at higher concentrations of Sr(II) in the organic phase. This value is close to the theoretically calculated value of 440 ppm for Sr(II) uptake by 0.005 M 18-crown-6 assuming 1:1 complex formation. Therefore, this observation further validates the formation of a 1:1 complex between Sr(II) and the 18-crown-6 molecule while getting stripped into the aqueous phase.



Figure 4-5: Stripping of Sr(II) as a function of Sr(II) concentration in the organic phase

4.2.7 Recovery of Sr

Studies were carried out to investigate whether Sr(II) stripped using 18-crown-6 can be precipitated and hence recovered quantitatively. For this purpose, 0.05 M 18-crown-6 in 4 M HNO3 was loaded with 4500 ppm of Sr(II) which is the maximum amount of Sr(II) which can be stripped for this concentration of 18-crown-6 forming a 1:1 complex with it. To this solution, solid potassium sulfate was added to obtain a saturated solution of 0.69 M (120 g / L). From this saturated solution, precipitation of strontium sulfate was observed. The solubility product (K_{sp}) of Strontium Sulphate is 3.44 x 10⁻⁷ (mol/lit)². It was found that 80% of the Sr(II) was

precipitated as SrSO₄. This precipitation ensured further purification of Sr(II)from the traces of Am(III) and trivalent lanthanides co-stripped along with Sr(II), which remain in the strip solution. Precipitation of Sr(II) was also achieved by the addition of potassium carbonate to the strip solution. However, addition of potassium carbonate neutralized the acidic strip solution and effervescence was observed during precipitation. Therefore, the amount of potassium carbonate required for precipitating Sr(II) was higher and it was observed that on the addition of approximately 322 g/L(2.33 M) of potassium carbonate, 99.9% of the Sr(II) is precipitated as SrCO₃. Hence, these results established that the Sr(II) stripped using 18-crown-6 can be quantitatively recovered from the strip solution by precipitation.

4.2.8 Distribution of 18-crown-6

Since 18-crown-6 is a water soluble macro cyclic ether, hence it has been used in the aqueous phase as a stripant for Sr(II) in our studies. However, studies were also carried out by us to investigate the solubility of 18-crown-6 in the organic phase chosen for our experiments. For this purpose, different standard solutions of 18-crown-6 were prepared in 5% isodecyl alcohol/*n*-dodecane. To each solution, a fixed concentration of tri-*n*-butyl phosphate (TBP) was added as an internal standard and these solutions were analysed using GC-MS. The chromatogram obtained for the analysis of one such standard solution is as shown in **Figure 4.6(a)**. The retention times of TBP and 18-crown-6 were obtained as 12.7 min and 15.5 min respectively. From the chromatograms obtained for the standard solutions, the peak areas corresponding to TBP and 18-crown-6 were obtained.



Figure 4-6 : (a) GC-MS chromatogram of 18-crown-6 in 5% isodecyl alcohol/*n*-dodecane with TBP as internal standard; (b) GC-MS chromatogram of 0.3 M TEHDGA – 5% isodecyl alcohol/*n*-dodecane equilibrated with 0.1 M 18-crown-6 in 4 M HNO₃

The ratio of the peak areas of 18-crown-6 and the internal standard TBP were plotted with respect to the ratio of their respective concentrations in each standard solution to obtain a calibration curve as shown in Figure 4.7. In order to investigate the uptake of 18-crown-6 by the organic phase used in our extraction studies, a solution of 0.1 M 18-crown-6 in 4 M HNO₃ was equilibrated with an equal volume of 0.3 M TEHDGA -5% isodecyl alcohol/*n*-dodecane phase for 30 minutes. Post equilibration and separation of the two phases, the organic phase was analysed using GC-MS after the addition of internal standard TBP, and the chromatogram was obtained as shown in Figure 4.6 (b). From this chromatogram, the peak area corresponding to 18-crown-6 extracted into the organic phase was obtained. The concentration of 18-crown-6 present in the organic phase was then calculated by taking the ratio of its peak area to that of TBP and deducing the concentration from the calibration plot shown in Figure 4.7. From the calibration plot, the concentration of 18-crown-6 present in 0.3 M TEHDGA – 5% isodecyl alcohol/n-dodecane phase was obtained as 0.02 M for an initial aqueous concentration of 0.1 M 18-crown-6 in 4 M HNO₃. These results indicate a significant uptake of the stripant into the organic phase during stripping. To further investigate the above results, trace amount of ⁸⁵Sr was added to a solution of 0.1 M 18-crown-6 in 4 M HNO₃, which was then equilibrated with 5% isodecyl alcohol/n-dodecane for 30 minutes. It was observed that there was no uptake of Sr(II) by the above organic phase indicating that while 18-crown-6 has some finite solubility in the organic phase owing to the presence of a polar diluent isodecyl alcohol, its complex with Sr(II), Sr(NO₃)₂.18-crown-6, has no solubility in the organic phase and remains in the aqueous nitric acid medium. Hence, the solubility of 18-crown-6 in the organic phase does not interfere with the efficient stripping of Sr(II) from the loaded organic phase.



Figure 4-7: Calibration curve for the estimation of concentration of 18-crown-6 in 5% isodecyl alcohol/*n*-dodecane phase using internal standard TBP

4.2.9 Selectivity of striping

Studies were also carried out to determine the extraction and stripping of some other fission elements in order to understand their interference, if any, in the above described processes. For this purpose, elements Zr(IV), Mo(VI), Ru(III), and Nd(III) (as a representative element for trivalent lanthanides) were investigated for their possible co-extraction and co-stripping along with the target elements, Sr(II) and Am(III). These metal ions were chosen for the studies as these are the predominant fission products present in the HLW and important contributors to the beta and gamma radiations. These elements along with Sr(II) and Am(III) were first extracted using 0.3 M TEHDGA – 5% isodecyl alcohol/*n*-dodecane from 4 M HNO₃, followed by stripping with 0.05 M 18-crown-6 in 4 M HNO₃ for selective Sr(II) recovery, and subsequently stripping with 0.01 M HNO₃ for the recovery of Am(III) and trivalent lanthanides. The results obtained for the above studies are shown in **Table 4.1**.

Table 4-1: Extraction and stripping of Am(III), Sr(II) and other fission products

Extractant: 0.3 M TEHDGA - 5% Isodecyl alcohol/*n*-dodecane Aqueous Feed:Am(III), Ru(III), Mo(VI), Zr(IV), Nd(III) and Sr(II) in 4 M HNO₃ (298 K, 30 min equilibration, O/A: 1:1) Strippant I: 0.1 M 18-crown-6 in 4 M HNO₃ Strippant II: 0.01 M HNO₃

Metal Ion	Feed, ppm	Raffinate, ppm	Strip I, ppm	Strip II, ppm
Sr(II)	100	11	74	13
Am(III)	Tracer	N. D.	0.8%	99.2%
Ru(III)	72.1	62	N. D.	6.5
Mo(VI)	102.2	27	N. D.	76
Zr(IV)	42	1.2	N. D.	0
Nd(III)	84.5	N. D.	0.7	82.1

From **Table 4.1**, it can be seen that in a single contact of extraction for O/A = 1:1, the extraction by 0.3 M TEHDGA – 5% isodecyl alcohol/*n*-dodecane for each element are as follows: Sr (89%), Am (100%), Nd (100%), Zr (94%), Mo(74%), and Ru(14%). Stripping of the loaded organic phase with 0.1 M 18-crown-6 in 4 M HNO₃ resulted in a Sr(II) recovery of 83% in a single contact. The extracted elements Zr(VI), Mo(IV), and Ru(III) did not strip along with Sr(II), whereas both Am(III) and Nd(III) stripped to about 0.8%.

It was also observed that almost 99% stripping of Sr(II) can be achieved by giving three contacts of the stripant 18-crown-6. Further precipitation of Sr(II) from the strip solution as described earlier ensures further purification of it from the traces of Am(III) and trivalent lanthanides present in the strip solution. Stripping of the Sr(II) stripped organic phase with 0.01 M HNO₃ resulted in the complete recovery of loaded Am(III), Nd(III), and Mo(IV). About 64% of the loaded Ru(III) was also recovered, whereas Zr(VI) did not strip and remained in the organic

phase. It has been reported that scrubbing of the loaded organic phase with 0.2 M oxalic acid - 0.05 M HEDTA in 4 M HNO₃ back-extracts Mo(IV) and Zr(VI) almost completely, which then prevents the stripping of these elements along with Am(III) and trivalent lanthanides when using 0.01 M HNO₃. Hence, in view of the above results, it can be said that the fission products do not interfere in the stripping of Sr(II) with 18-crown-6, and this method can be successfully applied for the extraction and separation of Sr(II) and Am(III) from actual HLW. Based on the studies conducted by us, an optimized process flow sheet for separation of Am(III) and Sr(II) from the HLW is shown in **Figure 4.8**.



Figure 4-8: Optimized process flow sheet for separation of Am(III) and Sr(II) from HLW

4.3 Separation of Sr using TEHDGA-Supported liquid membrane studies

Solvent extraction processes suffer from third phase formation, large volume of secondary waste generation, handling of large volumes of solvent large volume of inflammable diluents. Quest for environmentally benign techniques have led to the development of various greener technologies like supported liquid membrane where requirement of solvent is minimal. SLM based techniques have also been very useful for separation of radionuclides like U, Pu and Am where the concentration of radionuclides are very low as of the order of ppm.

Pyrex glass cell consisting of two compartments (volume 6 mL each) was used for SLM transport experiments. The effective area of the membrane flat sheet was determined and found to be 2.50 cm^2 . The feed and strip solutions were stirred at 250 rpm to prevent concentration polarization between membrane interfaces and bulk of the solutions. Transport of hydrogen ion was monitored by volumetric titrations. The transport studies were carried out at ambient temperatures (24-26°C). In all cases 0.05 M 18-Crown-6 in 4 M nitric acid was added in feed and 0.01 M nitric acid was used as stripant. The PTFE membranes were soaked in the carrier solution (0.3 M TEHDGA + 5% IDA/n-dodecane) for 60 minutes. During experiments, aliquots were removed from the feed as well as the receiver compartments at regular intervals and analyzed radiometrically using high purity germanium detector coupled with 8K MCA analyzer. Measured radionuclide concentration of feed and stripant solution were used to calculate the transport of radionuclides using following equation:

$$\%T = \frac{C_{r,t}}{C_{f,0}} x100$$
(4.6)

94

where, Cr,t is the concentration of the metal ion in the receiver phase at a given time 't'.

The transport of metal ion through SLM partly depends on physical properties of membrane such as membrane pore size, membrane thickness and tortuosity of membrane. More importantly, the relative complexation properties of metal ions with ligand played major role towards separation of metal ion. Emphasis has therefore been placed in present study includes development of process and optimization of process parameters for the separation of Sr(II) from Eu(III). This was attempted by employing highly Sr(II) selective ligand, 18-crown-6 along with carrier molecule, TEHDGA. Notably, Eu(III) used here as a representative of Am(III) owing to similar chemical properties of both the elements under present experimental conditions. For further purification of Am(III) from Sr(II), SLM was considered as most suitable technique as diffusion controlled mechanism can be utilised for transport of the metal ion. In line with earlier solvent extraction studies TEHDGA is used here as carrier molecule. Upon contact with TEHDGA, the complexes of Am(III) and Sr(II) formed during extraction (4 M nitric acid) can be represented as in **Figure 4.9** below:



Figure 4-9: Representative structure of (a) Am(III)-TEHDGA (b) Sr(II)-TEHDGA complex

The metal ions are then subsequently be stripped to stripant solution (0.01 M nitric acid). In view of the relative stability of the complexes and their different diffusion rate, a significant different in transport can be expected. However, during our SLM studies, using only TEHDGA as carrier molecule, no separation has been observed. Further experiments was therefore carried out by addition of 18-crown-6 in the feed compartment. This was done with expectation that Sr(II) will form a stable Sr-Crown ether complex (**Figure 4.10**).



Figure 4-10: Sr(II)- 18crown6 complex

Since the stability of Sr(II)-Crown ether complex is more than Sr-TEHDGA complex, the probability of Sr(II) transport is expected to be decreased and hence better separation can be achieved. Indeed, results in-line with our expectation. Under this condition, process parameters were optimised and results are presented below.

4.3.1 Optimizing the membrane parameters

Table 4.2 depicts the results of Eu(III) and Sr(II) transport as a function of membrane pore size. For the case of membrane having pore size $0.45 \ \mu m$ (lowest membrane pore size tested), about 99.6% for Eu(III)and 7% for Sr(II) was found to be transported through SLM in 60 minutes. Separation of these two radio nuclides can be attributed to the formation of stronger Sr-crown ether complex. The membrane of higher pore size employed in this study has poor transport for both the radionuclides. This is possibly due to leaching of carrier molecules from membrane. Based on these results 0.45 μ m membrane has been selected for further process optimization studies.

Membrane pore size (µm)	Eu transport (%)	Sr transport (%)
0.45	99.6	7.0
1.2	90.2	6.4
5	86.1	6.1

Table 4-2: Effect of membrane pore size on Am(III) and Sr(II) transport

Membrane thickness is one of the important parameters needs to be optimized in SLM studies. A thicker membrane can accommodate more carrier molecule. As transport of metal ion proceeds through diffusion controlled mechanism the presence of large pool of solvent molecule may results in better separation. On the other hand, higher membrane thickness may lead to diffusional resistance across the membrane and resulting in decreases in metal ion transport rate. To optimize this parameter, the effect of membrane thickness on metal ion transport was studied using membranes having pore size of $0.45 \,\mu\text{m}$ and varying thickness ranging from 80 to 320 μm . **Table 4.3** shows the effect of membrane thickness on metal ion transport.

Membrane thickness (µm)	Eu transport (%)	Sr transport (%)
80	99.6	7.0
160	93.1	6.6
240	89.5	6.4
320	87.2	6.2

Table 4-3: Effect of membrane thickness on Am(III) and Sr(II) transport

It can be seen that transport of Eu(III) decreases steadily with the increase in membrane thickness while the Sr(II) transport remains unaltered. This shows the diffusional resistance across the membrane played crucial role in metal ion transport. Based on the above results the membrane porosity of 0.45 μ m and thickness of 80 μ m was optimized. The optimized membrane characteristics are summarized in **Table 4.4** for reference.

Table 4-4: Various physical parameters of membrane

Properties	Value
Pore Size (µm)	0.45
Thickness (µm)	80
Porosity, π	0.64
Tortuosity, T	1.44

4.3.2 Kinetics of transport

Figure 4.11 shows the results of metal ion transport rate as a function of time. Almost 99.6 % of Eu(III) was transported to strip solution within 60 minutes and thereafter remained constant till

end of experiment duration, i.e. 240 minutes. Whereas a low amount of Sr(II) (~ 7 %) was transported in initial 60 minutes. The rate of Sr(II) transport was found to increase continuously and reached ~21% after 240 minutes. The results indicate that termination of experiment after 60 minutes would result in a Sr(II) rich feed solution, which is almost free from Eu(III) contamination.



Figure 4-11: Kinetics of Eu(III) and Sr(II) transport using TEHDGA as carrier molecule and 18-crown-6 as complexing agent for Sr(II)

4.3.3 Role of nitric acid on metal ion transport

Effect of feed nitric acid concentration on the metal ion transport was studied by varying the nitric acid concentration ranging from 2 to 6 M. The other parameters such as crown ether concentration in feed, stripant (0.01 M nitric acid) and membrane composition have been kept same. Result of metal ion transport as a function of nitric acid concentration is shown in **Figure 4.12**.



Figure 4-12: Aqueous feed acid dependency of Eu(III) and Sr(II) transport using TEHDGA as carrier molecule and 18-crown-6 as complexing agent for Sr(II)

The transport of Sr(II) was found to increase slowly with the increase in nitric acid concentration in feed. The increase in Sr(II) transport can be explained by increase in protonation of 18-corwn-6 with increase in nitric acid concentration and hence resulting in poor coordination between Sr(II) and 18-Crown-6. At lower feed acidity of ~2 M nitric acid, Sr(II) transport was as low as ~5 %, ensuring stable complexation between Sr(II) and 18-Crown-6. Under the conditions the nature of Eu(III) transport was found to be different from Sr(II) transport. Initially, up to 4 M acidity, a steep rise of Eu(III) transport was noted and thereafter it decreases. This is also in accordance with the complexation behavior of Eu(III) with TEHDGA as a function of acidity if the medium. Below 4 M acidity, salting out effect of nitric acid resulted in higher transport. At higher acidity, TEHDGA forms adduct with nitric acid. Thus, free concentration of TEHDGA available for complexation with Eu(III) decreases which resulted in poor transport of Eu(III). It was also observed that at higher feed acidity nitric acid transport increases resulting in increase in stripant acidity, which may possibly be responsible for the decrease in Eu(III) transport.

4.3.4 Effect of 18-Crown-6 on metal ion transport

Figure 4.13 depicts the effect of 18-crown-6 concentration on the transport of Eu(III) and Sr(II). Feed solution used in this study was prepared by adding varying concentration of 18-crown-6 to a mixture of Sr(II) and Eu(III) at nitric acid concentration of 4 M. Sr(II) transport was found to decrease with increase of 18-crown-6concentration in feed. The Sr(NO₃)₂-18-crown-6 complex (Fig.4.10) is not extracted by 0.3 M TEHDGA in 5% IDA + *n*-dd as revealed in our earlier studies. Hence the decrease in Sr(II) transport can be attributed to lesser availability of free Sr(II) at higher 18-Crown-6 concentration. At 0.1 M 18-Crown-6 concentration Sr(II) transport was as low as 3%. It was also found that Eu(III) transport is independent of 18-Crown-6 concentration and remains almost constant for all concentration studied.

Results of above SLM studies also opens up the possibility of Sr recovery from feed compartment after complete transport of Eu(III). For this purpose, solid potassium carbonate was added to feed solution containing 0.05 M both 18-crown-6 and Sr(II) in 4 M HNO₃. Solid potassium carbonate was added to completely saturate the solution which initially neutralizes nitric acid and then precipitation of strontium carbonate was observed. It was found that more than 99% of the Sr(II) was precipitated as SrCO₃. Higher concentration of 18-crown-6 (0.1M) hinders Sr(II) precipitation and results in poor recovery. This method provides final purification of Sr(II) from the traces of Eu(III). The precipitate was filtered off and filtrate was contacted with dichloromethane to recover 18-Crown-6. Dichloromethane phase was evaporated to dryness to get back 18-Crown-6.



Figure 4-13: 18-Crown-6 concentration dependency of Eu(III) and Sr(II) transport using TEHDGA as carrier molecule and 18-crown-6 as complexing agent for Sr(II)

4.4 Study on Tc separation using TEHDGA

Apart from Sr(II), ⁹⁹Tc is also co-extracted along with minor actinides for TODGA solvent system during actinide partitioning. Another glycolamides namely TEHDGA is currently used for actinide partitioning. No detailed study on Tc (VII) extraction has been studied under HLLW condition has been reported earlier. We have carried our detailed solvent extraction studies pertaining to extraction of ⁹⁹Tc with TEHDGA. Different parameters like effect of acidity, effect of interfering metal ion, nitrate ion concentration and kinetics of extraction were studied to develop a process flow sheet for separation of technetium.

4.4.1 Role of nitric acid concentration

Prior to evaluating distribution behavior of Tc(VII) with respect to various parameters, extraction of Tc(VII) was studied at different equilibration time, the kinetics of extraction was very fast and equilibrium was achieved within 10 minutes. Hence, for all the experiments contact time was kept as 30 minute to ensure complete attainment of equilibrium. Extraction of Tc(VII) as a function of nitric acid concentration for solvent 0.3 M TEHDGA + 5 % IDA/*n*-dodecane is shown in **Figure 4.14**.



Figure 4-14: Extraction of Tc(VII) using TEHDGA as a function of initial aqueous phase nitric acid concentration

 D_{Tc} value increases with increase in nitric acid concentration up to 0.5 M nitric acid (D_{Tc} = 50.21), thereafter D_{Tc} decreases and only 2.01 is obtained at 4 M nitric acid. The same trend of Tc(VII) extraction from nitric acid medium was observed for other neutral solvents like TBP or DHOA.

As TcO_4^- is having low hydration energy compared to nitrate therefore it gets easily extracted at lower nitric acid concentration. However, with increase in nitric acid concentration D_{Tc} value falls off rapidly because of exchange of TcO_4^- with nitrate ion. Probable extraction mechanism could be solvation of $HTcO_4$ which at higher acidity is replaced by HNO_3 molecules. The extent of extraction of Tc(VII) found in our studies are quite similar to D_{Tc} value reported by Zhi-Xuan Zhu etal. Using another well studied glycolamide, TODGA. The D_{Tc} value reported for a solvent composition of 0.1 M TODGA in *n*-dodecane is ~ 1.2 for a feed acidity of 2.9 M nitric acid, which is 1.4 for TEHDGA under same solvent composition and feed acidity.

4.4.2 Role of nitrate ion on Tc extraction

To elaborate more on detrimental effect of high nitric acid and nitrate ion concentration on extraction of Tc(VII), D_{Tc} was determined at feed acidity of 0.5, 2.0 and 4.0 M nitric acid with increase in nitrate concentration by addition of sodium nitrate salt and the plot is shown in **Figure 4.15**. D_{Tc} is found to decrease with increase in nitrate concentration for all the nitric acid concentrations mainly due to exchange of pertechnetate ion by nitrate and also by increase in uptake of nitric acid by TEHDGA at higher nitrate concentrations.



Figure 4-15: Extraction of Tc(VII) as a function of nitrate ion concentration

Nitric acid uptake of 0.3 M TEHDGA+5% IDA/*n*-dodecane for feed acidity of 4 M nitric acid at different sodium nitrate concentration is shown in **Table 4.15**. It is found that with increase in sodium nitrate concentration, extraction of nitric acid increases, at 4 M sodium nitrate concentration, nitric acid in the organic phase is about 1.31 M while it is only 0.66 M in absence of any sodium nitrate salt. This is explained by salting out effect of sodium nitrate. More acid extraction leads to decrease in Tc(VII) extraction with increase in sodium nitrate concentration.

Table 4-5: Effect of	of sodium nitrat	e on uptake c	of nitric acid by	TEHDGA.	Organic I	hase: 0.3	M
TEHDGA + 5	5 isodecyl alcoh	ol/n-dodecan	e; Aqueous Ph	ase: 4 M nitr	ric acid +	NaNO3.	

HNO3 (M)aq	NaNO3[M]aq	HNO ₃ (M) org
4	0	0.66
4	1	0.86
4	2	1.02
4	3	1.15
4	4	1.31

4.4.3 Mechanism of extraction

Figure 4.16 shows the log-log plot of D_{Tc} vs. nitrate concentration of sodium nitrate at 2 M nitric acid exhibiting a linear decrease with a slope of -1, suggesting the exchange of TcO₄⁻ by one mole of NO₃⁻ ion in the extraction process. Experimental results indicated exchange of TcO₄⁻ with nitrate ion or HNO₃.



Figure 4-16: log [D] versus log [NO₃-] plot for Tc(VII) extraction

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To gain an insight into the stoichiometry of complex between TEHDGA and HTcO₄, dependence of D_{Tc} on TEHDGA concentration was determined. Typical log-log plot of D_{Tc} vs. TEHDGA concentration is shown in **Figure 4.17.**The slope of this plot is found to be 1 indicating a 1:1 complex between TEHDGA and HTcO₄. In acidic solution Tc(VII) exists as HTcO₄, it is extracted by interaction with basic amidic moiety of TEHDGA molecule resulting in formation of solvated adduct as HTcO₄.TEHDGA. For monodentate solvating ligands like TBP or DOHA, formation of a 3:1 complex with HTcO₄ was observed where as in the present case because of higher denticity of TEHDGA the stoichiometric ratio is found to be less. The stoichiometry of complexation is found to be independent of nitric acid concentration whereas in case of TBP or DOHA stoichiometry changed with nitric acid concentration.



Figure 4-17: log [D] versus log [TEHDGA] plot for Tc(VII) extraction

Based on the above results of log-log plots, extraction mechanism at lower acidity up to 0.5 M proceeds as adduct formation:

$$TcO_4_{aq} + H^+_{aq} + TEHDGA_{org} \longrightarrow HTcO_4.TEHDGA_{org}$$

Whereas, at higher acidity above 0.5 M nitric acid, decrease in extraction of Tc(VII) takes place due to extraction of nitric acid over HTcO₄ and also with increase in nitrate ion concentration extraction of technetium decreases due to exchange of TcO_4^- with nitrate ion. The reaction would then proceeds as:

$$HTcO_4.TEHDGA_{org} + HNO_3 \overleftrightarrow HNO_3.TEHDGA + HTcO_4$$
$$HTcO_4.TEHDGA_{org} + NO_3^{-} \overleftrightarrow HNO_3.TEHDGA + TcO_4^{-}$$

Where the subscript 'org' refers to species in organic phase and 'aq' subscript refers to those present in aqueous phase.

4.4.4 Role of phase modifier in Tc extraction

Glycolamide based solvents are prone to third phase formation during extraction at higher nitric acid concentration and in the presence of high amount of extractable species. To mitigate the third phase formation, phase modifier like isodecyl alcohol (IDA) has been used while constituting TEHDGA solvent. The role of IDA concentration on HTcO₄ extraction has been studied and shown in **Figure 4.18**. It is observed that with increase in IDA concentration up to 50% v/v, D_{Tc} remained constant. In our earlier studies on extraction of Am(III) and Sr(II) with TEHDGA/IDA/*n*-dodecane solvent we have reported a decrease in extraction of these metal ions with increase in IDA concentration in the solvent phase due to intermolecular hydrogen bonding between TEHDGA and IDA which results in decrease of donor sites of TEHDGA molecule. However, in the present case due to strong acid-base interaction between HTcO₄ and TEHDGA the role of IDA in decreasing the extraction of HTcO₄ is negligible; rather it helps in solvation of HTcO₄ due to its high polarity.


Figure 4-18: Extraction of Tc(VII) as a function of IDA concentration

Stripping of TcO_4^- from loaded solvent was studied with deionized water and dilute sodium hydroxide solution. Five contacts of deionized water at 1:1 phase ratio was needed to strip about 99% of loaded technetium, while three contacts with 0.1 M NaOH resulted in complete stripping of technetium from loaded solvent.

4.4.5 Extraction of other metal ions

Based on the above experiments a flow sheet is designed for removal of Tc(VII) from acidic intermediate level waste. TEHDGA is characterized for high extraction of trivalent actinides, lanthanides and relatively low extraction for strontium, zirconium and molybdenum from nitric acid medium. The composition of the solution and distribution ratio of each metal ion (D_M) is shown in **Table 4.6.** It was found that only Mo(VI) is co-extracted significantly while other metal species are extracted to a lesser extend their distribution ratio varies from 0.08 for Sr(II) to 0.8 for Am(III).

Table 4-6: Results of test run with optimized flow sheet for extraction of Tc(VII) Extractant: 0.3 M TEHDGA + 5% isodecyl alcohol/*n*-dodecane Aqueous Feed: Tc(VII), Ru(III), Mo(VI),Zr(IV), Nd(III) and Sr(II) in 0.5 M HNO₃ (298 K, 30 min equilibration, O/A: 1:1)

Metal Ion	Feed (mg/L)	D _{M(Ext)}	% Stripping
Tc(VII)	Tracer (~10 ⁻⁷ M)	30.16	99.7
Mo(VI)	11.2	2.0	98.5
Nd(III)	2	0.45	99.5
Fe(III)	4140	0.06	>99
Ru(III)	40	0.18	>99
Sr(II)	1.6	0.08	>99
Cs(I)	5.2	0.01	>99
Na(I)	2500	<0.01	>99

4.5 Summary of the results

Separation of Tc and Sr is achieved using same TEHDGA solvent system used in actinide partitioning process and results are as follows:

 Minor actinides Am/ lanthanides are co-extracted along with Sr using a modified solvent composition of TEHDGA. Sr is selectively stripped leaving minor actinides in the organic phase using a water soluble crown ether namely 18-crown-6.

- 2. Experimental conditions were optimized for quantitative recovery of Sr with minimum contamination from other radionuclides.
- 3. The mechanism of Sr with crown ether was established and it was found that stoichiometry of the complex is 1:1. Kinetics of the stripping is fast and equilibrium is achieved within 30 minutes.
- Process was validated with simulated HLW solution. Sr can be recovered from the strip solution using precipitation method. Process has also been developed for recovery of 18crown-6 from the strip solution.
- 5. The same process was tested in supported liquid membrane mode and it was observed that the desired separation can be achieved by this process also. The properties of the membrane were optimized for better Eu and Sr separation.
- 6. Process developed opens up the possibility of separating Sr in radiochemically pure form using the same solvent system employed n actinide partitioning.
- 7. The TEHDGA solvent composition was found to extract Tc from 0.5 M nitric acid medium with a D value of 57. Extraction is higher compared to other neutral ligands reported in the literature.
- Mechanism of extraction was established for Tc extraction and it was found that HTcO4 is extracted by TEHDGA by forming an adduct through hydrogen bonding.
- 9. Extraction of other metal ions at low acidity was tested and results shows significant amount of Mo is co-extracted along with Tc.
- 10. It was concluded that Tc can be extracted using TEHDGA solvent system by changing the feed nitric acid concentration to lower values 0.5 to 1.0 M.

5 Chapter 5: Separation of Trivalent Actinides from Sr(II) using BEHGA

Chapter 5 Separation of Trivalent actinides from Sr(II) using BEHGA

5.1 Introduction

In actinide partitioning process using glycolamides (TEHDGA), co-extraction of Sr(II) along with lanthanides and minor actinides is accomplished. This aspect has elaborately been discussed in Chapter 1 and Chapter 4 of the present thesis. The prerequisite for minor actinides management is that it has to be separated from Sr and lanthanides before their transmutation in fast reactor or in ADS. In chapter 4, separation of Sr from bulk of trivalent actinides and lanthanides was addressed by selective stripping of Sr(II) from loaded TEHDGA phase using water soluble 18-crown-6. Though the process has high efficiency in separation of Sr(II) from minor actinides but this increases process steps and generate high volume of secondary waste. Hence attempt was made to synthesize a ligand which can selectively extract minor actinides and lanthanides over Strontium. Towards this a new ligand Bis 2-ethylhexyl glycolamide (BEHGA) was synthesized and tested for this purpose. The results of ligand synthesis, characterization and solvent extraction studies have been discussed in this chapter.

5.2 Synthesis of BEHGA

The ligand, BEGHA, has been synthesized by following procedure. In the first step, α -chloro N, N di-2-ethyl hexyl acetamide (2.1 mol) was reacted with sodium acetate. In the next step, the acetate substituted product was hydrolyzed using sodium hydroxide in methanol. The structural formula of the compound is presented in Figure 5.1.



Figure 5-1: Structure of BEHGA

5.3 Characterization

5.3.1 GC-MS

The ligand was characterized by GCMS and FTIR. The GCMS spectrum has been shown in **Figure 5.2.** The chromatogram has two major peaks one at 17.35 minutes (peak area ~4%) and another at 18.95 minutes (peak area ~96%). Peak corresponding to BEHGA is the second one as confirmed from the MS spectrum. The overall purity of the compound 96% as observed from the chromatogram. **Figure 5.3** shows the Mass spectrum of BEHGA and it can be found that the m/z +1 peak of the compound is 300 with base peak at 102.



Figure 5-2: Gas chromatogram of BEHGA



Figure 5-3: Mass spectrum of BEHGA

5.3.2 FTIR

The FTIR spectrum of the compound is shown in **Figure 5.4.** The major peak observed in the spectrum are 3408 cm⁻¹(O-H stretching), 1649 cm⁻¹ (amide stretching), and 2948 cm⁻¹(C-H

stretching). The presence of free –OH and Carbonyl functional group which can bind with metal ion is confirmed from the FTIR analysis. Apart from this several other peaks are found in the spectrum which is not important for the present study.



Figure 5-4: FTIR spectrum of BEHGA

5.4 Solvent Extraction Studies

5.4.1 Role of ligand concentration on metal ion extraction

After confirming the purity, the ligand is tested for extraction of metal ions from nitric acid solution. Prior to evaluating the distribution ratios with respect to various parameters, the time of equilibration for Am(III) from 4 M HNO₃ for 0.3 M BEHGA/*n*-dodecane was investigated. It was observed that the extraction equilibrium was attained within 5 minutes of contact time, and the D_{Am} remained constant thereafter. Therefore, all other extraction experiments were carried out for a contact time of 15 minutes to ensure that the equilibrium is reached. Experiments were

carried out to determine the distribution ratio for Am(III) and Eu(III) as a function of BEHGA concentration. Figure. 5.5 shows the variation of D_{Am} and D_{Eu} with the variation in the BEHGA concentration at a constant aqueous HNO3 concentration of 4 M. It was observed that at 4 M HNO₃, D for both Eu(III) and Am(III) increases with increase in glycolamide concentration. For 0.3 M BEHGA/n-dodecane system at 4 M HNO₃, D_{Am} and D_{Eu} were observed to be 10 and 8 respectively. Therefore, BEHGA, though a monoamide, showed a high extraction ability for Am(III) and Eu(III). It is of interest to known which property of BEHGA is helping for high extraction of these metal ions. Replacing the α -OH of BEHGA with α -OMe or α -OEt, as in N, N-bis(2-ethylhexyl)-2-methoxyacetamide or N, N-bis(2-ethylhexyl)-2-ethoxyacetamide, did not results in any extraction of Am(III) or other metal ions. Therefore, it is the effect of α -OH and C=O together acting as a bidentate donor sites responsible for bonding. Thus, it is proposed that intra-molecular hydrogen bonding between the α-OH and C=O group in BEHGA forms a preorganised five membered rigid structure which possibly retains its geometry during complex formation with trivalent actinides and lanthanides, thereby favouring extraction. The absence of hydrogen bonding and pre-organised binding sites as in case of methoxy and ethoxy homologues of BEHGA did not results in any extraction.



Figure 5-5: Plot of D for Am(III) and Eu(III) as a function of BEHGA concentration

5.4.2 Effect of Nitric acid Concentration

Further, the effect of aqueous nitric acid concentration on the uptake of Am(III) and Eu(III) by 0.3 M BEHGA/*n*-dodecane was examined as shown in **Figure.5.6**. It was observed that the *D* values obtained for both Am(III) and Eu(III) were very low (< 0.5) up to 2 M aqueous HNO₃ and increased rapidly thereafter with an increase in aqueous HNO₃ concentration. In fact, strong extraction of Am(III) was observed at high HNO₃ concentration of 8 M, where D_{Am} and D_{Eu} were observed to be close to 400. This indicates the possible participation of HNO₃in complex formation which favours extraction of metal ions at higher concentrations. The very low *D* values obtained at low aqueous HNO₃ up to 2 M for 0.3 M BEHGA/*n*-dodecane indicate that the extracted metal ions can be stripped easily at lower aqueous acidity. Hence, based on these

observations, the extracted Am(III) and Eu(III) were back extracted quantitatively (99%) from the loaded organic phase using 0.01 M HNO₃ in a single contact.



Figure 5-6: Plot of D for Am(III) and Eu(III) as a function of aqueous nitric acid concentration for 0.3 M BEHGA/ n-dodecane

5.4.3 Third phase formation

It was observed that 0.3 M BEHGA/*n*-dodecane did not form a third phase at high acid or high metal loading. Hence, the use of a phase modifier to prevent third phase formation may not be necessary in this case. This was an advantage over TEHDGA which forms third phase and requires a phase modifier such as isodecyl alcohol during the extraction of trivalent lanthanides and actinides. Since, third phase formation cannot be ruled out at extreme conditions of high metal loading and high nitric acid concentrations, the effect of the phase modifier, isodecyl alcohol, commonly used in our actinide separation programme with TEHDGA on the uptake of Am(III) by 0.3 M BEHGA/*n*-dodecane was also examined. **Figure. 5.7** shows the variation of

 D_{Am} for 0.3 M BEHGA + isodecyl alcohol/*n*-dodecane system with an increase in isodecyl alcohol concentration in the organic phase. It was observed that D_{Am} decreased with an increase in the volume percentage of isodecyl alcohol in the organic phase. This may be attributed to the disruption in the intramolecular hydrogen bonding in BEHGA molecules due to isodecyl alcohol, also a hydrogen bonding reagent, thus resulting in the disruption of the pre-organised binding sites necessary for metal ion complexation and extraction.



Figure 5-7: Role of IDA in Am/Eu extraction with BEHGA

5.4.4 Mechanism of Extraction

An attempt was made to evaluate the nature of the complex extracted during the extraction of trivalent actinides and lanthanides by BEHGA. In order to find out the stoichiometry of the metalextractant complex i.e., the number of extractant molecules bonded to each metal ion in the metalextractant complex, the slope of the log-log plot of D versus the extractant or BEHGA concentration for Am(III) was determined as shown in **Figure 5.8**. From the figure, it is seen that the plot of log D_{Am} versus log BEHGA concentration gives a straight line with a slope equal to 4. This, therefore, indicates that four molecules of BEHGA co-ordinate to each Am(III) ion.



Figure 5-8: Log plot of DAm(III) as a function of glycolamide concentration

Similarly, the plot of log D_{Am} versus log NO₃⁻ concentration gives a straight line with a slope closer to 3, indicating that 3 NO₃⁻ ions take part in complexation in the presence of HNO₃. The plot of log D_{Am} versus log HNO₃ concentration at constant ionic strength of 4 M (H+Na)NO₃gives a straight line with a slope closer to 2 as shown in **Figure 5.9**, suggesting the presence of nearly 2 nitric acid molecules in the extracted complex.



Figure 5-9: Log plot of $D_{Am(III)}$ as a function of HNO₃ concentration for constant ionic strength This, therefore, confirms that neutral HNO₃ molecules contribute to the extraction reaction and hence the influence of aqueous nitric acid concentration on the extraction process becomes significant at higher nitric acid concentration. Based on these results, the extraction of Am(III) by BEHGA in aqueous nitric acid medium can be written as:

$$Am^{3+}(aq.) + 4 BEHGA(org.) + 2 HNO_{3}(aq.) + 3 NO_{3}(aq.) \implies Am(NO_{3})_{3}.4BEHGA.2HNO_{3}(org.)$$

5.4.5 Selectivity of extraction

Among fission products, some of them such as Sr(II), Ru(III), Zr(IV) and Mo(VI), usually extracted by glycolamide based ligands, were investigated for extraction with 0.3 M BEHGA/*n*dodecane. At 4 M HNO₃, it was observed that Sr(II) and Ru(III) were not extracted ($D_{Sr(II)} = 0.01$ and $D_{Ru(III)} = 0.07$) while Zr(IV) and Mo(VI) have very high distribution coefficients ($D_{Zr(IV)}$, and $D_{Mo(VI)} > 500$). The extracted Zr(IV) and Mo(VI) were also held very strongly by the organic phase and were not stripped with 0.01 M HNO₃. Complete stripping of the extracted Zr(IV) and Mo(VI) could be achieved only by using 0.2 M oxalic acid + 0.5 M NaNO₃ at 0.2 M HNO₃ in three contacts at 1:1 organic to aqueous ratio.

Element	D
Am (tracer)	10.4
Nd	8.84
Sr	0.01
Ru(III)	0.07
Zr	>500
Мо	>500

Table 5-1: Extraction of fission products with 0.3 M BEHGA/n-dodecane

5.4.6 Separation between Eu and Sr

The Sr extraction was carried out with different concentration of BEHGA at 4 M nitric acid and the separation factor is calculated as shown in **Figure 5.10.** For this purpose, both ¹⁵²⁺¹⁵⁴Eu and ⁸⁵⁺⁸⁹Sr tracer solution was added to 4 M nitric acid (final concentration of metal ion ~10⁻⁷ M) and contacted with BEHGA solution for 30 minutes in glass vials. As both Sr and Eu are poorly extracted at low BEHGA concentration hence separation factor is low at this end and it increases with BEHGA concentration. This signifies that Sr extraction does not increase with increase in BEHGA concentration.



Figure 5-10: Selective extraction of Eu over Sr at different BEHGA concentration

High level liquid waste contains significant amount of inactive salt mostly sodium nitrate. It plays crucial role in extraction of metal ion during solvent extraction. Hence extraction of Eu and Sr was carried out after adding sodium nitrate in the feed solution. D values were measured for both Sr and Eu for different sodium nitrate concentration ranging from 0 to 2.5 M and shown in **Figure 5.11.** It is found that separation factor increases with increase in nitrate concentration. D value for Eu increases with increase in sodium nitrate in greater extent compared to Sr resulting in higher separation factor at higher salt concentration. So it can be stated that BEHGA can separate the two radionuclides at higher sodium nitrate concentration during actinide partitioning.



Figure 5-11: Role of sodium nitrate on separation of Eu and Sr using BEHGA (0.2 M in *n*-dodecane)

Lanthanide concentration in HLLW is \sim 1- 6 g/l depending on the nature of fuel and burn up in reactor. Hence BEHGA was tested at higher Eu concentration for its effectiveness towards separation of Eu from Sr. Concentration of inactive Europium nitrate was varied from tracer to 0.7 M and shown in **Figure 5.12.** It was found that separation factor decreases with increase in Europium concentration as ligand gets saturated Europium ions.



Figure 5-12: Role of Europium nitrate on separation of Eu and Sr using BEHGA (0.2 M in *n*-dodecane)

5.5 Separation studies using solvent impregnated resins

Solvent extraction studies described above has major disadvantages like large volume of organic requirement which is hazardous from environmental point of view. Hence Solvent Impregnated Resin (SIR) was prepared by incorporation of BEHGA (liquid extracting reagent) into a XAD-7 (porous polymer matrix). By doing this the volume of organic waste to be generated decreases significantly. This incorporation is done by physical impregnation process. We followed dry method of preparation of SIR. In a typical experiment 5 g of the pre-treated Amberlite XAD-7 was taken in 25 ml of dichloromethane (DCM) under constant agitation. DCM is used as carrier owing to its high solubility of ligand and easy removal from the resins. Solvents having such properties (good solubility of the ligand and lower boiling points), like methanol, acetone etc. can also be used. In fact, such greener solvents is preferred for bulk scale production of such

resins. Into this resin slurry, 5 g of BEHGA was added and agitated for 10 hrs. The solvent was removed by evaporation in a vacum rotary evaporator rotor-vapor until constant weight of resin material. The loading of the resin was found to be 50% measured by weight difference between the dry resin and SIR.FTIR studies of the XAD loaded with BEHGA showed the presence of 1649 cm⁻¹ of amide and peak at 3408 cm⁻¹ corresponding to O-H stretching frequency present in BEHGA as shown in **Figure 5.13.** Thermal analysis of the XAD-BEHGA SIR showed minor loss of ~2-3 % (due to moisture) at ~100 0 C and ~20-25% weight loss at around 450 0 C which could be attributed due to loss of extractant molecule. Scanning Electron Microscopy of the XAD-BEHGA resin at 500 × magnifications showed the resin coating in the XAD support as shown in **Figure 5.14**.



Figure 5-13: FTIR spectrum of XAD and XAD-loaded BEHGA



Figure 5-14: SEM micrograph of XAD-loaded BEHGA

5.5.1 Kinetics of removal

Kinetics of sorption is an important factor for determination of efficiency of SIRs. Hence sorption kinetics of Am(III) was measured for SIRs impregnated with BEHGA by measuring the distribution ratio of Am(III) at different time intervals. Known weight of resin material was contacted with aqueous solution having 3M HNO₃ concentration spiked with tracer concentration of Am(III) for different time intervals. The plot of distribution ratio of Am(III) against different time intervals is shown in **Figure 5.15** which shows that the sorption kinetics of Am(III) on the BEHGA loaded resin was slow and it required ~120 minutes to attain the equilibrium with no further change for longer contact time. Hence in further experiments contact time was maintained at 180 minutes. In order to investigate the controlling mechanism of the sorption process, the kinetics data were tried to be fitted with different kinetic models viz, pseudo-first order and pseudo-second order. The equation describing the pseudo-first order kinetics is given by following equation:

$$\ln(q_{eq}-q_t) = \ln q_{\max}-k_1.t$$

Where q_{eq} and q_t are the concentrations of Am(III) absorbed per gram of resin at equilibrium and at time t respectively, q_{max} is the maximum sorption value and k_1 (min⁻¹) is the rate constant of the pseudo-first order rate kinetics. For sorption following pseudo-first order kinetics, linear regression analysis of $ln(q_{eq} - q_t)$ vs t gives the value of q_{max} (slope) and k_1 (-slope). But the observed plot of the resin material containing BEHGA (**Figure 5.16**) was non-linear in disagreement (R²= 0.93) with pseudo-first order kinetics. Hence the observed kinetics data was tried to fit in pseudo-second order model:

$$\frac{\boldsymbol{t}}{\boldsymbol{q}_{t}} = \frac{1}{\boldsymbol{k}_{2} \cdot \boldsymbol{q}_{\max}^{2}} + \frac{\boldsymbol{t}}{\boldsymbol{q}_{\max}}$$

Where $k_2 \text{ (min}^{-1}\text{)}$ is the rate constant for pseudo-second order rate constant. The results were found to be fitted best with this mechanism (**Figure 5.17**, $R^2 = 0.9994$). Hence the sorption of Am(III) in the resin was found to be following pseudo-second order mechanism. The value of k_2 calculated from the slope and intercept was found to be 3.556×10^{-7} g µmol⁻¹min⁻¹.



Figure 5-15: Kinetics of sorption for Am(III) using XAD-loaded BEHGA



Figure 5-16: Kinetic model plot according to pseudo first order kinetics for sorption of Am(III) using XAD-loaded BEHGA



Figure 5-17: Kinetic model plot according to pseudo second order kinetics for sorption of Am(III) using XAD-loaded BEHGA

5.5.2 Role of nitric acid concentration

The effect of nitric acid concentration in the feed solution on the sorption efficiency of Am(III) for BEHGA loaded resin is shown in **Figure. 5.18.** Raw XAD-7 without BEHGA impregnation showed no sorption of Am(III) for up to 4MHNO₃ and even for 6.4 M HNO₃ there was very less sorption of Am(III) (~5%). This results from interaction anionic Am(III) complex through interaction with the oxygen of partially hydrolyzed ester groups. The hydrolysis of the resin material takes place at higher acid concentration. The trend for XAD-7 loaded with BEHGA shows continuous increase in distribution ratio of Am(III) with increasing nitric acid concentration in the feed. The reason behind this increase is due to higher complexation of Am(III) with BEHGA at higher nitric acid concentration due to increasing nitrate ion concentration.



Figure 5-18: Role of nitric acid concentration on Am(III) sorption by XAD loaded BEHGA ation. It was pointed out that BEHGA acts as a neutral bidentate chelating ligand which bonds through hydroxyl and carbamoyl oxygen atoms. At the same time with increasing acidity in the feed phase, extractant-nitric acid interaction becomes more important leading to lower concentration of free BEHGA on the surface of solid and hence the distribution ratio value reaches a saturation value.

5.5.3 Determination of sorption capacity

The sorption capacity of the XAD-BEHGA resin material was determined by batch equilibration method. Am(III) in this experiment was replaced with Eu(III) due to associated radiation dose with high concentrations of Am(III). Inactive solution of Eu having required concentration range was spiked with tracer of ¹⁵²⁺¹⁵⁴Eu and sorption studies were carried out as a function of Eu concentration. **Figure 5.19** shows the equilibrium sorption capacity (q_e) for different concentrations of Eu. Initial concentration of Eu provides an important driving force in

overcoming the mass transfer resistance to Eu(III) ions between aqueous and solid phases. Therefore a higher Eu(III) concentration initially will enhance the sorption process but will slow down with further increase in Eu(III) concentration. This is due to increasing concentration for the active sites in the resin material. The maximum amount of Eu(III) sorbed in the resin material was calculated to be 3.2 mg/g for the resin.



Figure 5-19: Equilibrium sorption capacity (qe) for different concentrations of Eu for XAD loaded BEHGA

Sorption isotherms are indicators of how the metal ions interact with the active sites of the sorbent surface. Therefore isotherm analysis is important to determine the maximum sorption capacity of the sorbent. The most commonly used isotherms are Langmuir and Freundlich, the linear forms of which are given in **Table 5.2**.

Isotherm	Linearized eqn.	Plot	Parameters
Langmuir	$\frac{C_{e}}{q_{e}} = \left(\frac{1}{b \cdot q_{\max}}\right) + \left(\frac{Ce}{q_{\max}}\right)$	$\frac{C_{e}}{q_{e}} vsC_{e}$	q _{max} =(1/slope); b=slope/intercept
Freundlich	$\log q_e = \log K_f + (1/n) \log c_e$	$\log q_e v_s \log c_e$	$K_f = intercept, n = 1/slope$

Table 5-2: Adsorption isotherm model used in the present study

The data from the isotherm study of Eu for SIR containing BEHGA are shown in **Figure 5.20.** Langmuir isotherm based on the assumption that only one monolayer of sorbing species can be sorbed on the surface of the sorbent, all sites of the sorbent are equivalent and the ability of molecule to sorb at a given site is independent of the nature of the neighbouring sites. We observed a linear plot for (C_e/q_e) vs C_e with a very good regression co-efficient (0.9927) suggesting that the sorption of Eu on SIR obeys Langmuir model. The Langmuir fitting constants q_{max} and b were obtained to be 3.27 mg/g and 0.03 respectively. Thus the calculated value of q_{max} (3.27 mg/g) is in excellent agreement with the experimental value (3.2 mg/g). The Langmuir constant b in the present study is < 1 (0.03) indicating that the sorption process is favourable. The data was also fitted with Freundlich isotherm model and the plot is shown in Figure 5.20 with poor regression co-efficient (0.968). Thus the sorption of Eu(III) on the SIR proceeds via a chemical reaction and it is limited by the availability of the ligand complexing sites due to saturation effect according to Langmuir model and it is also proved that there is no multilayer sorption of Eu(III).



Figure 5-20: Isotherm study for Eu adsorption using XAD loaded BEHGA (a) Langmuir model and (b) Freundlich isotherm

5.5.4 Reusability of the resin

The applicability of the resin materials depend on the repeated use of the material for sorption of Am(III) and this requires back extraction of the extracted Am(III) from the resin material. Solvent extraction studies of BEHGA showed that Am(III) can be stripped from extracted BEHGA using 0.5M HNO₃. But when we tried de-sorb the loaded Am(III) from the resin, quantitative de-sorption was found not be possible even after repeated contacts with the strippant. The reason behind this behaviour was not known and requires further investigation. Hence a complexing mixture of 0.2M Oxalic acid in 0.2M HNO₃ was studied for de-sorption of the extracted Am(III) from XAD-BEHGA and it was observed that quantitative stripping was possible in 3 contacts with the complexing solution.

After achieving complete de-sorption of the Am(III) from XAD-BEHGA, we carried out reusability experiments with the same material. For this purpose, the XAD-BEHGA material was subjected to multiple sorption- de-sorption cycle. The result (**Table.5.3.**) shows that the SIR consisting of XAD-BEHGA could be used at least for six cycles of operation without any reduction of the extraction performance.

Cycle Number	% Sorption	% Desorption (1 st Contact)	% Desorption (2 nd Contact)	% Desorption (3 rd contact)
1	98.90	80.26	15.67	3.89
2	98.72	79.76	15.98	4.45

Table 5-3: Reusability study of XAD-BEHGA resins

3	99.01	81.28	15.12	3.51
4	98.76	80.28	16.16	3.25
5	99.10	82.81	15.75	1.25
6	98.97	80.79	14.66	4.33

5.5.5 Selectivity of extraction

As reported earlier, BEHGA has very negligible extraction of Cs(I), Sr(II) and Ru but it does show significant extraction for trivalent actinides, lanthanides as well as tetravalent elements Zr(IV), Pu(IV). To investigate the performance of the SIR containing BEHGA, batch equilibration experiment was carried out using a simulated feed solution containing ²⁴¹Am(III), ¹⁴⁴Ce(III), Nd(III), ¹⁵²⁺¹⁵⁴Eu(III), ²³⁹Pu(IV/III), ²³⁸U(VI), Zr(IV), Mo(VI), ¹³⁷Cs(I), Sr(II), Ru in 4M HNO3. Except for the radionuclides which were kept in tracer concentrations ²⁴¹Am(III), ¹⁴⁴Ce(III), ¹⁵²⁺¹⁵⁴Eu(III), ²³⁹Pu(IV/III), ¹³⁷Cs(I) all other elements were kept at 100 ppm concentrations. The results (**Figure 5.21.**) showed identical behavior compared to solvent extraction results. We found excellent extraction performance except for Cs, Ru and Sr and all other elements were found to be extracted with large distribution ratio (> 3000). All the extracted elements were found to be stripped quantitatively in 3 contacts using 0.2M Oxalic acid in 0.2M HNO3.



Figure 5-21: Extraction of other radionuclides using XAD-BEHGA resins

5.5.6 Column studies

After obtaining various sorption parameters of the resin in batch equilibrium mode, performance of the resin was tested in column mode. For this a glass column having the dimensions of (15 cm × 1 cm) was used with 1 g of the XAD-BEHGA resin. Pre conditioning of the resin material was done by passing 3M HNO₃ through the column prior to the introduction of the sample. The column operations were carried out at room temperature $(25 \pm 2)^{0}$ C with flow rates of 6 ml/hr during loading and 3 ml/hr during elution. The concentration of Am(III) (mg/L) was plotted as a function of volume of feed/eluent passed through the column to obtain the loading and elution curves.

The loading and elution curves for Am(III) using XAD-BEHGA is shown in **Figure 5.22**. The feed solution for this experiment was 10.2 mg/L Am in 3M HNO₃. As evident from the Figure 5.22, breakthrough for Am(III) was observed after passing 300 ml of feed solution suggesting capacity of 3.06 mg of Am per gm of resin. The equilibrium loading capacity of XAD-BEHGA resin is found to be 3.27 mg/g in batch equilibration mode. The column capacity of Am was found to be slightly lower which can be due to non-equilibrium conditions in column and slow sorption kinetics of Am(III) on the resins. After reaching the breakthrough, passing of the feed solution was continued through the column till cent percent breakthrough of Am(III) was observed. Then the column was washed with 50 ml of 3M HNO₃ to remove any un-complexed and physically sorbed Am(III) from the column. There was no leaching of Am(III) from the column during washing step as can be seen from the Figure 5.22. Finally, the loaded Am(III) could be quantitatively eluted using 250 ml of 0.2M Oxalic acid in 0.2M HNO₃.



Figure 5-22: Loading and elution curves for Am(III) using XAD-BEHGA in fixed bed column mode

5.6 Summary of the results

- BEHGA has been synthesized and tested for selective extraction of minor actinides and lanthanides over Sr. The ligand is found to extract minor actinides and lanthanides preferentially over Sr.
- The mechanism of extraction is purely solvation and stoichiometry of the extracted species was determined from log-log plot. It was observed that –OH group present in the α position plays crucial role in metal ion extraction.
- 3. Selective extraction of Am over Sr is unaltered even in presence of high amount of nitrate salts.

- 4. Another important aspect of the ligand is that it does not form third phase at higher nitric acid concentration or high metal ion concentration.
- 5. The ligand is found to retain its high extraction performance when also impregnated in innert matrices like XAD. The detailed characterisation of the SIR using techniques like TG-DTA, SEM and FTIR proves ~50 % impregnation of the ligand in XAD matrix.
- The Kd for Eu is as high as 3000 whereas extraction of Sr is insignificant under the same chemical conditions.
- 7. Apart from its high sorption capacity, it was also established that the adsorbed metal ions can be desorbed from the resins and the resins can further be used in for further six cycles.
- The sorption mechanism is found to follow pseudo second order kinetics model and Langmuir isotherm adsorption model.
- The resin was also tested in column mode and the maximum loading capacity was found to ~3 mg/g.
- 10. BEHGA has all desired properties to be used as an extractant for extraction of minor actinides from acidic waste solution both in solvent extraction and SIR column model.

6 Chapter-6: Separation of ¹⁰⁶Ru from HLLW for Use as a Radiation source

Chapter-6 Separation of ¹⁰⁶Ru from HLLW for Use as a Radiation source

6.1 Introduction

As indicated in the scope of the work, the work on separation of ¹⁰⁶Ru was undertaken with the objective to use it as a radiation source. Though no regulatory limit pertaining to its purity requirement for the said application is available, the concentration of any radionuclides less than 1 Bq/mL is considered as the acceptance criteria. With this set target, process development work for the separation of the radioelement was under taken. Amongst the available processes, the feasibility of using ion exchange and solvent extraction based processes has been explored initially. Afterwards, these processes were abandoned due to poor Ru uptake performance. These processes are not also suitable to meet the stringent quality requirement of the product. In the latter part, dedicated efforts were made to establish a process involving oxidation of Ru to RuO4 followed by its collection either by distillation or extraction in suitable solvent. Since the RuO4 is highly volatile, volatilization behaviour of the species were studies and the inference has been used in process optimization. The optimized process developed has been demonstrated successfully for the recovery of ¹⁰⁶Ru from actual waste solution and used to prepared brachytherapy source (plaque source) suitable for treatment of cancer of the eye.

In this chapter, the properties of ¹⁰⁶Ru responsible for eye cancer treatment application and results of the study are discussed in detailed.

6.2 Decay characteristics of ¹⁰⁶Ru

The unique decay characteristics of ¹⁰⁶Ru are presented in Fig. 6.1 below. As can be seen from the figure that the ¹⁰⁶Ru (half-life of 368 days) is main fission product produced in thermal fission of uranium. It is a low energy beta emitter. However, its daughter, ¹⁰⁶Rh emits high energy beta radiation which is very useful for the brachytherapy applications, particularly for the treatment of eye cancer.



Figure 6-1: Decay characteristics of ¹⁰⁶Ru

6.3 Utility of ¹⁰⁶Ru source in brachytherapy application

As indicated above, the high beta energy emitted by ¹⁰⁶Rh source is used for the treatment in eye cancer. Since ¹⁰⁶Ru-¹⁰⁶Rh are in secular equilibrium, the separated ¹⁰⁶Ru is therefore used to make sealed source in form of a plaque and used for the treatment of eye cancer. Different kinds of eye
cancers, such as intraocular melanoma including choroidal melanoma and retinoblastoma can be treated by the ¹⁰⁶Ru plaque. In fact, plaque brachytherapy among the various treatment modalities scores very high when eye and vision salvage are considered as prime criteria. It is to be noted that plaque brachytherapy is being practiced over the last three decades. Few ophthalmic oncologists in India are also using such imported sources. The high cost of the imported sources and stringent regulatory measures while importing the sources, makes it's inaccessible to the small ophthalmic centre of the country.

Preparation of ruthenium plaque involves separation of the radioelement from nuclear waste solution in radiochemically pure form, electro-deposition of the radioelement on silver substrate and finally preparation of the sealed source. The first step to make such sources for the patients of our country is process development for the generation of radiochemically pure ¹⁰⁶Ru. Sustained efforts have been made during this PhD work led development of a process which in turn helped to prepare ¹⁰⁶Ru plaque. Results of process development study are discussed below.

6.4 Origin of waste for the separation of ¹⁰⁶Ru

Process flowsheet shown in Figure 1-9 represents present practices for the management of HLW through partitioning route. In this scheme, the raffinate generated after 3rd cycle operation, i.e., after separation of minor actinides by TEHDGA is used as feed for the separation of ¹⁰⁶Ru. Typical composition of the waste solution used in the present study is shown in **Table 6.1**.

Parameters	Quantity		
Acidity (HNO3)	2.5 M		
Gross a	10 ⁻⁵ mCi/L		
¹⁰⁶ Ru	8.47 mCi/L		
¹³⁷ Cs	10 ⁻³ mCi/L		
¹²⁵ Sb	6.25 mCi/L		

Table 6-1: Typical composition of acidic ILW used for separation of ¹⁰⁶Ru

6.5 Screening of the processes for the separation of ¹⁰⁶Ru

It is known that Ru as ruthenium nitrosyl complexes are present in the waste solution originated from reprocessing plants. Moreover, various cationic, anionic and neutral complexes of Ru-NO are present simultaneously in the same solution. This complex aquatic chemistry of Ru is responsible for the very low DF factors as represented in section 1.6.6.

In view of the above speciation, feasibility of using room temperature ionic liquid containing liquid cation and anion exchange moieties has been examined. A brief outcome of the results is discussed in section 6.6 below.

Since the above process did not yield desirable results, efforts were made to develop process for the separation through oxidation of Ru species to RuO₄. In this process, the formation of sole neutral complex (RuO₄) is expected to give better purification.

6.6 Studies on Ru separation using Room Temp Ionic liquid

Ru can exist as cationic, anionic or neutral species depending on the chemical environment in solution. Keeping this in mind, we have synthesized room temperature ionic liquids by reacting liquid cation exchangers with anion exchangers like Aliquat336-DEHPA (AD), Aliquat336-DNPPA (ADN) and Primene JMT-DEHPA (PD). A typical synthesis procedure is shown below:



Figure 6-2: Synthesis Scheme of Ionic liquids

The Ionic Liquids did not extract Ru from nitric acid (M) solutions rather they weakly extracted Ru from solution having pH more than 2. Among the three IL, ADN was found to have the maximum extraction performance and Using 0.2 M ADN, D_{Ru} was found to be 0.92 for a feed pH of 8 with actual intermediate level waste. Almost 63% pure ¹⁰⁶Ru was extracted in 3 stages during counter current extraction at A/O=1. Ru extraction remain unaltered by increasing IDA concentration in the organic phase. Changing to other diluents like 1-octanol, NPOE does not increase Ru extraction. Ruthenium can be successfully stripped in three contacts using 4 M nitric acid as stripant. Hence further efforts were made to develop a process for extraction of Ru from highly acidic solution with better recovery.

6.7 Studies on Ru separation through oxidation route

Though the process involving oxidation of Ru to RuO₄ is known from a long time, systematic study for the large scale recovery of ¹⁰⁶Ru is scarce. Moreover, most of the work in this direction is limited with simulated waste solution and therefore these data can-not be used to predict the performance due to differences of the speciation in simulated and real waste solution. During the study, systematic research in two broad areas viz., (i) volatilization behavior of RuO₄ and (ii) extraction behavior of RuO₄ to CCl₄ has been carried out. Results of the study helped to finalize a process scheme for the separation of ¹⁰⁶Ru from HLW. The utility of the scheme towards production of radio chemically pure ¹⁰⁶Ru has been successfully demonstrated with actual waste and the recovered ¹⁰⁶Ru has been used to make plaques for the treatment of eye cancer.

6.8 Studies on the volatilization behavior of RuO₄

The oxidation of the Ru species to RuO₄ can be accomplished using oxidant having oxidation potential more than 1.4 volt. Strong oxidant such as KMnO₄, KIO₄ or Ozone can therefore be used for this purpose. In this study, KIO₄ has been selected as oxidant for the oxidation of Ru species. The standard electrode potential of the IO_3^-/IO_4^- couple is approximately 1.6 V and hence it is capable of oxidising all ruthenium species to RuO₄. Further, selection of KIO₄ as oxidant was done mainly because of the two reasons viz., (i) oxidation can easily be accomplished under ambient conditions and (ii) oxidation performance of the reagent is superior or equivalent when compared to other reagents tested earlier. The oxidation of Ru by KIO₄ can be represented as follows.

8 Ru³⁺_{aq} + 5 IO₄⁻_{aq} + 12 H₂O
$$\rightarrow$$
 8 RuO_{4 aq} + 5 I⁻_{aq} + 24 H⁺_{aq}......(6.1)

It can be seen that the formation of RuO4 depends on various factors such as concentration of acid, oxidant, temperature and time. Further, the resultant oxidation product, ruthenium tetroxide (RuO4), is a colorless liquid and has low boiling point (around 40 °C) and high solubility of RuO4 in water (2% w/v at 20 °C). Despite its low boiling point, the high solubility of RuO4 in water (2% w/v at 20 °C) may keep the generated RuO4 in the solution. In order to drive out the RuO4 from solution, an external driving force like increase of temperature may be required. It can be noted that all RuO4volatilization data reported in literature was based on the measurement of Ru concentration in solution either by using ICP or radiometric analysis before and after experiments. Further detailed study on volatilization behavior of RuO4 from nitric acid and role of different process parameters, such as concentration of acid, oxidant, temperature and time, have not been reported. It is believed that such data are important towards adaptation of best practices, particularly, for recovery of radio-ruthenium from nuclear waste solution. During the present work, efforts have been made to devise a simple technique for real time monitoring of RuO4 volatilization from aqueous solution. The process utilizes conversion of Ru(III) to RuO4 by addition of metaperiodate followed by monitoring of its UV-Vis profile as a function of time.

6.8.1 UV-Vis study for identification of RuO₄

UV-Vis spectra of Ruthenium in 1 M HNO₃ solution both before and after addition of KIO₄ are presented in **Figure 6-3.** The Ru(III) solution do not have any absorption peak between 350 to 450 nm. In contrast, well defined absorption peak at 385nm was observed after addition of KIO₄. The absorption peak appeared at 385 nm is the signature peak of RuO₄.Based on the literature reports by G.B.Barton et al., Lambert-Beers law is followed for RuO₄ solutions having concentration in the range of ≤ 1 mM and molar extinction coefficient (ϵ) is reported to be 930 mol⁻¹ lit cm⁻¹. This value was used to calculate the Ru(VIII) concentration in solution.



Figure 6-3: UV-Vis spectrum of 0.27mM ruthenium solution before and after oxidation using KIO₄

It is indicated from **equation 6.1** that the RuO₄ formation is dependent on various factors like initial concentration of Ru(III), concentration of IO_4^- , acidity of the solution and temperature of the system. The volatilization behavior of RuO₄ as a function of these process variables have been studies as described below.

6.8.2 Effect of KIO₄ concentration

Figure 6-4 shows the effect of KIO₄ concentration towards formation of RuO₄ from initial 1 mM RuCl₃ in 1 M HNO₃ medium.KIO₄ concentration in this study was varied from 0.5 to 3 wt% (21 mMto 130 mM). As described earlier, the concentration of RuO₄was determined form reported molar extinction coefficient. It can be seen from **Figure 6-4** that rate of RuO₄ formation increases with the increase of IO_4^- concentration from 0.5 to 2wt% and thereafter it remained same. For lower KIO₄ concentration, particularly 0.5 and 1 wt%, formation of RuO₄ was mostly completed within 3

minutes of KIO₄ addition and reached to a steady value after about 15 minutes. Thereafter it remains constant upto 30 minutes. It is seen that about 85 and 95 % of initial RuO₄ was formed by oxidation of RuCl₃using 0.5 and 1 wt% of KIO₄respectively. Complete oxidation of Ru(III) to RuO₄was obtained using 2.0 wt% or higher amount of KIO₄.



Figure 6-4: Effect of KIO₄ on formation of RuO₄ from RuCl₃ in 1 M HNO₃

6.8.3 Kinetics of volatilization

Though RuO₄ is highly volatile species, no appreciable amount of RuO₄ loss was observed during KIO₄ variation study noted above. Further experiments were therefore conducted to study kinetics of RuO₄ formation and volatilization of RuO₄ over an extended period. In this study, 2%

KIO4 was used for oxidation of 0.5 mM RuCl₃ and the generated RuO₄ concentration in solution was monitored by measuring the absorbance at 385 nm as a function of time over a period of 120 minutes. Results of the study are presented in **Figure 6-5**. It can be noted that there are three distinct portions of the plot, marked as 'a', 'b' and 'c', respectively. In portion 'a' RuO₄ concentration increases steadily, indicating oxidation of Ru(III) to Ru(VIII) is in progress and finally reaches a maximum at around15 minutes. Portion 'b' is a plateau region where RuO₄ concentration attained an equilibrium value. This is possible when all RuCl₃has converted to RuO₄ and there is no significant volatilization of RuO₄from solution. Another possibility is that rate of formation of RuO₄ concentration in solution, complete conversion of RuCl₃ to RuO₄is accountable and thus volatilization loss of RuO₄ is insignificant at that stage. After about 30 minutes, RuO₄ concentration in solution was found to decrease slowly with time (portion 'c'). This clearly indicated that RuO₄is escaping from solution. At the end of 2 hours, about 15% of RuO₄ is volatilized from the system.



Figure 6-5: Kinetics of RuO4volatilization in 1 M nitric acid

As indicated in equation 6.1, the concentration of RuCl₃ will have a significant effect on the rate of formation of RuO₄ and also rate of its volatilization. Evaluation of such effect was studied with three different RuCl₃ bearing solutions (RuCl₃ concentration 0.25, 0.50 to 0.75mM). In all cases, 2% KIO₄ and 1 M HNO₃ was used. The volatilization kinetic for all three concentrations is shown in **Figure 6-6**. The volatilization % is found to be10 for solution having 0.25 mM Ru whereas it is 15 and 19% for both 0.5 and 0.75 mM Ru(III) solution. This concludes that extent volatilization is dependent on Ru concentration and increases with increase in Ru(III) concentration.



Figure 6-6: Dependence of RuO4volatilization kinetics concentration on initial Ru concentration

The kinetics data obtained at different Ru concentration were fitted according to first and second order kinetics equation and shown in **Figure 6-7**.



Figure 6-7: Determination of order and rate constant of kinetics of RuO₄ volatilization (a) first order and (b) second order kinetics model

The plot of log $[A]_t$ v/s time shows straight line at all three concentrations (0.25, 0.5 and 0.75 mM)with correlation coefficients as 0.96, 0.96 and 0.99 whereas plot of 1/A_t v/s time gives correlation coefficient as 0.94, 0.95 and 0.97 indicating that volatilization process fits well with first order kinetics. The value of different parameters is shown in **Table 6-2**.

		Ru Conc. (mM)		
		0.25	0.5	0.75
1 at	K (min ⁻¹)	5.6*10-4	8.4*10-4	9*10 ⁻⁴
1 st	R ²	0.96	0.96	0.99
Order				
2 nd	K (min ⁻¹ mMol ⁻¹)	0.004	0.005	0.003
order	R ²	0.95	0.95	0.95

Table 6-2: Values of rate constant for volatilization kinetic of RuO₄

6.8.4 Role of nitric acid

Nitric acid, being an oxidizing agent, may play crucial role in the redox processes. Hence the extent of volatilization was evaluated at different nitric acid concentration and shown in **Figure 6-8.** Extent of volatilization is same for all nitric concentration up to 40 minutes. But it can be noted that in case of 4 M nitric acid the volatilization rate is slightly higher in the window of 40 -100 minutes. There is no difference in volatilization pattern in case of 1 and 2 M nitric acid when other experimental parameters are kept constant. Finally, for all nitric acid concentration, magnitude of volatilization is same at the end 120 minutes. This confirms that role of nitric acid is insignificant in the nitric acid concentration range studied.



Figure 6-8: Kinetics of RuO₄ volatilization at different nitric acid concentrations

6.8.5 Effect of Temperature

To understand the effect of temperature in RuO₄ volatilization, kinetics of volatilization was studied at different temperature and has been shown in **Figure 6-9**. As expected, the rate of volatilization is found to increase with the increase of temperature. At the end of 2 hours of experiment, almost 82% Ru(VIII) was found to be volatilized at 70 $^{\circ}$ C whereas it is 15 at 25 $^{\circ}$ C.



Figure 6-9: Kinetics of RuO₄ volatilization at different temperature

The kinetics data obtained at different temperature were fitted according to first and second order kinetics equation and shown in **Figure 6.10**.



Figure 6-10: Determination of order and rate constant of kinetics of RuO₄ volatilization (a) first order and (b) second order kinetics model

The plot of Log $[A]_t$ v/s time shows straight line at all three temperatures with correlation coefficients as 0.96, 0.97 and 0.98 whereas plot of 1/A_t v/s time gives correlation coefficient as 0.95, 0.95 and 0.95 indicating that volatilization process fits well with first order kinetics at all three temperatures. The value of different parameters is shown in **Table 6-3**.

		Temperature		
		25 ⁰ C	45 ⁰ C	70 ^о С
1 et	K (min ⁻¹)	8.4*10-4	0.002	0.0059
I st Order	R ²	0.96	0.97	0.98
2 nd	K (min ⁻¹ mMol ⁻¹)	6.18*10 ⁻⁴	0.0026	0.0139
order	R ²	0.95	0.95	0.95

Table 6-3: Values of rate constant for volatilization kinetic of RuO₄

It can be seen from Table 6-3, the rate constant of Ru(VIII) volatilization is 8.4×10^{-4} , 0.002 and 0.0059 at 25, 45 and 70 °C respectively. Activation energy of the process was calculated from log K v/s 1/T plot (**Figure 6-11**) and is found to be 3.9×10^{-3} J/mol. The value of pre-exponential factor was also calculated from **Figure 6-11** and is found to be 0.002 min⁻¹.



Figure 6-11:Arrhenius Plot (log K vs.1/T) for Ruthenium volatilization process

During initial stages of extraction, it was observed that a black precipitate is appeared on keeping the solution of RuO₄/CCl₄ for more than 30 minutes. This was attributed to the formation of RuO₂.In order to avoid RuO₂ precipitation, CCl₄ was pre-equilibrated withCl₂ gas and used in all further solvent extraction studies.

Based on these studies, a series of unique data on RuO4 volatilization under different process conditions such as rate constant, activation energy, etc., have been generated. Some of the data are used towards optimization of process flowsheet, as described below.

6.9 Studies on the extraction of RuO₄

In this section, process optimization towards extraction of generated RuO₄ is described. It can be noted that the generated RuO₄ can be collected by distillation. Since RuO₄ has a strong tendency to absorp on surfaces, the distillation process not attempted. Another option is that it can be extracted into chloroalkanes. Based on literature report, extraction of RuO4 in CCl₄ has been selected for further process optimization study.

During initial stages of extraction, it was observed that a black precipitate is appeared on keeping the solution of RuO₄/CCl₄ for more than 30 minutes. This was attributed to the formation of RuO₂.In order to avoid RuO₂ precipitation, CCl₄ was pre-equilibrated withCl₂ gas and used in all further solvent extraction studies.

Initial process optimization study was carried out with 25 mL simulated waste spiked with ¹⁰⁶Ru radiotracer. The conversion of Ru nitrosyl nitrate to RuO₄ was carried out by addition of KIO₄. Further optimization with regard to extraction of RuO₄ in CCl₄ has been carried out by conducting a series of experiments, by varying phase ratio (organic and aqueous), using different concentration of HNO₃ in waste feed, extraction time, etc. Details the experimental process and waste feed used have been mentioned under each section.

6.9.1 Optimizing nitric acid and potassium meta-periodate concentration

Table 6-4 depicts the results of preliminary solvent extraction studies using with and without Cl₂ equilibrated CCl₄, different nitric acid and potassium meta-periodate concentrations. It can be seen that extraction of ¹⁰⁶Ru remained unaltered by pre-equilibrating the organic phase with chlorine gas. For both solvents about 75% of ¹⁰⁶Ru extraction was observed. It is also evident that nitric acid concentration has no apparent role on extraction of RuO₄. On the other hand, the concentration of metaperiodate has a significant role, particularly for the conversion of Ru(III) to RuO₄. Optimum requirement of KIO₄ for the oxidation reaction is around 2% and about 15 minutes is necessary for complete conversion to RuO₄. The mechanism of extraction is shown in equation 6.2.

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KIO4 (wt%)	KIO ₄ (mM)	HNO ₃ (M)	% E (Ru)
2	86.9	1.5	74*
2	86.9	1.5	75
2	86.9	2.5	75
2	86.9	3.8	76
0.5	21.7	1.5	69
1	43.7	1.5	72
1.5	65.2	1.5	75
*with Cl ₂ equilibra	ted CCl ₄		

Table 6-4: Role of nitric acid and potassium metaperiodate on ruthenium extraction

6.9.2 Kinetics of extraction

Figure 6-12 presents effect of contact time on extraction of RuO₄ in CCl₄. Feed solution used in this study was prepared by spiking high level liquid waste in 1 M nitric acid solution. In all cases, equal volume of aqueous and organic phase mixture was used. About ~75% of ¹⁰⁶Ru was found to be extracted in 5 minutes and thereafter no significant increase in RuO₄ was noted even after 30 minutes of equilibration. This indicates that whatever Ru species were converted to RuO₄, can be quantitatively extracted within 5 minutes.



Figure 6-12: Kinetics of RuO₄ extraction in carbon tetrachloride

6.9.3 Ru extraction in cross current mode

To have better extraction performance the extraction process was operated in cross current mode. In this experiment fresh organic was introduced in each extraction step and the raffinate was used as feed for the next step. Before solvent extraction 2wt% KIO₄ was added in each step. As it can be shown from **Figure 6-13**, % E was found to be around 75in the first cycle and increases to 82 in the second cycle. No further increase in ruthenium extraction was found in 3rd and 4th cycle of operation. Hence it can be concluded that maximum ruthenium is oxidised in single step and gets extracted to the organic phase.



Figure 6-13: RuO₄ extraction by carbon tetrachloride in cross current mode 6.9.4 *Optimizing the O/A ratio*

Figure 6-14 depicts the role of aqueous to organic phase ratio in ruthenium extraction. Extraction was carried out varying the organic to aqueous from 1 to 3. It was found that \sim 73 % extraction takes place in A/O of 1 whereas extraction is only 32% in case of A/O of 3. As the extraction mechanism involves dissolution of ruthenium tetroxide in carbon tetrachloride, hence with increase in A/O value, as the amount of CCl₄ decreases % E decrease.



Figure 6-14: Effect of aqueous /organic ratio on extraction of ruthenium

6.9.5 Selectivity of Ru extraction

Extractions of other radionuclides were studied as radiochemical purity of ¹⁰⁶Ru is important for source preparation. Tracer quantity of ¹³⁷Cs, ¹⁵²Eu, ⁸⁵⁺⁸⁹Sr was added to the waste solution and extraction was studied. Extraction data of other fission products like ¹³⁷Cs, ¹⁵²Eu, ⁸⁵⁺⁸⁹Sr and ¹²⁵Sb is shown in **Table 6-5**. This indicates high radiochemical purity of the¹⁰⁶Ruextracted to organic phase.

Metal ion	% E
¹⁰⁶ Ru	75.0
¹³⁷ Cs	< 0.1
¹⁵² Eu	< 0.1
⁸⁵⁺⁸⁹ Sr	< 0.1
¹²⁵ Sb	< 0.1

Table 6-5: Extraction of other fission products along ruthenium extraction

6.9.6 Stripping of Ru from loaded organic phase

Fig 6-15 represents the striping of RuO₄ from CCl₄ using various reagent mixture. The preference in selection of strip solution was given on the basis of its usefulness as catholyte for electrodeposition of Ru during fabrication of plaque. It is known that Ru(III) in sulphamic acid solution forms a stable solution and has been used for electro deposition. The stripping efficiency of sulphamic acid solution was found to be very poor. Hydrazine sulphate in 1 M nitric acid was employed in stripping back the ruthenium into aqueous phase. Results show that almost entire Ru was stripped in single contact using hydrazine sulphate a phase ratio of O/A of 2. The extracted ruthenium was completely stripped back using 0.1 M hydrazine sulphate in 1 M nitric acid.



Figure 6-15: Screening of stripant solution

6.9.7 Recyclability Studies of carbon tetrachloride

Feasibility of recyclability of carbon tetrachloride was studied in 10 mL scale and the results are shown in **Figure 6-16**. Before each step carbon tetrachloride was equilibrated with chlorine. It was found that the extraction performance for ruthenium of the solvent remains unaltered in 5 cycles of operation. Selectivity of ruthenium extraction was also retained.





6.9.8 Designing the process flowsheet

Based on the outcome of the study discussed above, a process flow diagram has been developed which is presented in **Figure 6-17**.



Figure 6-17: Flow chart developed to purify ¹⁰⁶Ru from high level waste

6.9.9 Demonstration of process with actual waste solution

7Ru extraction performance of the process (presented in Figure 6-17) has been demonstrated successfully with three different scale 25mL and 50 ml scale with actual HLW and shown in Table 6-6.

Batch No.	Ru in Feed (mCi/L)	Feed Volume (mL)	%Ext	%Stripping	Ru in product (mCi/L)
1	30.15	25	73	99	21.23
2	30.15	25	78	99	23.32
3	30.15	50	73	99	21.82

Table 6-6: Performance evaluation of process flow sheet with actual HLLW

The final product solution has been analyzed using HPGE detector for gamma emitting radionuclides and ZnS for alpha. An assay of the product solution is presented in along **Figure 6-18** with its γ -spectrum.



Figure 6-18: γ spectrum of Ru(III) solution obtained after stripping and which was further used as catholyte in electro-deposition

It is worthy to be recorded here that a substantial amount of ¹⁰⁶Ru has been separated using this process in several batches. The process performance has been found to be well reproducible and more importantly the radiochemical purity of the product solution obtained from different batches meets stringent quality requirements. Approximately 25 mCi of Ru has been separated till date. This recovered ¹⁰⁶Ru has successfully been used for the fabrication of eye plaques. The fabrication of eye plaque involves electro-deposition of ¹⁰⁶Ru on silver substrate and then fabrication of sealed source after incorporation of the quoted plate in between two silver disks. The sealed disk is then bending to required radius to give plaque shape. A pictorial representation of the whole process scheme along with photograph of actual plaque is presented below for reference.

Separation of ¹⁰⁶Ru from radioactive waste and preparation of sources for treatment of eye cancer





Figure 6-19: A thumbnail view of the process for production of Ru Plaque

6.10 Summary of the results

- A process based on oxidation of Ru species followed by its extraction has been developed for selective separation of the radionuclides from acidic actual waste solutions. Demonstration of the process with actual waste at 25 mL scale shows 73% extraction of the metal ion in a single contact.
- 2. As RuO₄ is a volatile compound and may escape from the system depending on the experimental conditions hence detailed study was carried out to understand the volatilization behavior of Ruthenium Tetroxide. And towards this role of several parameters like initial Ru concentration, time, nitric acid and temperature was evaluated.
- 3. Volatilization rate was found to be fast at higher nitric acid concentration whereas extent of volatilization increases with increase in temperature
- 4. RuO₄ volatilization was found to follow first order kinetics. Activation energy of the process was also calculated from the rate constant at different temperature.
- 5. This Ru volatilization study is first of its kind which has been done with so much details.
- 6. The extracted Ru can be quantitatively stripped using a single contact using reducing agent hydrazine sulfate in nitric acid.
- The process is found to have high decontamination factor over other radionuclides like Cs, Sr, Eu, Sb and actinides, as required for fabrication of radiation sources to be treatment of eye cancer.
- Kinetic of extraction is very fast whereas it takes almost 60 minutes for complete stripping.
- 9. Ru extraction does not increase significantly in multiple batch extraction as obtained from cross current extraction data.

10. Separated Ru meets all radiochemical properties for fabrication of radiation source to be used for eye cancer treatment. Approximately 25 mCi of Ru has been separated using this process and used for fabrication of Ru eye Plaques.

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- **3.** Title of the Thesis: Synthesis and evaluation of specific extractants for separation processes in back-end of fuel cycle

<u>Keywords</u>

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- 2. Ligands
- 3. Separation studies
- 4. Solvent extraction
- 5. Extraction Chromatography
- 6. Supported liquid membrane
- 7. Ruthenium
- 8. Strontium
- 9. Technetium
- 10. Plaque brachytherapy

Thesis Highlight

Title of thesis: Synthesis and evaluation of specific extractants for separation processes in back-
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Name of the Student: Prithwish Sinharoy
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Thesis Title:
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High level liquid waste generated from reprocessing of spent nuclear fuel contains bulk of fission products along with minor actinides. Efforts has been made in recent past in India for separation of radioelements in radiochemically pure which can be further used either in medical or industrial applications or preparation of target material for transmutation. During the present thesis work, development of selective solvents and efficient process for the recovery of some important radionuclides have been addressed. The key highlights of the thesis work are as follows:

Synthesis of ligands like N, N, N', N' tetra-isobutyl pyridine di-glycolamide (PDGA), *N,N,N',N'*-tetra(2ethylhexyl) di-glycolamide (TEHDGA) & N, N-bis(2-ethyl hexyl)glycolamide (BEHGA) was carried out and characterized using GC-MS and FTIR. The ligand PDGA in NB/ Ionic liquid diluent has higher selectivity for tetravalent plutonium over minor actinides, alkali and alkaline earth metal ions. The second ligand TEHDGA extracts both minor actinides, lanthanides & Sr(II) from nitric acid medium and from the loaded organic phase Sr has been selectively stripped using 18-crown-6 resulting into separation of Sr from trivalent elements. TEHDGA is also found to extract Tc from low nitric acid concentration. BEHGA a neutral extractant, similar to TEHDGA, showed extraction for Am, lanthanides, Zr and Mo at higher acidities and negligible extraction for Sr. BEHGA exhibited bi-denticity through a pre-organized five-member ring formed due to intramolecular hydrogen bonding between its α -OH and C=O groups. An innovative process was developed for recovery of treatment of cancer of the eye.



Figure 1. Schematic of separation of metal ions using ligands from nuclear waste solution

Figure 2. A thumbnail view of the process for production of Ru Plaque