DECLARATION

I declare that the thesis entitled “NOVEL ION EXCHANGE RESIN FOR THE SEPARATION OF ACTINIDES FROM PUREX WASTE” submitted to the University of Madras by me for the degree of Doctor of Philosophy is the record of work carried out by me during the period from 2005 to 2015 under the guidance of Dr.S.V.NARASIMHAN and has not formed the basis for the award of any degree, diploma, associateship, fellowship, titles in this or any other University or other similar institution of Higher learning.

Signature of the Candidate

Jaya Balakrishna Variyar
Scientific Officer E
Kalpakkam Reprocessing Plant
Bhabha Atomic Research Centre facilities
Department of Atomic Energy
Kalpakkam-603102
Dedicated to

FAMILY AND FRIENDS
ACKNOWLEDGEMENT

First and foremost I am deeply indebted to my research guide Dr. S.V.Narasimhan, for his valuable guidance, critical comments, tolerance and constant encouragement during the entire course of this study. I take this opportunity to state that his keen interest and valuable suggestions were of immense help in the entire study.

I wish to express my gratitude to Dr. S.Velmurugan, Head, WSCD, Kalpakkam for his active help and constant support rendered to me. I wish to express my sincere gratitude to Shri.S.Basu, former Director, Bhabha Atomic Research Centre Facilities (BARCF), Dr. P.R.Vasudeva Rao, Director, Indira Gandhi Centre for Atomic Research (IGCAR), Shri. B.Shreekumar, Plant Superintendent, KARP for allowing me to pursue my research work. I express my sincere gratitude to Dr.T.Kumar, Supdt. (PC & R)Lab, KARP for continuous help and support at all stages of this study. I wish to express my thanks to Shri. N.Vijayakumar, in-charge, PC Lab for the cooperation rendered to me in carrying out the work.

I owe my special thanks to Dr.P.V.Achuthan, NRB, Mumbai, for his constant support and valuable suggestions in interpretation of results. I am pleased to acknowledge inspiration rendered by Dr. K.N.Sabharwal in carrying out the synthesis of ion exchange resins and for valuable discussions had with me. I am grateful to Shri. K.A. Venkatesan, FchD, Chemistry Group, IGCAR for technical support and suggestions which were of immense help in enriching my knowledge. I wish to thank Dr.V.Chandramouli, MPCS, Chemistry Group, IGCAR for performing elemental analysis of synthesised resin.
I owe my special thanks to Shri. V.K. Madhavan Kutty for his constant encouragement and for many useful discussions. I wish to thank Shri. V. Srinivasa Rao for his timely help in carrying out high active works, Smt. P. Revathy for carrying out ICP-AES analysis and support rendered during the course of my work, Shri. Pawan Kumar Singh for carrying out alpha spectrometry. I am pleased to acknowledge the support and constructive criticism of my friends Smt. Letha Sebastian, Smt. R. Manjula, Smt. Seema M. Nair, Smt. R. Shanthakumari, Smt. Padma Priya, Smt. S. Vijayalakshmi and Smt. Padma S. Kumar.

Finally, I would like to express my special indebtedness to my colleagues of laboratory whose continuous support was unremitting source of inspiration for this work.

Whatever I am today is because of my parents, who had created a very good environment for education and whatever I had achieved today is by the support and sacrifices made by my husband Mohandas and my son Varun. Nothing is going to be complete without saying thanks to my parents, my in-laws, my brothers and family for rendering support during the period of my research work.

Jaya Balakrishna Variyar
SYNOPSIS

NOVEL ION EXCHANGE RESIN FOR THE SEPARATION OF
ACTINIDES FROM PUREX WASTE

1. Introduction:

Nuclear Energy is an important source of energy as the conventional energy sources are fast depleting. Nuclear power contributes ~16% to global electricity. Presently some 441 nuclear power reactors are in operation in 32 countries. Most of these reactors derive energy from fission of U\textsuperscript{235} that occur in nature.

Though the nuclear power is sustained source of energy, the management of spent fuel arising from nuclear power production has long been considered as an important issue due to political, economical and societal implications associated with it. Spent fuel discharged from reactors contains appreciable quantities of fissile (U\textsuperscript{235} and Pu\textsuperscript{239}), fertile (U\textsuperscript{238}), and highly radioactive fission products. For long-term nuclear power production, there are two fuel cycle options that are of relevance and under consideration at the present juncture, viz. the Open cycle with permanent disposal of spent fuel and the closed fuel cycle with reprocessing and recycle of uranium and plutonium. The closure of fuel cycle by means of reprocessing and recycling in fast breeder reactors is considered as a standard strategy. Indian nuclear power programme is based on closed nuclear fuel cycle for efficient utilization of its nuclear resources. Closed fuel cycle emphasizes on the reprocessing of the spent fuel.

India has entered in the field of spent fuel reprocessing in early sixties. India’s first spent fuel reprocessing plant was commissioned at Trombay to reprocess spent fuel arising from research reactors. With passage of time, the country has entered in the field of reprocessing of spent fuel arising from power reactors.
During reprocessing of spent nuclear fuel, the elements plutonium and uranium are separated by PUREX process which is basically a solvent extraction process, leaving behind the fission products which are subsequently concentrated to yield the High Level Waste (HLW). HLW, generated from concentration of first cycle raffinate contains almost all the radioactivity associated with the spent fuel. These streams are acidic in nature with 3-4 M HNO$_3$ having gross beta and gamma activity in the range of 100 -120 Ci/l. The HLW solution consists of long lived alpha emitting radio-nuclides such as Am, Cm and Np (referred to as minor actinides) apart from small amount of un-recovered plutonium and uranium as well as beta / gamma emitting fission products(representing a total of about 1/3 of the periodic table) and significant concentrations of structural materials and process chemicals.

Management of High Level Radioactive Liquid Waste (HLW) generated during reprocessing of spent nuclear fuel, is a challenging task considering acidic nature of waste as well as presence of long lived radioactive elements. Minor actinides having half-lives of several million years are the major concern for the safe disposal of HLW. Americium being a long-lived alpha emitter is the greatest contributor to the radio toxicity of the waste in the 300- 70,000 year time frame after removal from the reactor. The lanthanides, representing about 40% of the mass of fission products are neutron poisons. The most accepted strategy for the safe management of HLW is to vitrify it in glass matrix and deposit in repository. The presence of transuranic elements in waste placed in a repository requires engineering of the repository to ensure safe performance for hundreds of thousands of years. Ensuring repository performance over such a large lapse of time is beyond human experience. Because of this, there has been growing interest in closing the nuclear fuel cycle in a manner that allows long lived radionuclides to be recycled back into fuel cycle with only a minimum residence in repository. Once recovered these actinides can be burnt separately in reactors and transmuted to short lived nuclides. Special efforts are on among various countries for
efficient Partitioning and Transmutation (P & T) process depending on the nature of the waste generated.

Various solvent extraction processes have been developed to separate long lived actinides and lanthanides from HLW like TRUEX, DIAMEX, DIDPA and TRPO which employ octyl(phenyl)-N,N-diisobutyl carbamoyl methyl phosphine oxide (CMPO), N,N-dimethyl-N,N-dibutyl tetradecyl malonamide (DMDBTDMA), diisodecyl phosphoric acid (DIDPA) and trialkyl phosphate oxide (TRPO) as the extractants, respectively[1]. All these reagents have their advantages and limitations. This led to the search for alternative and efficient separation technique for actinide partitioning purpose.

Ion exchange is one of the oldest separation techniques finding application in almost all fields of separations [2]. They are advantageous to solvent extraction process in their ability to separate the target metal present even at extremely low concentrations. Ion exchangers have been used in nuclear industry for purification of uranium from uranium bearing deposits and purification of plutonium during the tail end of PUREX process. More recent developments have focused on synthesis of ion exchangers with highly specific functional groups and enhanced radiation resistance. Polymer supported reagents with ligands designed for ion-specific interactions are reviewed by S.D.Alexandratos. They incorporate ligands capable of chelating or coordinating with a target metal ion, eg: amines, crown ethers, phenolics, phosphonates, azo and amidoxime ligands [3-5]. The success of Phosphorus based solvents like TBP, TOPO, CMPO in the field of actinide separation under high acidic conditions led to the synthesis of resins with phosphorus containing ligands. Ion exchange resins with phosphorus based ligands received wide attention within the context of dual mechanism bifunctional polymers. They became an important group of metal chelating agents especially in the field of actinide separation [6-8]. Vasudeva Rao [9] et al has studied the synthesis and properties of bifunctional phosphinic acid resin. These resins were used to
sorb uranium and some of the fission products from high acid media. In this phosphorus based resins the selectivity is due to the precise structure of phosphorus ligand. Literature survey shows phosphinic acid resin outperforms sulphonic acid resins for actinide separation in high acid region due to strong coordinating ability [10]. But the main disadvantages of phosphorus based resins are that they suffer from low kinetics of complexation. Different parameters which enhance the complexation rates are particle size, percent of cross linking, types of cross-linking agent, macroporosity. Apart from these parameters introduction of nonselective sulphonic acid group also found as another means of enhancing the complexation rates [11-13]. S.D. Alexandratos have reported the uptake data of several actinide ions and transition metal ions from solutions of various compositions by a newly synthesised resin Diphonix [14-17]. Diphonix is essentially a sulphonated gem diphosphonate resin. It is reported that introduction of sulphonic acid group is responsible for the increased rates of complexation.

2. Scope of the study:

Literature survey shows that in order to enhance kinetics of phosphonic acid resin, Alexandratos introduced sulphonic acid group into the phosphonic acid resin. Earlier he had shown that enhancement has been achieved with phosphonic acid based resins. Uptake studies were carried out with Eu(III) from nitric acid media show enhanced levels of complexation as well as improved kinetics. In view of this property of phosphinic acid based resins, the suitability of the resin for the separation of actinides from waste generated in PUREX process.

The objectives of the present study are:

1. Synthesis and characterisation of phosphinic acid resin,

2. Sulphonation of phosphinic acid resin and its characterisation.
3. Evaluation of the above resins by carrying out uptake studies with selected elements from actinides and lanthanides from varying concentrations of nitric acid media

4. Kinetics Studies to evaluate the influence of Sulphonic acid group

5. Experiments with Sulphonated phosphinic acid resin for the removal of actinides from Simulated HLW.

6. Application of the above to actual ILW.

7. Studies with the secondary waste generated in laboratory.

3. Organization of thesis:

The thesis consists of six chapters. The first chapter gives general introduction and background of this study. The second chapter deals with synthesis, characterisation, experimental procedures and principles of different instrumental techniques that are utilized in this study. The following chapters discuss research work done in detail. Each chapter has brief introduction and experimental details, if specific method is employed. This is followed by results and discussions and all the findings from each section are summarized at the end of each chapter. The last chapter gives the overall conclusions and salient findings from this study. The content of each chapter is as given below.

Chapter 1: GENERAL INTRODUCTION:

This chapter deals about the role of nuclear energy and evolution of reprocessing in nuclear industry. It includes details regarding the role of actinides and lanthanides chemistry relevant to fuel reprocessing and nuclear waste management. The importance of separation of minor actinides and long-lived fission products from radioactive waste for better waste management purpose is discussed in detail. It describes the source and type of radioactive waste along with the environmental impact of the radionuclides present in those wastes. Major aim of radioactive waste management is to separate long lived, alpha emitting elements which belong to the actinide series of the periodic table. Chemistry of the actinides
which is important for separation of the elements has been discussed in brief. A brief description of the separation techniques which are used for actinide separation like solvent extraction, membrane technique etc. is also given in this Chapter. Literature reports on actinide separation using different class of extractants have also been summarized. Various methods were experimented for the separation of these actinides and lanthanides for the safe disposal of high level waste arising from reprocessing. A detailed literature survey of the various ion exchange materials employed in the fuel reprocessing and nuclear waste management forms part of this chapter. This Chapter deals with the history and development of various ion exchange resins, with the passage of time. Advantages of ion exchange resins compared with other separation techniques and their different mechanisms of exchange of ions. It also includes a note of ion exchange resins used for specific purposes. This chapter concludes with the scope of the present work.

**Chapter 2 EXPERIMENTAL:**

The second part of this chapter mentions about the instruments and various analytical techniques followed during the course of the whole work. Plutonium and Americium was analysed by radiometry using scintillation counters. Mainly spectrophotometric method was followed for the analysis of U(VI). Atomic emission spectroscopy was used for the analysis of Eu and Nd. Preparation and purification of various standards are included in this Chapter. Methods to adjust the oxidation state of Pu are described in this Chapter. Purity of the different oxidation states of Pu was checked by spectrophotometry.

**Synthesis and characterisation:** First half of this chapter explains the methods used for the synthesis of phosphinic acid and sulphonated phosphinic acid resins and observations made during the process of synthesis. It also explains the laboratory scale set up and details of
chemicals used for the synthesis. The synthesised resins were characterized by checking various parameters.

**Chapter 3. DISTRIBUTION STUDIES:**

This chapter deals with the studies carried out to find the distribution coefficient of various systems on the synthesized phosphinic as well as in sulphonated phosphinic acid resin. Actinide elements selected are Pu(IV), U(VI) and Am(III) and the lanthanides selected are Eu(III) and Nd(III). Batch extraction studies were carried out to find K_D for the said elements at different nitric acid concentrations from 0.5 to 6 M. Performance of this resin is compared with commercially available strong cation exchanger Dowex 50W X 8. This chapter also deals in detail about the probable mechanism responsible for higher distribution ratios of the elements at higher acidity. In order to prove the role of phosphorus ligand and their ability to strongly coordinate, studies were carried out to find out the variation in K_D with the concentration of U(VI) from a system of constant nitric acid(0.5M) and varying ionic strength maintained with the addition of NaNO_3(0.5 – 6M). Studies carried out for the extraction of Pu(IV) from varying concentrations of sulphuric acid ranging from 0.5 to 6M are also discussed in this chapter. Plutonium generally exists in varying oxidation state like +3, +4 and +6 in acidic medium due to disproportionation even though +4 is the most stable state. This chapter briefly describes the studies carried out to establish the extraction of varying oxidation states of Pu from 1 M HNO_3.

**Chapter 4. KINETICS OF EXTRACTION OF Pu(IV):**

This chapter deals with kinetics of sorption of Pu from nitric acid. Studies show that introduction of sulphonic acid group into the specific phosphinic acid resin enhances the complexation as well as the kinetics of extraction. Hence a system was selected to find the effect of sulphonation on rate of extraction. A detailed description on the studies done with Pu(IV) at two different acidities i.e. 0.5 and 6 M HNO_3 is presented in this chapter. Samples
were drawn at regular intervals of time and time required to reach the fractional attainment of equilibrium is calculated. An attempt is made in this chapter to explain the probable mechanism of enhanced extraction. This chapter includes the kinetics studies done with Dowex 50W a strong cation exchange resin for the extraction of Pu(IV) from HNO3 media and the performance of these resins are compared.

**Chapter 5. SEPARATION STUDIES:**

The chapter deals with the Separation studies of actinides and lanthanides by the sulphonated phosphinic acid resin from various wastes. The first part of this chapter deals with the separation of actinides and lanthanides from waste streams that generate in due course of PUREX process viz HLW, ILW. The extraction of Pu, U, Am, Eu and Nd from the Simulated High Level Waste by the sulphonated resin was carried out on column at two different acidities. Separation studies were carried out using a solution of High Level Liquid Waste (HLW) generated in plant to check for the actual extraction ability in presence of high ionic strength as well as high dissolved solids. Studies were carried out with the actual ILW generated in plant. Since all the results are encouraging the second part of this chapter extends to the separation of Pu and U from the secondary waste generated in laboratory in due course of analysis as well as the separation of Plutonium from the oxalate supernatant generated in Reconversion laboratory. The chapter deals in detail about the various waste generated in laboratory.

**Chapter 6. SUMMARY AND CONCLUSIONS:**

Some important conclusions arrived based on the results discussed in the previous chapters are presented in this chapter. Scope for further work in this area of research is also discussed briefly.
4. Salient observations and conclusions from this study:

1. Synthesis and characterisation of phosphinic acid resin from polystyrene–DVB matrix was carried out. The increase in capacity and decrease in phosphorus content after functionalization is attributed due to the presence of sulphonic acid group.

2. Among the three resins studied, for the extraction of Pu(IV) from varying concentrations of nitric acid, the highest $k_d$ values were obtained on sulphonated phosphinic acid resin in the acidity range studied. High $K_D$ values shown by phosphinic acid and sulphonated phosphinic acid resin for the extraction of Pu are due to the presence of $\text{P=O}$ which coordinates Pu(IV) even at high acidities. Compared with phosphinic acid resin, Sulphonated phosphinic acid resin shows a two fold increase in $K_D$ even at high acidities due to the presence of sulphonic acid group. The sulphonic acid group imparts the hydrophilicity required for uptake of metal ions from solution.

3. From $K_D$ data for the extraction of U(VI) from varying concentrations of nitric acid, Dowex resin shows very less $K_D$. Compared to phosphinic acid resin, sulphonated resin shows high $K_D$, due to the presence of sulphonic acid group. Even from highly salted solutions of NaNO₃ (0.5-6M) sulphonated phosphinic acid resin shows high $K_D$ compared to phosphinic acid resin. The results suggest the suitability of the resin for the separation of U(VI) from acidic medium containing high salt content.

4. Studies carried out for the extraction of Am(III) shows that both Dowex and phosphinic acid resin shows very less $K_D$ at all acidities of nitric acid. Sulphonated phosphinic acid resin also shows a decrease in $K_D$ with increase in acidity, but shows higher $K_D$ compared to other resins up to an acidity of 3 M and with further increase in acidity it merges with that of other resins. The results suggest that the resin can be effectively used for the separation of Am(III) up to an acidity of 3M.

5. The ion exchange kinetics of phosphinic acid resin was found to be slow. On sulphonation it was found that the resin reached equilibrium within 30 minutes compared to phosphinic acid resin which took more than two hours to reach
equilibrium. The increase in kinetics appears to be because of an access mechanism provided by sulphonic acid group incorporated into the phosphinic acid resin.

6. Separation studies carried out with this resin shows that removal of actinides and lanthanides can be easily accomplished using sulphonated phosphinic acid resin from various waste streams generated under PUREX conditions. Removal of Actinides and Lanthanides from HLW is possible with sulphonated phosphinic acid resin. At high acidity it removes more than 99% of Pu and U and almost 70% of Am and lanthanides. At lower acidity it removes more than 99% of all Actinides and Lanthanides.

**Scope for future Study:**

Elution agents for the recovery pose a challenge. So the important area of future study is to find an appropriate eluting agent from the resin phase. The separation of actinides can be fully effective when the sorbed ions are stripped back from the resin phase. The high $K_D$ values shown by the actinide ions especially Plutonium and Uranium at different concentrations of nitric acid shows that stripping of these ions from the resin is a matter of concern. Possible stripping agents must be reducing agents, complexing agents or a mixture of both. In the case of other ions like Am, Eu and Nd the decrease in $K_D$ with increase in acidity suggest it may be possible to strip these ions at higher concentrations of nitric acid.
REFERENCES:

# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td><strong>Introduction</strong></td>
<td>1</td>
</tr>
<tr>
<td>1.1</td>
<td>Nuclear Energy</td>
<td>1</td>
</tr>
<tr>
<td>1.2</td>
<td>Nuclear Reactors</td>
<td>2</td>
</tr>
<tr>
<td>1.3</td>
<td>Nuclear Energy Programme in India</td>
<td>4</td>
</tr>
<tr>
<td>1.4</td>
<td>Spent Fuel Reprocessing or closed fuel cycle</td>
<td>5</td>
</tr>
<tr>
<td>1.5</td>
<td>Separation Techniques</td>
<td>6</td>
</tr>
<tr>
<td>1.5.1</td>
<td>Precipitation process</td>
<td>7</td>
</tr>
<tr>
<td>1.5.2</td>
<td>Solvent Extraction</td>
<td>7</td>
</tr>
<tr>
<td>1.5.3</td>
<td>Ion Exchange</td>
<td>8</td>
</tr>
<tr>
<td>1.6</td>
<td>History of reprocessing</td>
<td>8</td>
</tr>
<tr>
<td>1.6.1</td>
<td>Dry Process</td>
<td>9</td>
</tr>
<tr>
<td>1.6.1.1</td>
<td>Fluoride volatility process</td>
<td>9</td>
</tr>
<tr>
<td>1.6.1.2</td>
<td>Pyro chemical reprocessing of molten salt fuels</td>
<td>9</td>
</tr>
<tr>
<td>1.6.2</td>
<td>Wet Process</td>
<td>10</td>
</tr>
<tr>
<td>1.6.2.1</td>
<td>Bismuth Phosphate method</td>
<td>10</td>
</tr>
<tr>
<td>1.6.2.2</td>
<td>Butex Process</td>
<td>10</td>
</tr>
<tr>
<td>1.6.2.3</td>
<td>Hexone process</td>
<td>11</td>
</tr>
<tr>
<td>1.7</td>
<td>PUREX Process</td>
<td>11</td>
</tr>
<tr>
<td>1.7.1</td>
<td>Head End Treatments</td>
<td>13</td>
</tr>
<tr>
<td>1.7.2</td>
<td>Co-decontamination cum partition cycle</td>
<td>14</td>
</tr>
</tbody>
</table>
1.7.3. Product Purification Cycle 15
1.7.4. Waste evaporation cycle 15
1.8 Radioactive waste 15
1.8.1 Low Level Waste 16
1.8.2 Intermediate Level waste 17
1.8.3 High Level Waste 17
1.8.4 Management of radioactive waste 19
1.9 Chemistry of Actinides and Lanthanides 21
1.9.1 Oxidation state 23
1.9.2 Disproportionation 25
1.9.3 Complex formation of actinides 25
1.10 Actinide partitioning 26
1.10.1 TRUEX Process 26
1.10.2 TRPO process 26
1.10.3 DIDPA Process 27
1.10.4 TALSPEAK Process 27
1.11 Ion Exchange 28
1.12 Role of Ion exchangers in nuclear industry 31
1.13 Literature survey on phosphorus based ion exchange resins 32
1.14 Scope of present work 33
1.15 References 36
2. **EXPERIMENTAL**

**PART I** Synthesis and Characterisation

2.1 Introduction

2.1.1 Preparation of ion exchange resins

2.1.2 Solution polymerisation

2.1.3 Emulsion polymerisation

2.1.4 Suspension polymerisation

2.2 Selective polymer supported resins

2.3 Capacity

2.3.1 Weight capacity

2.3.2 Volume capacity

2.3.3 Apparent capacity

2.3.4 Sorption capacity

2.3.5 Breakthrough capacity

2.3.6 Salt splitting capacity

2.4 Functionalization of phosphinic acid resin

2.5 Sulphonation

2.5.1 Sulphonation of phosphinic acid resin

2.6 Characterisation

2.6.1 Total Capacity

2.6.2 Phosphorus Content
2.6.3  P-H bond capacity  
2.6.4  Sulphur content  
2.7  Chemicals and preparation of solutions  

**PART II**  

2.8  Instrumentation  
2.8.1  Spectrophotometer  
2.8.2  Alpha Spectrometry  
2.8.3  ICP – AES  
2.8.4  Scintillation counter  
2.8.4.1  ZnS (Ag) Scintillation Counter  
2.8.4.2  NaI (Tl) Scintillation Counter  
2.9  Analytical Methods  
2.9.1  Estimation of uranium  
2.9.1.1  Spectrophotometric method  
2.9.1.1.1  Bromo-PADAP Method  
2.9.1.1.2  Ammonium Thiocyanate Method  
2.9.1.2  Davis and Gray method  
2.9.2  Estimation of plutonium  
2.9.3  Estimation of americium  
2.10  References  

**3. DISTRIBUTION STUDIES**  

3.1  Introduction
| 3.1.1 | Ion exchange equilibria | 71 |
| 3.1.2 | Selectivity | 72 |
| 3.1.3 | Selectivity coefficient | 73 |
| 3.1.4 | Ion exchange isotherms | 74 |
| 3.1.5 | Separation factor | 74 |
| 3.1.6 | Distribution coefficient | 75 |
| 3.1.7 | Dependence on temperature | 76 |
| 3.2 | Experimental Methods | 76 |
| 3.2.1 | Batch extraction | 76 |
| 3.2.2 | Column operations | 77 |
| 3.3 | Uptake Measurements | 78 |
| 3.3.1 | Effect of amount of resin | 78 |
| 3.3.2 | Extraction of Pu(IV) from nitric acid medium | 80 |
| 3.3.3 | Extraction of Pu(III) and Pu(VI) from nitric acid medium | 82 |
| 3.3.4 | Extraction of Pu(IV) from sulphuric acid medium | 83 |
| 3.3.5 | Extraction of U(VI) from nitric acid medium | 85 |
| 3.3.6 | Extraction of Am(III) | 87 |
| 3.3.7 | Extraction of Eu(III) | 88 |
| 3.3.8 | Extraction of Nd(III) | 89 |
| 3.3.9 | Extraction of uranium at different salt strengths | 90 |
| 3.3.10 | Effect of temperature on extraction | 93 |
## RESULTS AND DISCUSSION

### PART II

1. **Importance of Analytical services in reprocessing industry**
   - **Process control analysis**: 136
   - **Plant control analysis**: 136
   - **Quality control analysis**: 137
   - **Miscellaneous analysis**: 137
   - **Accountability analysis**: 137
   - **Pu reconversion process operation**: 137

2. **Classification of secondary wastes**
   - **Oxalate analytical waste**: 140
     - **Importance of Free Acidity**: 140
     - **Analytical procedure**: 141
     - **Waste disposal**: 141
   - **Titrimetric analytical waste**: 142
     - **Importance of analysis of uranium concentration**: 142
     - **Analytical procedure (Davis-Gray method)**: 143
     - **Waste disposal**: 143
   - **Potentiometric analytical waste**: 144
     - **Importance of Pu analysis**: 144
     - **Analytical procedure** *(modified Drummond and Grant method)*: 145
5.5.3.3 Waste disposal 145

5.6 Experimental 146

5.6.1 Batch equilibration studies using oxalate supernatant 146

5.6.2 Batch equilibration studies using oxalate analytical waste 146

5.6.3 Batch equilibration studies using titrimetric analytical waste 147

5.6.4 Batch equilibration studies using potentiometric analytical waste 147

5.7 Results and Discussion 147

5.8 Conclusion 151

6. SUMMARY AND CONCLUSION 154

6.1 Scope for future Study 159

List of Publications 161

List of corrections incorporated in the thesis after a suggestion from examiners 162
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig 1.1</td>
<td>Schematic presentation of India’s 3 stage nuclear programme</td>
<td>4</td>
</tr>
<tr>
<td>Fig 1.2</td>
<td>Schematic representation of Closed Nuclear fuel</td>
<td>6</td>
</tr>
<tr>
<td>Fig 1.3</td>
<td>Schematic layout of purex process</td>
<td>12</td>
</tr>
<tr>
<td>Fig 1.4</td>
<td>Partitioning of minor actinides- Impact on waste management</td>
<td>20</td>
</tr>
<tr>
<td>Fig 2.1</td>
<td>Experimental set up for synthesis</td>
<td>49</td>
</tr>
<tr>
<td>Fig 2.2</td>
<td>Synthesis scheme of phosphination</td>
<td>53</td>
</tr>
<tr>
<td>Fig 2.3</td>
<td>Synthesis scheme of sulphonation</td>
<td>54</td>
</tr>
<tr>
<td>Fig 3.1</td>
<td>Variation of $K_D$ of Pu(IV) with weight of resin</td>
<td>79</td>
</tr>
<tr>
<td>Fig 3.2</td>
<td>Extraction of Pu(IV) from the nitric acid medium</td>
<td>81</td>
</tr>
<tr>
<td>Fig 3.3</td>
<td>Extraction of Pu(IV) from sulphuric acid medium</td>
<td>84</td>
</tr>
<tr>
<td>Fig 3.4</td>
<td>Extraction of U(VI) from nitric acid medium</td>
<td>86</td>
</tr>
<tr>
<td>Fig 3.5</td>
<td>Extraction of Am(III) from nitric acid medium</td>
<td>87</td>
</tr>
<tr>
<td>Fig 3.6</td>
<td>Extraction of Eu(III) from nitric acid medium</td>
<td>89</td>
</tr>
<tr>
<td>Fig 3.7</td>
<td>Extraction of Nd(III) from nitric acid medium</td>
<td>90</td>
</tr>
<tr>
<td>Fig 3.8</td>
<td>Variation of $K_D$ of uranium on phosphinic acid resin and sulphonated phosphinic acid resin with acidity</td>
<td>96</td>
</tr>
<tr>
<td>Fig 3.9</td>
<td>Variation of log $K_D$ with log acidity of uranium on sulphonated phosphinic acid resin</td>
<td>97</td>
</tr>
<tr>
<td>Fig.4.1</td>
<td>Extraction of Pu(IV) by phosphinic acid resin</td>
<td>112</td>
</tr>
<tr>
<td>Fig 4.2</td>
<td>Ft vs. time of Pu(IV) on phosphinic acid resin</td>
<td>113</td>
</tr>
<tr>
<td>Fig 4.3</td>
<td>Bt vs. time of Pu(IV) on phosphinic acid resin</td>
<td>114</td>
</tr>
</tbody>
</table>
Fig.4.4 Extraction of Pu(IV) by sulphonated phosphinic acid resin 115
Fig4.5 Ft vs. time of Pu(IV) on sulphonated phosphinic acid resin 116
Fig 4.6 Ft vs. time of Pu(IV) on different resins at 0.5 M HNO₃ 117
Fig 4.7 Ft vs. time of Pu(IV) at 6 M HNO₃ 118
Fig 4.8 Bt vs. time of Pu(IV) by sulphonated phosphinic acid resin 119
Fig.5.1 Breakthrough curve for Pu(IV) on
sulphonated phosphinic acid resin at 3M HNO₃.

List of Tables

Table 1.1 Computed HLW Composition (burn up –7000 MWD/ T and cooling time 1 year) 18
Table 1.2: Major contributors of beta and gamma activities in HLW 19
Table 1.3 Electronic configuration of actinides and lanthanides 22
Table 1.4 Oxidation states of actinides 24
Table 1.5 Isotopes of actinides and their half-lives 24
Table 2.1 Functional groups of selective ion exchangers 45
Table 2.2 Characterization of synthesised resins 53
Table 3.1 Extraction studies with Pu(III) and Pu(VI) from 1 M HNO₃ 83
Table 3.2. Effect of NaNO₃ concentration in the extraction of U(VI) =1 g/ L with acidity 0.5M 91
Table 3.3 Effect of temperature on extraction of U(VI) from 1M HNO₃ 93
Table 5.1 Batch equilibration studies with SHLW 129

xxvi
Table 5.2  Column experiment for 100% breakthrough capacity of Pu(IV) on Sulphonated phosphinic acid resin

Table 5.3  Column studies with SHLW, H⁺ = 3 M

Table 5.4  Column studies with SHLW, H⁺ = 0.5 M

Table 5.5  Column studies with HLW

Table 5.6  Batch equilibration studies with ILW

Table 5.7  Batch equilibration studies with Pu oxalate supernatant

Table 5.8  Batch equilibration studies with oxalate analytical waste

Table 5.9  Batch equilibration studies with titrimetric analytical waste

Table 5.10 Batch equilibration studies with potentiometric analytical waste