SOLID PHASE EXTRACTION BEHAVIOR OF Am(III) AND Eu(III) IN SOLVENT IMPREGNATED RESINS CONTAINING CMPO, TEHDGA AND HDEHP AND THEIR DEGRADATION STUDIES

By

G. SAIPRIYA

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Bhabha Atomic Research Centre, Mumbai

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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 G. Saipriya entitled "**Solid phase extraction behavior of Am(III) and Eu(III) in solvent impregnated resins containing CMPO, TEHDGA and HDEHP and their radiolytic degradation studies**" and recommend that it may be accepted as fulfilling the thesis requirement for the award of Degree of Doctor of Philosophy.

Chairman - Dr. S. Velmurugan **Date:** 19.04.2018

Guide / Convener - Dr. M. P. Antony **Date:** 19.04.2018

Examiner - Dr. Ashok Khanna Ashok Khanna **Date:** 19.04.2018

Member 1- Dr. N. Sivaraman N. Sivaraman **Date:** 19.04.2018

Member 2- Dr. C. Mallika CMallika **Date:** 19.04.2018

Technology Adviser- Dr. T. Kumar 19/4/18 **Date:** 19.04.2018

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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.

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List of Publications arising from the thesis

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3. "Studies on the adsorption behavior of americium and europium on radiolytically degraded solvent impregnated resin containing neutral and acidic extractants" G. Saipriya, R. Kumaresan, P. K. Nayak, K. A. Venkatesan, T. Kumar and M. P. Antony, *J. Radioanal. Nucl. Chem.,* **2017**, 314(3), 2557-2568.

Conferences

1. Studies on the extraction of Am (III) and Eu(III) in TEHDGA-HDEHP system. K. Saipriya, R. Kumaresan, P. K. Nayak, K. A. Venkatesan, T. Kumar and M. P. Antony, Proceedings of DAE-BRNS Biennial Symposium on Emerging Trends in Separation Science and Technology (SESTEC 2016), IIT- Guwahathi, India, p-55.

2. Single-cycle extraction chromatographic method for separation of trivalent actinides from simulated high level waste. K. Saipriya, R. Kumaresan, P. K. Nayak, S. Rajesh, K. A. Venkatesan, T. Kumar and M. P. Antony, International conference on Recent Advances in Analytical Science (RAAS-2016), IIT-Varanasi (BHU), India, p-111.

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Dedicated to my beloved father

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CONTENTS

Title	Page no.
SYNOPSIS	i
LIST OF FIGURES	xiv
LIST OF TABLES	xx
Chapter 1: Introduction	**1**
1.1. Nuclear Energy	1
1.2. Nuclear fuel cycle	2
1.3. Indian nuclear power programme	4
1.4. Reprocessing of spent nuclear fuel	7
1.5. Radiotoxicity of HLLW	10
1.6. Partitioning and Transmutation	11
1.7. Partitioning of minor actinides	14
1.8. Solvent extraction processes for minor actinide partitioning	15
1.8.1. Solvent extraction	15
1.8.2. Extractants for the metal ion recovery	16
1.8.3. Types of extractants	17
1.8.3.1. Acidic extractants	18
1.8.3.2. Basic (Anionic) extractants	19
1.8.3.3. Neutral extractants	20
1.8.3.4. Chelating extractants	21

1.8.4. Two-cycle separation of minor actinides from HLLW **21**

1.8.4.1. Lanthanide-Actinide(III) co-extraction (Group separation) **21**

1.8.4.2. Mutual separation of lanthanides and actinides **22**

1.8.5. Single-cycle separation of minor actinides from HLLW **24**

1.8.5.1. Direct separation of trivalent actinides from lanthanides **24**

1.8.5.1.1. BTP process **24**

1.8.5.1.2. BTBP process **25**

1.8.5.2. Single-cycle separation using a combination of solvents **25**

1.8.5.2.1. TRUSPEAK process **26**

1.8.5.2.2.PALADIN process **26**

1.9. Solid phase separations for minor actinide partitioning **29**

1.9.1. Solid phase extraction **29**

1.9.1.1. Methods for the preparation of solvent impregnated resins **32**

1.9.1.2. Methods for the preparation of Levextrel resins **33**

1.9.1.3. Solid-phase extraction sorbents **33**

1.9.1.4. Solid-phase extraction sorbents for actinides and lanthanides separations **35**

1.9.1.4.1. Polymer based solvent impregnated resins for actinide and lanthanide extraction studies **37**

1.9.1.4.2. Silica based solvent impregnated resins for actinide and lanthanide extraction studies **39**

1.10. Adsorption Isotherms **40**

1.10.1. Langmuir isotherm **40**

1.10.2. Freundlich isotherm **41**

1.10.3. Temkin isotherm **41**

1.10.4. Dubinin – Radushkevich isotherm **42**

1.11. Radiolytic stability of solvent impregnated resins **43**

1.12. Scope of the present study **44**

1.13. References **46**

Chapter 2: Experimental **61**

2.1. Chemicals and reagents **61**

2.1.1. Radioactive tracers **62**

2.1.2. Organic materials and solvents **62**

2.1.3. Aqueous solutions and complexing agents **64**

2.2. Extractants used in distribution studies **66**

2.2.1. Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) **66**

2.2.2. Tetra-bis(2-ethylhexyl) diglycolamide (TEHDGA) **66**

2.2.3. Bis-(2-ethylhexyl) phosphoric acid (HDEHP) **67**

2.3. Instrumentation **69**

2.3.1. Gamma counter **69**

2.3.2. Gamma chamber for irradiation **70**

2.3.3. Rotary evaporator **70**

2.3.4. Thermostatted rotary water bath shaker **70**

2.3.5. pH meter **71**

2.3.6. Inductively coupled plasma-optical emission spectrometer **71**

2.3.7. NMR spectrometer **72**

2.3.8. FT-IR spectrometer **72**

2.3.9. Electronic single pan balance **72**

2.3.10. Column chromatography 75

2.3.11. Thin Layer Chromatography 75

2.4. Preparation of Fast Reactor Simulated High-Level Liquid Waste (FR-SHLLW) 75

2.5. Standard europium nitrate solution for adsorption studies 76

2.5.1. Potassium oxalate solution 78

2.5.2. Standard EDTA solution 78

2.6. Experimental procedures 78

2.6.1. Liquid - liquid extraction studies for checking the purity of extractants 78

2.6.2. Solid-liquid extraction studies for the uptake of Am(III) and Eu(III) metal ions 79

3.6.2.1. Preparation of solvent impregnated (extraction chromatographic) resins 79

3.6.2.2. Distribution coefficient measurements 80

3.6.2.3. Kinetic studies 81

3.6.2.4. Studies on selective separation of Am(III) 83

2.7. Irradiation experiments 83

2.8. Adsorption isotherms 84

2.9. References 85

Chapter 3: Extraction behavior of Am(III) and Eu(III) from nitric acid medium in CMPO-HDEHP impregnated resins 87

3.1. Introduction 87

3.2. Extraction of Am(III) in HDEHP impregnated resins 93

3.3. Extraction of Am(III) in CMPO impregnated resins 95

3.4. Extraction of Am(III) in combined resin **97**
3.5. Extraction of Eu(III) in individual and combined resins **98**
3.6. Extraction mechanism at 0.01 M nitric acid **99**
3.7. Extraction mechanism at 2 M nitric acid **101**
3.8. Selective separation of Am(III) **104**
3.9. Conclusion **105**
3.10 References **107**

Chapter 4: Extraction behavior of Am(III) and Eu(III) from nitric acid medium in TEHDGA-HDEHP impregnated resins 113

4.1. Introduction **113**
4.2. Kinetics of extraction **114**
4.3. Extraction of Am(III) in TEHDGA impregnated resin **118**
4.4. Extraction of Am(III) in HDEHP impregnated resin **121**
4.5. Extraction of Am(III) in 30%TEHDGA+10%HDEHP (combined) impregnated resin **121**
4.6. Extraction of Eu(III) in individual and combined resins **122**
4.7. Extraction mechanism of Am(III) and Eu(III) in combined resin **124**
4.8. Studies with fast reactor simulated high-level liquid waste **128**
4.9. Selective separation of Am(III) **130**
4.10. Conclusion **131**
4.11. References **132**

Chapter 5: Radiolytic degradation studies of solvent impregnated resins containing neutral extractants such as CMPO and TEHDGA in conjunction with an acidic extractant HDEHP 139

5.1. Introduction **139**

5.2. Extraction behavior of Am(III) and Eu(III) at 3 M nitric acid in CMPO+HDEHP and CMPO systems **141**

5.3. Extraction behavior of Am(III) and Eu(III) at 3 M nitric acid in TEHDGA+HDEHP and TEHDGA systems **144**

5.4. Extraction behavior of Am(III) and Eu(III) at 0.01 M nitric acid in CMPO+HDEHP and HDEHP systems **147**

5.5. Extraction behavior of Am(III) and Eu(III) at 0.01 M nitric acid in TEHDGA+HDEHP and HDEHP systems **150**

5.6. Separation factor of Eu(III) over Am(III) **153**

5.7. Conclusion **155**

5.8. References **156**

Chapter 6: Studies on the adsorption behavior of Eu(III) on irradiated and un-irradiated solvent impregnated resins containing neutral and acidic extractants 159

6.1. Introduction **159**

- 6.1.1. Langmuir adsorption isotherm **160**
- 6.1.2. Freundlich adsorption isotherm **160**
- 6.1.3. Temkin isotherm **161**
- 6.1.4. Dubinin-Radushkevich (D-R) isotherm **162**

6.2. Adsorption isotherm of Eu(III) **163**

6.3. Conclusion **176**

6.4. References 177

Chapter 7: Summary and Conclusions 181

7.1. Extraction behavior of Am(III) & Eu(III) in CMPO-HDEHP impregnated resins 181

7.2. Extraction behavior of Am(III) and Eu(III) in TEHDGA-HDEHP impregnated resins 182

7.3. Radiolytic degradation studies of SIRs containing neutral extractants such as CMPO and TEHDGA in conjunction with an acidic extractant HDEHP 183

7.4. Studies on the adsorption behavior of Eu(III) on irradiated and un-irradiated SIRs containing neutral (CMPO, TEHDGA) and acidic extractant (HDEHP) 184

Chapter 8: Scope of Future Studies 187

Appendix 191

Glossary 192

SYNOPSIS

1.Introduction

Energy is an important ingredient of life. Energy consumption has a major role to play in enhancing economic and civilization growth of human beings [1-2]. Energy consumption is often taken as the benchmark for quality life. The demand for energy has increased with phenomenal increase in human population followed by fast growing industrialization and urbanization [3]. Nearly 75 % of the world energy production has been predominantly catered by the fossil fuels such as coal, natural gas, and oil owing to their widespread availability [4, 5].The use of these fossil fuels leads to the generation of greenhouse gases, causing global warming [6].Therefore, to meet the world demand of electricity and to deal with the climate change objectives the usage of low carbon sources of electricity is essential [7]. Huge consumption of natural energy sources such as oil and gas, and limited technological progress in the development of renewable resources such as solar, tidal and wind etc., makes nuclear energy a proven source of low carbon electricity.Nuclear energy source is an inevitable option for the future energy demand. Currently nuclear energy contributes nearly 11% of the global electricity and 3% of total energy production in India[8]. The contribution of nuclear energy needs to be increased from the present 3 % to at least 25% in coming years to satisfy the future energy demand. According to the Indian nuclear three stage program [9], the first stage deals with the production of electrical energy through natural uranium fuelled pressurized heavy water reactors (PHWR). In the second stage, the depleted uranium and plutonium recovered from the spent fuels of PHWR would be used to fuel the fast breeder reactors (FBR) to generate electricity as well as to breed ^{233}U from thorium which is used as blanket. In the third stage, the fissile ^{233}U will be used in the ^{233}U based thermal breeder reactors to produce electricity as well as to further breed ^{233}U from thorium. The fuel discharged from reactor after energy production is called spent nuclear fuel (SNF). The spent nuclear fuel contains significant quantities of fissile elements, such as plutonium, depleted (unused) uranium, and several fission products formed during fission reaction. Therefore, it is necessary to reprocess the spent nuclear fuel for the recovery of the fissile elements for further use in the reactors as fuel to sustain the nuclear energy program in India.

Two major techniques based on aqueous and non-aqueous processes have been adopted for reprocessing of spent nuclear fuels. Among these, the aqueous process, namely PUREX (Plutonium Uranium Recovery by EXtraction) process has been widely used for the reprocessing of spent nuclear fuel [10, 11]. The PUREX process is a solvent extraction process, involving the dissolution of spent nuclear fuel in nitric acid medium and selectively extracting the fissile elements uranium(VI) and plutonium(IV) by 1.1 M tributyl phosphate (TBP) in n-dodecane. The aqueous product (PUREX raffinate) discarded after this process is known as “high level liquid waste” (HLLW).This HLLW solution comprises mixture of minor actinides, small amounts of unrecovered plutonium and uranium, lanthanides, other fission products, corrosion products arising from structural materials and process chemicals. Among the various elements present in HLLW, long-lived radiotoxic minor actinides (formed in small concentrations 0.1%) such as ^{237}Np, ^{241}Am, ^{243}Am, ^{244}Cm, ^{245}Cm, ^{243}Cm and heat emitting fission products like ^{99}Tc, ^{107}Pd, ^{93}Zr, ^{129}I, ^{135}Cs, ^{137}Cs and ^{90}Sr contribute to the maximum level of radio-toxicity. Since the half-lives of these isotopes are in range between few years to several hundred years, HLLW poses long-term risks to the public health and the environmental safety [12]. Therefore, the future nuclear energy depends on the safe management of HLLW. At present, the HLLW is vitrified in the form of borosilicate glass and is envisaged to be stored in deep geological repositories for long time [13-15]. However, such repositories require continuous long-term surveillance, due to the presence of these radiotoxic minor actinides as their half-lives are high. In case of accidental ground-water invasion into these repositories, the radiotoxic metal ions can be released into the environment owing to their significant solubility and higher mobility in aqueous medium. Therefore, the current disposal practice is a very expensive option. On the other hand, partitioning (P) of these minor actinides from HLLW and their subsequent transmutation (T) into stable or short-lived products by using fast reactors or accelerated driven systems (ADS) could reduce the radio-toxicity of HLLW [16]. Therefore, P&T strategy is a necessary option for the safe management of HLLW.

The partitioning of minor actinides from HLLW is one of the most challenging problems. The minor actinides separated from HLLW are accompanied by lanthanides, as the two groups of f-elements have very similar physical, chemical and extractive properties [17]. Currently, partitioning of trivalent actinides from HLLW is being carried out by a two-cycle approach namely (i) group separation of trivalent lanthanides and actinides together from HLLW, followed by the recovery using dilute nitric acid in the first-cycle, and (ii) mutual separation of lanthanides and actinides from dilute nitric acid medium in the second-cycle. The presence of lanthanides along with actinides reduces the efficiency of actinide transmutation, due to the high neutron absorption cross section of lanthanides.Apart from this, lanthanides do not form solid solutions in metal alloys or in mixed oxide transmutation targets. As a result they segregate into separate phases with a tendency to grow under thermal treatment. Thus, the minor actinides tend to concentrate in these phases and this will lead to an unacceptable non-uniform heat distribution in the transmutation fuel matrix under irradiation [18]. In view of these, complete separation of Ln(III) from An(III) is necessary prior to the actinide transmutation.

For the first cycle, several methods and extractants have been proposed for co-extraction of trivalent An(III) and Ln(III) from HLLW, such as TRUEX, DIAMEX, DIDPA which employ octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphineoxide (CMPO),N,Ndimethyl-N,N-dibutyltetradecylmalonamide(DMDBTDMA), diisodecylphosphoric acid (DIDPA) and trialkyl phosphine oxide (TRPO) as the extractants [19]. Along with these extractants, various DGAs studied so far, N,N,N',N' -tetra-octyldiglycolamide (TODGA) and N,N,N',N'-tetra-2-ethylhexyl diglycolamide (TEHDGA) have several advantages over other reagents [20]. In the second cycle lanthanide, actinide mutual separation was carried out by TALSPEAK (Trivalent Actinide – Lanthanide Separation by Phosphorusreagent Extraction from Aqueous Komplexes) process. This process involves the selective separation of An(III) from lactate buffered diethylenetriaminepentaaceticacid (DTPA) solution using bis-(2-ethylhexyl)phosphoric acid (HDEHP) in 1,4-diisopropylbenzene [21]. In recent decades, the extractants containing soft donor ligands capable of binding selectively actinides are being studied extensively for An(III)/Ln(III) separation.

In contrast to the two-cycle approach, single-cycle methods have been receiving much attention in the recent past, for the separation of trivalent actinides directly from HLLW.The literature showed that there are two approaches available for developing single cycle process. In one approach, actinides(III) can be directly extracted from

PUREXraffinate by using the extractant consisting of soft donor ligands. For example, 1-cycle SANEX process for direct selective separation of actinides(III) from PUREX raffinate by using a mixture of tetramethyl-5,6,7,8-tetrahydro-benzo-[1,2,4]-triazin-3-yl)-[2,2]-bipyridine (CyMe4BTBP) &tetraoctyldiglycolamide (TODGA) in a TPH/1-octanol solution [22]. Another approach deals with the co-extraction of both An(III)+ Ln(III) from nitric acid medium by a suitable solvent(combined neutral and acidic extractant). The selective separation of actinides(III) alone from the loaded organic phase can be achieved using soft donor stripping agents [23].

2. Scope of the present study:

Industrially, the separation methods are being widely used in actinide partitioning is based on solvent extraction mode. Though the liquid-liquid extraction is a promising technique, it has couple of limitations such as third phase formation and high solvent inventory [24]. To minimize these limitations solid phase extraction method was developed. In fact the solid phase extraction method (SPE) is an apt method for the separation of small quantities of trivalent actinides from a large volume of HLLW. Solid-phase extraction technique is a simple, rapid and low solvent inventory method, combines the selectivity of solvent extraction with the operational benifits of column chromatography [25]. Nevertheless, limited studies have been reported so far, for the separation of actinides by solid phase extraction (extraction chromatography) as compared to solvent extraction.

The aim of the present study is to develop a single cycle method for trivalent actinide partitioningby using a neutral extractant and an acidic extractant in solid phase separation mode. The extraction behaviour of Am(III) representing minor actinides and Eu(III) representing lanthanides from nitric acid medium was studied with solvent impregnated resins (SIR) containing either CMPO or HDEHP and a combination of CMPO and HDEHP. In this case, both Am(III) and Eu(III) are extracted to organic phase using combined solvent system followed by the selective stripping of Am(III) using Diethylenetriaminepentaacetic acid (DTPA)-Citric Acid (CA) solution. The distribution coefficient of Am(III) and Eu(III) was measured in various combinations of impregnated resins from different nitric acid concentrations.

In the same way, the extraction behavior of Am(III) and Eu(III) from nitric acid medium was studied with TEHDGA or HDEHP and a combination of TEHDGA and HDEHP impregnated resins. Mutual separation of Am(III) and Eu(III) was achieved with 0.005 M DTPA + 0.1 M CA + 1 M $NaNO_3$. A simulated solution corresponding to the composition of HLLW originating from Fast Reactor (FR-SHLLW) is proposed and the extraction behavior of metal ions present in FR-SHLLW was also studied extensively using 30% TEHDGA+10% HDEHP. The results indicate that 90% of trivalent lanthanides and Am(III) extracted in single contact of combined resin.

The radiation stability of CMPO-HDEHP and TEHDGA-HDEHP solvent impregnated resins were studied. Adsorption behavior of Eu(III) on CMPO-HDEHP and TEHDGA-HDEHP systems were studied. Different isotherm models were fitted to find the maximum adsorption capacity of resins and the type of adsorption.

3. Organization of the thesis:

3.1. Chapter 1

The first chapter describes the role of electricity and nuclear energy for the sustainable development of nation. It explains about nuclear fission and the three-stage Indian nuclear energy programme. This chapter also deals with brief introduction to nuclear fuel cycle and importance of spent nuclear fuel reprocessing to recover fissile and fertile materials to provide fresh fuel for the existing and future nuclear power plants. This chapter explains about Partitioning and Transmutation (P&T) strategy for the safe management of HLLW and provides the detailed literature survey on various methods proposed for the partitioning of actinides from HLLW and tells the need for mutual separation of lanthanides and actinides. It points out the merits and demerits of various processes and reagents proposed for the separation of long-lived radiotoxic actinides. This chapter also compares the single cycle and two cycle process for actinide partitioning. It also discusses the separation of actinides by different techniques. It explains about the merits of solid phase extraction technique over conventional liquid-liquid extraction used for actinide partitioning.

3.2. Chapter 2

This chapter deals with the details of various chemicals and reagents used for the present work. This also includes the detailed impregnation procedures on inert polymeric support. Methodologies adopted for the measurement of radioactivity of various radioisotopes using sodium iodide thalium NaI(Tl) detector is discussed. Usage of inductively coupled plasma-optical emission spectroscopy (ICP-OES) for the determination of concentration of various metal ions presents in FR-SHLLW, and thereby the distribution ratio measurements etc., are explained.

3.3. Chapter 3

This chapter discusses the extraction behavior of Am(III) and Eu(III) by using a Chromatographic resin containing extractants such as octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphineoxide (CMPO) or bis-(2-ethylhexyl)phosphoricacid (HDEHP) or mixture of extractants (CMPO + HDEHP) in ingle cycle solid phase separation mode.The extraction of Am(III) and Eu(III) was studied over a range of nitric acid concentration with this combined resin. The effect of various parameters such as concentration of nitric acid in aqueous phase and the concentration of CMPO and HDEHP in the resin phase was studied and the results were given in this chapter. In a combined system, synergistic extraction was observed at lower nitric acid concentration (< 0.5M) and antagonism was observed at higher nitric acid concentration. The mechanism of extraction was probed by slope analysis method at 0.01 and 2M nitric acid concentrations. The recovery of Am(III) from the loaded organic phase was carried out by the optimized aqueous formulation composed of 0.001 M DTPA+0.1 M citric acid (CA) at pH 3.

3.4. Chapter 4

This chapter deals with the development of single-cycle process for the separation of Am(III) and Eu(III) using solvent impregnated resins containing extractants such as tetra-bis(2-ethylhexyl)diglycolamide (TEHDGA) or bis-(2-ethylhexyl)phosphoric acid (HDEHP) or mixture of TEHDGA + HDEHP. The rate of extraction of Am(III) and Eu(III) from 1 M nitric acid and the effect of various parameters, such as the concentration of nitric acid in aqueous phase and concentration of TEHDGA and HDEHP in resin phase was studied. The distribution coefficient of Am(III)and Eu(III) in HDEHP-impregnated resin decreased and that in TEHDGA-impregnated resin increased, with increase in the concentration of nitric acid. In TEHDGA + HDEHP – impregnated resin, synergistic extraction was observed at lower nitric acid concentration and antagonism at higher nitric acid concentration as similar to CMPO-HDEHP resin. The mechanism of Am(III) and Eu(III) extraction in the combined resin was investigated by slope analysis method. The extraction of various metal ions present in the fast reactor simulated high-level liquid waste was studied. The extraction of Am(III) was accompanied by the co-extraction of all lanthanides and unwanted metal ions such as Zr(IV), Y(III), and Pd(II) from FR-SHLLW. The co-extraction of unwanted metal ions is minimized by adding trans-1,2-diaminocyclohexane-N,N,N'N'-tetraacetic acid (CyDTA) to FR-SHLLW, prior to extraction. The separation factor of Am(III) over Eu(III) was studied using citrate-buffered diethylenetriaminepentaacetic acid(DTPA) solution.

3.5. Chapter 5

This chapter describes the radiolytic stability of CMPO-HDEHP and TEHDGA-HDEHP combined solvent impregnated resins (SIR) along with their individual extractant impregnated resin systems. The extractants to be employed for the separation of radiotoxic elements such as actinides and long-lived fission products invariably exposed to the high energetic radiation associated with them. Under these conditions, the covalent bonds in extractant may undergo cleavage to generate degradation products. Therefore, the reagents used for the actinide separations need to be strong with respect to high radiation. The degree of degradation was assessed by measuring the distribution ratio of Am(III), Eu(III) with irradiated resins as a function of absorbed dose of γ-radiation. Extraction behavior of irradiated systems at different dose rates were studied at both extraction and stripping conditions.

3.6. Chapter 6

This chapter explains about adsorption behavior of Eu(III) on CMPO-HDEHP and TEHDGA-HDEHP solvent impregnated systems. It describes the distribution of metals between the solid-liquid phases at equilibrium by using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) adsorption isotherm models.Adsorption isotherms describe the relationship between the equilibrium concentration of metal ions in solution and the amount of metal ions adsorbed on a specific adsorbent. Different concentrations of europium stock solutions were prepared and equilibrating with solvent impregnated resins to study the distribution of europium metal ion between solid-liquid phases. Results obtained were utilized to arrive the maximum adsorption capacity of the resins by applying the data on different adsorption isotherms models. The adsorption capacity values were compared with the irradiated systems. The Langmuir adsorption isotherm model described the adsorption of metal ions on homogeneous surface of an adsorbent. Each adsorptive site can be occupied only once in a one-to-one manner with constant adsorption energy without any interaction between the adsorbed ions. The Freundlich adsorption isotherm model is used to describe the adsorption of an adsorbate on a heterogeneous surface of an adsorbent by assuming multilayer adsorption. The temkin isotherm indicated that the heat of adsorption of all the molecules decreases linearly with coverage of adsorbent. It also gives the details about the type of adsorption process, like physisorption, chemisorptions or ion exchange based on adsorption energies calculated. D-R model expressed the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface.

3.2. Chapter 7

This Chapter provides the summary and conclusions of all the studies reported in the thesis. This chapter also discusses the scope for the future work in this field.

REFERENCES

1. Jose Goldenberg, editor. Energy: What Everyone Needs to know, Oxford University Press 2012.

2. Hiranmoy Roy, RajaiahJayaraj, Anshunan Gupta, Energy consumption and human development: global perspective, Economics and Policy of Energy and Environment, 1 (2015) 111-131, DOI: 10.3280/EFE2015-001008.
3. D. Dash, B. Mishra, M. K. Satapathy, Education for Sustainable Development, Indian Educational Review (NCERT) 47 (2010) 7-29.
4. S. David, Future Scenarios of fission based reactors, Nucl. Phys. A, 751 (2005) 429–441.
5. R. B. Grover, Nuclear energy: Emerging trends. Curr. Sci. 78 (2000) 1191.
6. Chandra pal, Environmental pollution and Development, Mittal Publications, 1st Edition (1999).
7. http://www.world-nuclear.org/focus/climate-change-and-nuclear-energy/nuclear-must-be-part-of-the-international-response.aspx.
8. S. A. Bhardwaj, Indian nuclear power programme–Past, present and future, Sadhana 38 (2013) 775-794.
9. H. J. Bhabha, The role of atomic power in India and its immediate possibilities, In: Proc. of the Internatl. Conf. on the Peaceful uses of Atoic Energy, 1, Geneva, 1955, p-103.
10. H.A.C.Mckay, J.H.Miles, J.L.Swanson,The PUREX Process. In: W.W. Schulz, J.D.Navratil, K.P. Bender (eds) Science and technology of tributyl phosphate vol III, CRC Press, Boca Raton Florida. (1990).
11. P. K. Dey, N. K. Bansal, Spent fuel reprocessing: A vital link in Indian nuclear power program, Nuclear Engineering and Design, 236 (2006) 723.
12. Status and Trends of Spent Fuel reprocessing, IAEA TECDOC-1103, 1999.

13. I. W. Donald, B. L. Metcalfe, R. J. Taylor. The immobilization of high level radioactive wastes using ceramics and glasses. J. Mater. Sci. 32 (1997) 5851-5887.

14. E. M. Gonzalez-Romero, Impact of partitioning and transmutation on the high level waste management. Nucl. Eng. Des. 241 (2011) 3436-3444.

15. K. Raj, K. K. Prasad, N. K. Bansal, Radioactive waste management practices in India. Nuclear Engineering and Design, 236 (2006) 914-930.

16. Implications of Partitioning and Transmutation in Radioactive Waste Management. IAEA Technical Reports Series, STI/DOC/010/435, 2004.

17. K. L. Nash, A review of the basic chemistry and recent developments in trivalent f-elements separation. Solvent Extr. Ion Exch. 11 (1993) 729-768.

18. V. Anastasov, M. Betti, F. Boisson, F. Depisch, F. Houlbreque, R. Jeffree, I. Khamis, S. Lattemann, J. C. Miquel, S. Nisan, P. K. Tewari, Status of minor actinide fuel development, IAEA Nuclear energy series No. NF-T-4.6. 2009.

19. J. N. Mathur, M. S. Murali, K. L. Nash, Actinide partitioning-a review, Solvent Extr. Ion Exch. 19 (2001) 357-390.

20. S. A. Ansari, P. N. Pathak, P. K. Mohapatra, V. K. Manchanda, Chemistry of diglycolamides: Promising extractants for actinide partitioning. Chem.Rev.112 (2012) 1751-1772.

21. M. Nilsson, K. L. Nash. A review of the development and operational characteristics of the TALSPEAK process, Solvent Extr. Ion Exch. 25 (2007) 665-701.

22. A. Wilden, C. Schreinemachers, M. Sypula, G. Modolo, Direct selective extraction of actinides (III) from purex raffinate using a mixture of CyMe4BTBP

and TODGA as 1-cycle SANEX, solvent. Solvent Extr. IonExch. 29 (2011) 190–212.

23. G. J. Lumetta, A. V. Gelis, F. Vandegrift, Solvent systems combining neutral and acidic extractants for separating trivalent lanthanides from the transuranic elements, Solvent Extr. IonExch. 28 (2010) 287–312.
24. P. R.VasudevaRao,Z.Kolarik,.: A review of third phase formationin extraction of actinides by neutral organophosphorusextractants. *Solvent Extr. Ion Exch.* 14(1996) 955–993.
25. E.P. Horwitz, D.R. McAlister, M.L. Dietz, Extraction chromatography versus solvent extraction: how similar are they, Sep. Sci. Technol. 41 (2006)2163–2182.

LIST OF FIGURES

Figure No.	Title of the Figure	Page No.
1.1.	Schematic representation of open and closed fuel cycles	**4**
1.2.	Schematic diagram of Indian nuclear power programme	**5**
1.3.	Schematic diagram of PUREX process	**9**
1.4.	Depiction of the advantage of P&T strategy over direct disposal of SNF for minimizing the radiotoxicity	**12**
1.5.	Graphical representation of two cycle and single cycle process	**28**
1.6.	Solvent impregnated resin bead	**30**
1.7.	Classification of impregnated resins	**31**
2.1.	Reaction scheme for the synthesis of diglycolamides	**68**
2.2.	Structure of extractants	**68**
2.3.	Block diagram of a typical ICP – OES instrument	**74**
3.1.	Variation of distribution coefficient of Am(III) as a function of nitric acid concentration.Resin = 30% CMPO/ADS 400 or 10% HDEHP/ADS 400 or 30%CMPO+10%HDEHP/ADS 400. Aqueous phase= HNO_3 from 0.01 M to 4 M	**94**
3.2.	Dependence of distribution coefficient on the concentration of HDEHP in resin phase for the extraction of Am(III) and Eu(III) at 0.01 M HNO_3	**94**
3.3.	Dependence of distribution coefficient on the concentration of CMPO in resin phase for the extraction of Am(III) and Eu(III) at 2 M HNO_3	**96**

3.4. Variation of distribution coefficient of Eu(III) as a function of nitric acid concentration. Resin = 30% CMPO/ADS 400 or 10% HDEHP/ADS 400 or 30%CMPO+10%HDEHP/ADS 400. Aqueous phase= HNO_3 from 0.01 M to 4 M **98**

3.5. Dependence of distribution coefficient on the concentration of CMPO in resin phase for the extraction of Am(III) and Eu(III). Resin = CMPO + 10% HDEHP/ ADS 400. Aqueous phase = 0.01 M HNO_3 **100**

3.6. Dependence of distribution coefficient on the concentration of HDEHP in resin phase for the extraction of Am(III) and Eu(III). Resin = HDEHP + 30% CMPO/ ADS 400. Aqueous phase = 0.01 M nitric acid **100**

3.7. Dependence of distribution coefficient on the concentration of CMPO in resin phase for the extraction of Am(III) and Eu(III). Resin = CMPO + 10% HDEHP/ ADS 400. Aqueous phase = 2 M HNO_3 **103**

3.8. Dependence of distribution coefficient on the concentration of HDEHP in resin phase for the extraction of Am(III) and Eu(III). Resin= HDEHP + 30% CMPO/ ADS 400. Aqueous phase = 2 M nitric acid **103**

4.1. Variation in the percentage extraction of Eu(III) and Am(III) as a function of time, fitted by using pseudo-first order rate equation. Resin phase= 10% HDEHP + 30% TEHDGA – impregnated resin (0.05 g), Aqueous Phase= 1M HNO_3 (5 mL) spiked with $^{(152+154)}$Eu(III) or ^{241}Am(III) tracer **115**

4.2. Variation in the percentage extraction of Eu(III) and Am(III) as a function of time, fitted by using pseudo-second order rate equation. Resin phase= 10% HDEHP + 30% TEHDGA – impregnated resin (0.05 g), Aqueous Phase= 1M HNO_3 (5 mL) spiked with $^{(152+154)}$Eu(III) or ^{241}Am(III) tracer **115**

4.3. Variation in the distribution coefficient of Am(III) as a function of nitric acid concentration. Resin = 30%TEHDGA/ADS 400 or 10%HDEHP/ADS 400 or 30%TEHDGA+10%HDEHP/ADS 400. Aqueous phase = nitric acid from 0.01 M to 3 M **120**

4.4. Dependence of distribution coefficient on the concentration of TEHDGA in resin phase for the extraction of Am(III) and Eu(III) at 3 M nitric acid concentration. Resin= TEHDGA/ADS 400 **120**

4.5. Variation in the distribution coefficient of Eu(III) as a function of nitric acid concentration. Resin = 30%TEHDGA/ADS 400 or 10%HDEHP/ADS 400 or 30%TEHDGA+10%HDEHP/ADS 400. Aqueous phase = nitric acid from 0.01 M to 3 M **123**

4.6. Dependence of distribution coefficient on the concentration of TEHDGA in resin phase for the extraction of Am(III) & Eu(III). Resin = TEHDGA+10% HDEHP/ADS 400. Aqueous phase=0.01 M HNO_3 **125**

4.7. Dependence of distribution coefficient on the concentration of HDEHP in resin phase for the extraction of Am(III) & Eu(III). Resin = HDEHP+30% TEHDGA/ADS 400. Aqueous phase=0.01 M HNO_3 **125**

4.8. Dependence of distribution coefficient on the concentration of TEHDGA in resin phase for the extraction of Am(III) and Eu(III). Resin = TEHDGA + 10% HDEHP/ ADS 400. Aqueous phase = 3 M nitric acid **127**

4.9. Dependence of distribution coefficient on the concentration of HDEHP in resin phase for the extraction of Am(III) & Eu(III). Resin = HDEHP + 30% TEHDGA/ ADS 400. Aqueous phase = 3 M HNO_3 **127**

5.1.(a) Variation of distribution coefficient of Am(III) as a function of absorbed dose. Resins = 30% CMPO/ADS 400 or 30%CMPO+10% HDEHP/ADS 400, Aqueous phase =3M HNO_3, v/m=100 **142**

5.1.(b) Variation of percentage extraction of Am(III) as a function of absorbed dose. Resins=30%CMPO/ADS 400 or 30%CMPO+10%HDEHP/ADS 400, Aqueous phase=3M HNO_3, v/m=100 **142**

5.1.(c) Variation of distribution coefficient of Eu(III) as a function of absorbed dose. Resins=30% CMPO/ADS 400 or 30% CMPO+10% HDEHP/ADS 400, Aqueous phase =3M HNO_3, v/m=100 **143**

5.1.(d) Variation of percentage extraction of Eu(III) as a function of absorbed dose. Resins=30%CMPO/ADS 400 or 30%CMPO+ 10%HDEHP/ADS 400, Aqueous phase =3M HNO_3, v/m=100 **143**

5.2.(a) Variation of distribution coefficient of Am(III) as a function of absorbed dose. Resins = 30% TEHDGA/ADS 400 or 30% TEHDGA+10% HDEHP/ADS 400, Aqueous phase= 3M HNO_3, v/m=100 **145**

5.2.(b) Variation of percentage extraction of Am(III) as a function of absorbed dose. Resins = 30% TEHDGA/ADS 400 or 30% TEHDGA+10% HDEHP/ADS 400, Aqueous phase= 3M HNO_3, v/m=100 **145**

5.2.(c) Variation of distribution coefficient of Eu(III) as a function of absorbed dose. Resins = 30% TEHDGA/ADS 400 or 30% TEHDGA+10% HDEHP/ADS 400, Aqueous phase= 3M HNO_3, v/m=100 **146**

5.2.(d) Variation of percentage extraction of Eu(III) as a function of absorbed dose. Resins = 30% TEHDGA/ADS 400 or 30% TEHDGA+10% HDEHP/ADS 400, Aqueous phase= 3M HNO_3, v/m=100 **146**

5.3.(a) Variation of distribution coefficient of Am(III) as a function of absorbed dose. Resins = 10% HDEHP/ADS 400 or 30% CMPO+10% HDEHP/ADS 400, Aqueous phase =0.01M HNO_3, v/m=100 **148**

5.3.(b) Variation of percentage extraction of Am(III) as a function of absorbed dose. Resins = 10% HDEHP/ADS 400 or 30% CMPO+10% HDEHP/ADS 400, Aqueous phase =0.01M HNO_3, v/m=100 **148**

5.3.(c) Variation of distribution coefficient of Eu(III) as a function of absorbed dose. Resins = 10% HDEHP/ADS 400 or 30%CMPO+10% HDEHP/ADS 400, Aqueous phase =0.01 M HNO_3, v/m=100 **149**

5.3.(d) Variation of percentage extraction of Eu(III) as a function of absorbed dose. Resins = 10% HDEHP/ADS 400 or 30%CMPO+10% HDEHP/ADS 400, Aqueous phase =0.01 M HNO_3, v/m=100 **149**

5.4.(a) Variation of distribution coefficient of Am(III) as a function of absorbed dose. Resin=10% HDEHP/ADS 400 or30%TEHDGA+10% HDEHP/ADS 400, Aqueous phase =0.01 M HNO_3, v/m=100 **151**

5.4.(b) Variation of percentage extraction of Am(III) as a function of absorbed dose. Resin=10% HDEHP/ADS 400 or 30%TEHDGA+10% HDEHP/ADS 400, Aqueous phase =0.01 M HNO_3, v/m=100 **151**

5.4.(c) Variation of distribution coefficient of Eu(III) as a function of absorbed dose. Resin=10% HDEHP/ADS 400 or 30%TEHDGA+10% HDEHP/ADS 400, Aqueous phase=0.01 M HNO_3, v/m=100 **152**

5.4.(d) Variation of percentage extraction of Eu(III) as a function of absorbed dose. Resin=10% HDEHP/ADS 400 or 30% TEHDGA+10% HDEHP/ADS 400, Aqueous phase =0.01 M HNO_3, v/m=100 **152**

6.1. The non-linear fitting of various adsorption isotherm models on un-irradiated 30% CMPO +10% HDEHP/ADS 400 resin. Aqueous phase = 3 M nitric acid **166**

6.2 The non-linear fitting of various adsorption isotherm models on 550kGyirradiated 30% CMPO +10% HDEHP/ADS 400 resin.Aqueous phase = 3 M nitric acid **167**

6.3. The non-linear fitting of various adsorption isotherm models on un-irradiated 30%CMPO/ADS400 resin.Aqueous phase=3 M nitric acid **168**

6.4. The non-linear fitting of various adsorption isotherm models on 550 kGyirradiated 30% CMPO /ADS 400 resin.Aqueous phase = 3 M nitric acid **169**

6.5. The non-linear fitting of various adsorption isotherm models on un-irradiated 30% TEHDGA+10% HDEHP/ADS 400 resin. Aqueous phase = 3 M nitric acid **170**

6.6. The non-linear fitting of various adsorption isotherm models on 550kGy irradiated 30% TEHDGA +10% HDEHP/ADS 400 resin. Aqueous phase = 3 M nitric acid **171**

6.7. The non-linear fitting of various adsorption isotherm models on un-irradiated 30% TEHDGA/ADS 400 resin. Aqueous phase = 3 M nitric acid **172**

6.8. The non-linear fitting of various adsorption isotherm models on 550kGy irradiated 30% TEHDGA/ADS 400 resin. Aqueous phase = 3 M nitric acid **173**

LIST OF TABLES

Table No.	Title of theTable	Page No.
1.1.	Half-lives of actinides due to natural decay and by fission with fast neutrons.	**13**
2.1.	Operating conditions and description of ICP-OES instrument.	**73**
2.2.	The simulated composition of fast reactor high-level liquid waste (FR-SHLLW). The composition is based on the HLLW arising from reprocessing of spent fast reactor fuel with a burn-up of 80,000 MWd/Te and 2 year cooling.	**77**
3.1.	Extraction of Am(III) and Eu(III) from the aqueous solution containing various concentration of DTPA and citric acid.	**105**
4.1.	Fitting Constants and the statistical parameters obtained for the rate of extraction of Am(III) and Eu(III) in TEHDGA+HDEHP- impregnated resin	**117**
4.2.	Percentage of extraction of metal ions from FR-SHLLW. Resin = 30% TEHDGA + 10 % HDEHP impregnated resin. Aqueous phase = FR-SHLLW in 3 M HNO_3. Weight or resin = 1 g. Volume of aqueous phase = 5 mL	**129**
4.3.	Extraction of Am(III) and Eu(III) from the aqueous solution containing various concentration of DTPA and citric acid. SF = $D_{Eu(III)}$ / $D_{Am(III)}$ Resin Phase = HDEHP + 30% TEHDGA – impregnated resin (0.05 g), Aqueous phase = 0.005 M DTPA + 0.1 M CA + 1 M $NaNO_3$.	**131**

5.1. Variation in the separation factor of Eu(III) over Am(III) at 3 M and 0.01 M nitric acid. Resins = 30% CMPO + 10% HDEHP, 30% TEHDGA + 10% HDEHP, 30% CMPO, 30% TEHDGA, 10% HDEHP (un-irradiated and irradiated up to 550 kGy). **154**

6.1. Fitting constants and statistical parameters obtained from various adsorption isotherms for un-irradiated SIR systems. **174**

6.2. Fitting constants and statistical parameters obtained from various adsorption isotherms for irradiated SIR systems (550 kGy). **175**

CHAPTER 1

Chapter 1: Introduction

1.1. Nuclear Energy

Electricity is indispensable for the livelihood of human beings and it plays an important role in the economic development of the country [1]. The per capita electricity consumption is directly related to per capita gross national production, which in turn is related to the quality life and health of the human population living in the country [2]. The demand for energy has increased roughly by 2-3% per annum on global scale, for the past two decades [3]. Although India is the fourth largest energy consumer in the world, about 19 percent of the populations do not have the access to electricity and majority of the population are still out of the reach of industrialization. The per capita electricity consumption in India is 1000 kWh, very much less compared to developed countries, whose average is nearly 15,000 kWh [4]. The total energy demand of India by the year 2050 is estimated to be 1000 GWe [5, 6]. Therefore, there is an urgent need to identify the suitable energy resources for meeting the heavy demand for energy in future. At present, 75% of energy in India is predominantly produced by power plants that use fossil fuels like coal, natural gas and oil [7]. However, there are several issues associated with the use of these fuels even though they provide reliable source of energy, at present. They emit green house gases, mostly co_2 emissions and causes global warming [8]. In addition the fossil fuels are consumed at a rapid rate and there is uncertainty in the technological progress in the renewable resources such as solar, tidal, wind etc. Therefore, in order to meet the future demand for energy and to resolve the issues associated with the climatological changes, it is envisaged to use a low carbon source of electricity production. All these factors make the nuclear option inevitable for catering the future energy demand [9, 10]. The potentiality of nuclear fuel lies in the enormous quantity of power it can generate in comparison to conventional fuels. The quantity of fuel required for nuclear power plants is very less as compared to other plants which burn fossil fuels. The energy production from one ton of natural uranium is much higher than that two to three million tons of coal or oil. Production of more fuel than that consumed in the nuclear reactor using breeding technology is feasible. Nuclear power plants produce the nuclear energy by fissioning of heavy nuclei into lighter nuclei of unequal masses. The fissile heavy elements such as ^{235}U, ^{233}U, ^{239}Pu, undergo fission by both slow and fast neutrons. The nuclear reactors are designed in such a way to obtain controlled release of energy. The heat energy liberated during fission is then converted into electrical energy [11]. India ranks 13th country in the world in terms of nuclear power generation, with installed capacity of 5.8 GW in 2014 from 21 reactors at seven sites. Six reactors, with a total capacity of around 4 GW are in the various stages of construction [4, 12]. Currently nuclear energy contributes nearly 11% of the global electricity and 3% of total energy production in India [2, 6].

1.2. Nuclear fuel cycle

Nuclear fuel cycle encompasses the science and technology associated with the various stages of production of electricity through a nuclear reactor. The various steps involved in the science and technology are the mineral exploration, mineral processing, purification of uranium/thorium, fuel fabrication, reactor operation, spent fuel reprocessing, radioactive waste management and recycling of fissile material [13]. The “Front End” of the fuel cycle includes stages from mining of the ore to the reactor operation, and the "Back End" of the fuel cycle includes the discharging of the irradiated fuel from the reactor and its subsequent reprocessing, recovery of valuables and treatment and disposal of high level waste. The fuel after sufficient use in the nuclear reactor is reffered as 'spent nuclear fuel'(SNF) [14], contains valuable materials such as depleted uranium (U), plutonium (Pu) and several radionuclides formed by the fission reaction, known as "fission products"(FPs). Along with this, some transuranium elements such as neptunium, americium and curium are also formed in small concentrations (~0.1%) as activated products. These elements are called as minor actinides (MA).

There are two options available for the management of the spent fuel [15, 16]: a) reprocessing and recycling of the fissile elements, known as closed fuel cycle option and b) direct geological disposal of spent fuel as waste, known as open fuel cycle option. The open fuel cycle option is not a suitable option for countries like India, where availability of uranium reserves are very limited. Apart from this, direct disposal of spent nuclear fuel is not an acceptable option for the public health and safety of the environment due to very long half-lives of these actinides. Open fuel cycle option also requires a continuous long-term surveillance making this option expensive. In India, closed fuel cycle option is followed, in which the spent fuel is reprocessed for the recovery of fissile elements and recycle them for fueling in the future reactors. Therefore, the closed fuel cycle, enables effective utilization of the fuel resources to sustain the nuclear energy programme in India [17]. Figure 1.1 illustrates the various stages involved in nuclear fuel cycle.

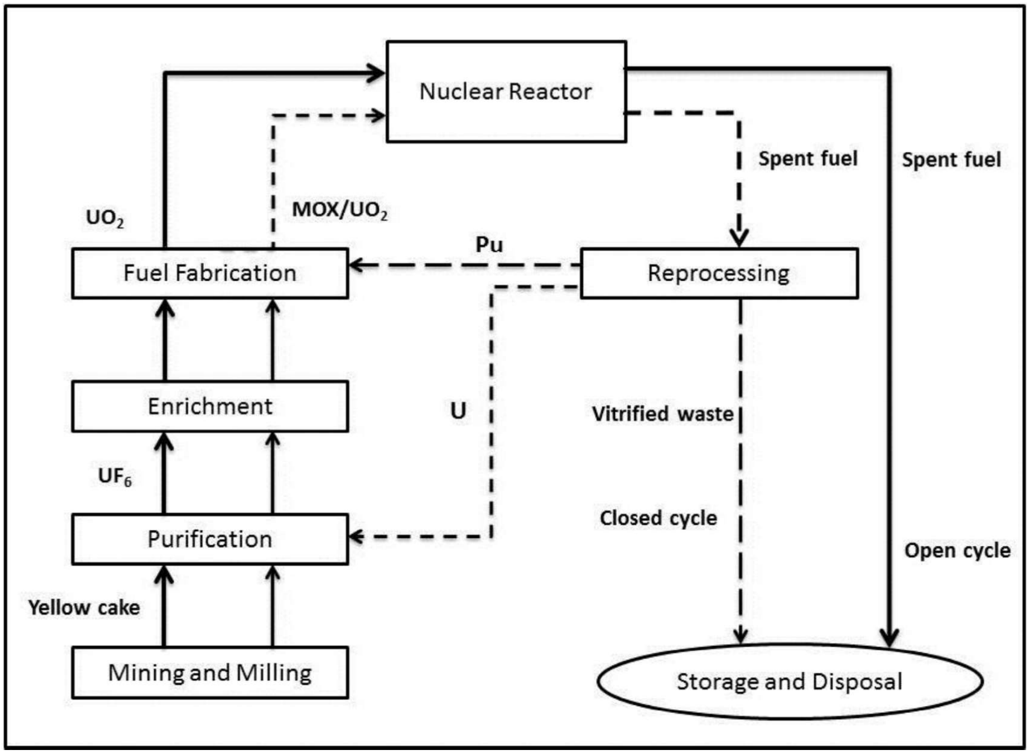


Figure 1.1. Schematic representation of open and closed fuel cycles.

1.3. Indian nuclear power programme

Natural uranium reserves of India is estimated to be ~1,72,000 tons of U_3O_8 while thorium is estimated as ~6,50,000 tons [18]. The amount of uranium available in India could set a limitation to the growth of nuclear energy as in the case of fossil fuels. However, the generation of ^{239}Pu and ^{233}U in breeder reactors overcomes this limitation. ^{239}Pu can be generated using natural uranium containing ^{238}U as fuel and ^{233}U can be generated by bombarding fertile ^{232}Th with neutrons. Keeping this in view, a three-stage programme has been envisaged [19] and implemented in our country by the visionary Dr. Homi Jehangir Bhabha in 1950's. This was initiated for the effective utilization of uranium and enormous thorium reserves for the production of energy to secure the country's long term energy requirement. It is based on a closed fuel cycle concept, requiring reprocessing of spent fuel from every reactor. A schematic of Indian three stage nuclear program is depicted in figure. 1.2.

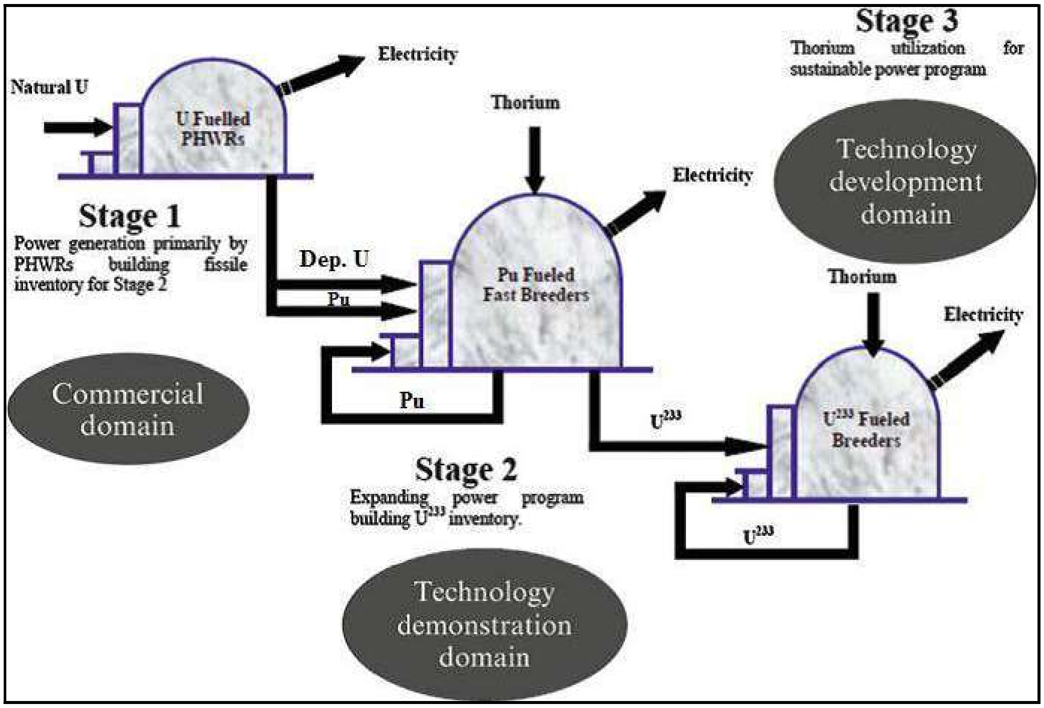


Figure 1.2. Schematic diagram of Indian nuclear power programme [20].

1. In the first stage of the programme, ^{235}U from the domestic natural uranium undergoes fission in a thermal reactor, and produces ^{239}Pu from fertile ^{238}U. At present all operating reactors in India are based on the use of either natural uranium (0.7% ^{235}U or enriched uranium (3-4% ^{235}U). Currently, there are eighteen PHWRs, two BWR, and two PWR (VVER) operating with a total capacity of 6780 MWe [21]. The spent fuel from PHWR contain small quantities of fissile ^{239}Pu, along with residual uranium (known as depleted uranium, in which predominantly ^{238}U). The spent fuel can be reprocessed chemically to separate plutonium and residual uranium from fission products. The product obtained in the first stage namely plutonium and depleted uranium is used for fueling in fast breeder reactors (FBRs) in the 2nd stage.

2. The second stage is based on the setting up of Fast Breeder Reactors (FBRs) which are fuelled by mixed oxide of ^{238}U and ^{239}Pu, recovered by reprocessing of the spent fuel from the first stage reactors. A 40 MWt Fast Breeder Test Reactor (FBTR) is in operation at Kalpakkam since 1985 [22] to demonstrate the second stage with indigenously developed mixed carbide ($U_{0.3}Pu_{0.7}$) as the fuel. India's first commercial fast reactor, the 500 MWe Prototype Fast Breeder Reactor (PFBR) is in the advanced stage of completion. In FBRs, ^{239}Pu undergoes fission, producing energy, and producing ^{239}Pu by transmutation of ^{238}U. Thus the FBRs produce energy and fuel, hence termed Breeders. FBRs are capable of generating more fuel than they consume and thus are technically capable of growing the nuclear capacity to a very high level. In the second stage nuclear power reactors, thorium (Th) is kept as blanket for converting the fertile Th into fissile ^{233}U, which will form fuel to the third stage of the programme [23].

3. In the third stage, the fissile ^{233}U will be used in thermal or fast breeders to produce electricity as well as to further breed ^{233}U from thorium. Thus the third stage of Indian nuclear power programme is purely based on the usage of plentiful resources of thorium available in India. A 30 KWt reactor, KAMINI at kalpakkam, India is the only reactor in the world, which uses ^{233}U as fuel [24]. In addition to this, Advanced Heavy Water Reactors (AHWRs) are also conceptualized to employ ^{233}U as fuel. According to the three-stage programme, Indian nuclear energy could grow to about 10 GW through PHWRs fueled by domestic uranium and the growth expected to come from FBRs will be about 50 GW. The third stage is to be deployed only after the successful achievement of 2nd stage [25].

1.4. Reprocessing of spent nuclear fuel

Reprocessing forms the vital link among the three stages of nuclear power programme and the success of the closed fuel cycle would depend on the efficient utilization of plutonium for power generation. Spent fuel reprocessing which forms an important part in the Back End of Nuclear Fuel cycle involves the separation of nuclear grade uranium and plutonium from spent fuel [26]. The spent nuclear fuels discharged from nuclear power reactors contain significant amounts of fissile element, plutonium and unused fertile element uranium. Nuclear fuel reprocessing is the chemical treatment of spent fuel involving separation of its various constituents .The spent fuel is reprocessed to recover and recycle the plutonium and uranium in the next stage reactors. The spent nuclear fuel can be reprocessed in two ways: aqueous reprocessing and non-aqueous reprocessing (pyrochemical process) methods. Though, pyrochemical process has attractive features such as less number of process steps, lower volumes of waste generated and easier waste management etc., it has several limitations compared to aqueous reprocessing such as lower separation factors for fission products, need for remote operation, need for sophisticated equipment, need for high purity inert atmosphere to enable handling of hygroscopic salts and reactive metals, high temperature operation etc [27, 28]. Among the aqueous based processes, Plutonium Uranium Recovery by Extraction (PUREX) process has been widely employed for reprocessing of spent nuclear fuel [29, 30]. This process involves the chemical separation of plutonium and uranium from spent nuclear fuel by a liquid-liquid separation process. PUREX process developed at Knoll Atomic Power laboratory (KAPL) and the Oak Ridge National Laboratory (ORNL) and after several modifications has been industrially employed as the primary process for the recovery of uranium and plutonium from spent nuclear fuel. In India PUREX plants are being successfully operated at Trombay, Tarapur and Kalpakkam. It uses tri-*n*-butyl phosphate (TBP) diluted with *n*-dodecane as solvent to extract uranium and plutonium. Because of the ability of actinides to form strong solvation type complexes with extractant such as Tri-*n*-butyl phosphate (TBP) resulted in the separation of actinides from fission products. The PUREX process consists of three major steps. These are (i) head end step, which includes de-cladding of fuel, dissolution, and feed preparation, (ii) solvent extraction using tri-*n*-butyl phosphate (TBP), which involves co-extraction and partitioning of uranium and plutonium, and (iii) final purification and conversion of uranium and plutonium to their respective oxides [26].

In detail, PUREX process (Figure 1.3), the head end step involves the chopping of irradiated fuel pins into smaller pieces and then leached with hot 8-10 M nitric acid. The acidity of dissolver solution is then adjusted to 2-3 M and the valence state of plutonium was adjusted to Pu(IV) using NO_2 gas. The aim of this second step is to separate uranium and plutonium from whole of fission products as well as from each other. This is effected by extracting both U(VI) and Pu(IV) together into 30% TBP in aliphatic hydrocarbon diluents such as, *n*-dodecane leaving behind the whole of fission products, which goes as high active waste (HAW). The loaded organic is subjected to scrub with 2 M HNO_3 to remove the carried over fission products. Partitioning of uranium and plutonium is carried out by the selective reduction of Pu(IV) to Pu(III) in the organic phase, which then comes back to the aqueous phase of lower acidity nitric acid. This reduction is generally carried out by uranous nitrate stabilized with hydrazine. Also, hydrazine helps in stabilizing U(IV) in the nitric acid medium by scavenging the nitrite ions. The uranium in the organic phase is finally stripped using 0.01 M $NaNO_2$. After an additional cycle of purification, the uranium is concentrated and precipitated as ammonium diuranate, filtered and calcined to U_3O_8. Similarly, plutonium in the aqueous phase is also passed through an additional cycle of purification by solvent extraction or anion exchange, precipitated as oxalate and calcined to PuO_2 [26].

The raffinate rejected after the extraction of uranium and plutonium by PUREX process is known as “high-active waste” (HAW). The HAW is composed of fission products, activation products, lanthanides, the remaining minor actinides (^{241}Am, ^{243}Am, ^{245}Cm and ^{237}Np) and additives. This high active waste is generally concentrated ~ 20 times to obtain “high-level liquid waste” (HLLW).

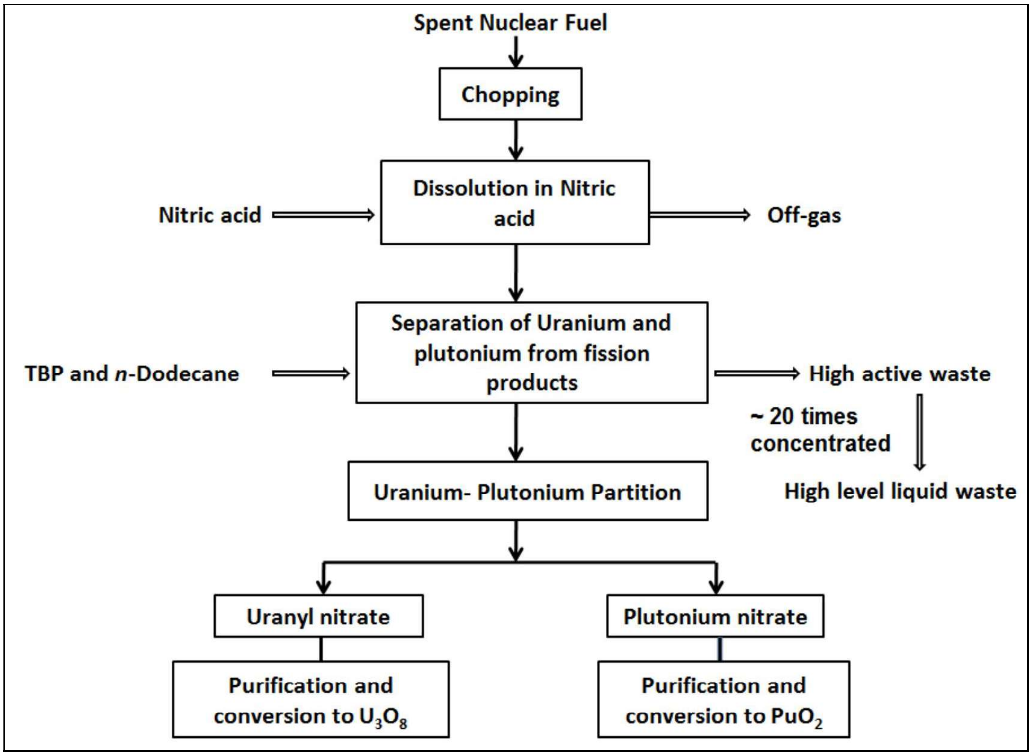


Figure 1.3. Schematic diagram of PUREX process.

1.5. Radiotoxicity of HLLW

The long-term radiotoxicity of high level liquid waste (HLLW) generated in spent nuclear fuel reprocessing is governed by the content of several long-lived minor actinides (MA) and some specific fission products. The HLLW contains un-extracted U, Pu, minor actinides (such as Am, Np, Cm), lanthanides, fission product elements such as Tc, Pd, Zr, I, Cs, and Sr, transition metal elements including Fe, Ni, Co, Zr, and some salts of Fe, Al, and Na [31]. Minor actinides so called since they constitute less than 0.1% of spent fuel composition. Since the half lives of minor actinides and some of the fission products range from few hundred to millions of years, HLLW poses a long term radiological risk to the public health and environment [32]. Figure 1.4 shows the radiotoxicity of spent nuclear fuel and high-level liquid waste over the range of time. It can be seen that the estimated time for the radiotoxicity of spent nuclear fuel and HLLW, to decay to the background level (equal to natural uranium) is $10^5 - 10^6$ years. In the first 100 years after discharge from nuclear reactor, the radiotoxicity of SNF is essentially contributed by fission products [33]. It is then determined by Pu and other minor actinides such as Np, Am and Cm. Since plutonium is recovered from the spent nuclear fuel by reprocessing and used as fuel for future reactors, the long-term radiotoxicity of HLLW is essentially contributed by the minor actinides such as ^{237}Np, ^{241}Am, ^{243}Am, ^{244}Cm, ^{245}Cm, ^{243}Cm and fission products such as ^{99}Tc, ^{107}Pd, ^{93}Zr, ^{129}I, ^{135}Cs, ^{137}Cs, and ^{90}Sr. The sustainability of the future nuclear energy depends on the safe management of HLLW which must be safe guarded to human health as well as the ecology.

At present, the most accepted approach for the management of HLLW is to vitrify the waste in a glass matrix followed by interim storage to allow the decay of heat-dissipating nuclides such as ^{137}Cs and ^{90}Sr and its subsequent disposal in deep geological repositories [34, 35]. The half lives of a few minor actinides and some fission product elements range between a few hundreds to millions of years. Therefore, storing vitrified blocks for such a long period is not favorable option from an economic, as well as an environmental safety point of view. There is also the possible risk of the migration of long-lived minor actinides from the repository to the aquatic environment owing to their significant solubility and higher mobility in aqueous medium. Partitioning and Transmutation (P&T) strategy is another accepted method to remediate the radiotoxicity of HLLW. P&T involves the separation of minor actinides from HLLW, followed by transmutation of them into short-lived or stable isotopes [36, 37]. Details of P&T are explained in section 1.6. As shown in Figure 1.4, if the actinides are not removed from the spent fuel, it will require millions of years to reduce its radiotoxicity to the level of natural uranium ore [38]. Thus, the safe management of nuclear waste plays an important role in the success of nuclear energy.

1.6. Partitioning and Transmutation

The P&T process envisages the complete removal of minor actinides from radioactive waste and their subsequent transmutation (T) into stable or short-lived products. This P&T process will lead to generation of extra energy and at the same time would alleviate the need for long term surveillance of geological repositories. After partitioning of the actinides along with the long lived fission products, the residual waste can be vitrified and buried in subsurface repositories at a much reduced risk and cost. Several countries worldwide are currently exploring the strategy of P&T (Partitioning and Transmutation), which aims to reduce the radiotoxicity of the waste by prior separation of uranium, plutonium, minor actinides, and other long-lived fission products. This strategy reduces the radiotoxicity of HLLW to a large extent, and simplifies the management of HLLW. Figure 1.4 depicts advantage of P&T strategy in minimizing the radiotoxicity of HLLW [38]. The great decrease in radiotoxicity is because of the removal of plutonium as well as the complete burning of minor actinides in the fast reactor. Therefore, P&T is inevitable for safe management of HLLW. Table 1.1 compares the natural half-lives of actinides before and after transmutation. It is interesting to note that the average half-life of HLLW can be dramatically reduced to very small values by transmutation [39].

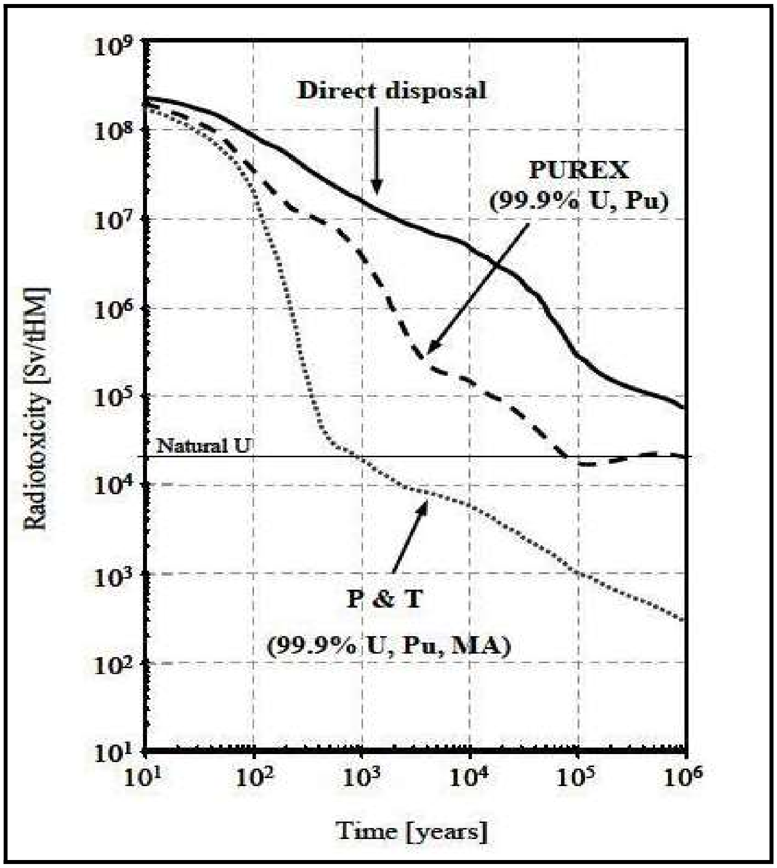


Figure 1.4. Depiction of the advantage of P&T strategy over direct disposal of SNF for minimizing the radiotoxicity [38].

Table 1.1. Half-lives of actinides due to natural decay and by fission with fast neutrons [39]

Actinide	$t_{1/2}$ (natural decay) in years	$\tau_{1/2}$ (transmutation) in years
^{237}Np	2.14×10^6	2.46
^{238}Pu	88	1.61
^{239}Pu	2×10^4	1.76
^{240}Pu	6×10^3	2.35
^{241}Pu	14	1.95
^{242}Pu	4×10^5	2.83
^{241}Am	433	2.40
^{242m}Am	152	1.72
^{243}Am	7×10^3	2.89
^{242}Cm	0.44	1.93
^{243}Cm	30	1.46
^{244}Cm	18	1.97
^{245}Cm	8×10^3	1.60

1.7. Partitioning of minor actinides

The success of P&T strategy depends on efficient separation of minor actinides and burning in ADS. However, in order to transmute minor actinides, they must be separated from the lanthanide fission products also present in HLLW. This separation is necessary, since the lanthanides act as neutron poisons during transmutation of actinides in ADS and prevents transmutation of minor actinides. In addition, the lanthanides do not form solid solutions easily with americium and curium during the preparation of targets for transmutation in the form of metal-alloy or oxide [40]. They also tend to segregate upon thermal treatment. In view of these, the complete separation of Ln(III) from An(III) is very important prior to the actinide transmutation.

Partitioning of trivalent actinides from HLLW is one of the most challenging problems. It involves the selective separation of trivalent actinides from the chemically similar lanthanides present in HLLW. The stable oxidation state of trans-plutonium actinides (Am and Cm) in HLLW is +3. The concentration levels of these actinides are very small in HLLW. In contrast to this, the trivalent lanthanides (Ln(III)) in HLLW as fission products present in substantially high concentrations. As the two groups of f-elements have very similar physical, chemical and extractive properties, it is difficult to separate the trivalent actinides alone from HLLW [41]. Moreover, the high concentration of nitric acid (3-4 M) prevailing in HAW also complicates the separation procedure to a great extent. Therefore, the current method for partitioning involves the liquid-liquid extraction of An(III) and Ln(III) together from HLLW in the first extraction cycle, followed by lanthanide-actinide separation in the second cycle. Details are discussed in sections 1.8.4 & 1.8.5.

In contrast to this traditional approach, a single-cycle approach has been developed in which the actinides are separated directly from HLLW in a single processing cycle. To improve efficiency and reduce the cost associated with partitioning the TRU elements from irradiated fuel, a single process for separating minor actinide elements from the PUREX process raffinate is desirable. The literature showed that there are two approaches available for developing single cycle process. In one approach, actinides (III) can be directly extracted from PUREX raffinate by using the extractant consisting of soft donor ligands. Another approach deals with the co-extraction of both An(III) and Ln(III) from nitric acid medium by a suitable solvent (combined neutral and acidic extractant). The selective separation of actinides(III) alone from the loaded organic phase can be achieved using soft donor stripping agents. Several methods and reagents have been developed and studied for these separations. Details are discussed in 1.8.6 section. The separation methods mostly used in actinide separations are based on liquid-liquid extraction mode.

1.8. Solvent extraction processes for minor actinide partitioning

1.8.1. Solvent extraction

Solvent extraction is a versatile technique for the separation of desired products from a complex mixture of other metal ions present in the aqueous medium [42, 43]. It plays a very important role in various industries such as nuclear, metallurgical, pharmaceutical, food and beverage, chemical, petrochemical, biochemical, catalysis, polymers etc.,

Solvent extraction essentially depends on the distribution of a solute (for example a desired metal ion, M) between two immiscible/partially miscible liquids generally aqueous and organic liquids in contact with each other. The distribution ratio of a solute M (D_M) is defined as the ratio of the activity or concentration of the solute in organic phase ($[M]_{org}$) to that in aqueous phase ($[M]_{aq}$) at equilibrium, as shown in equation 1.1.

$$D_M = \frac{(a_M)_{org}}{(a_M)_{aq}} \, or \, \frac{[M]_{org}}{[M]_{aq}} \tag{1.1}$$

The distribution ratio of solute is constant for a given pair of liquids at constant temperature. In metal recovery operations, the valuable component is a metal ion or metal complex contained in aqueous solution. This aqueous solution is mixed with an immiscible organic phase containing the active extractant, for the complexation of metal ions to form neutral hydrophobic species in the organic phase. The extractant transfers metal ion from aqueous phase into organic phase by a series of chemical reactions, referred as “extraction”. The organic phase loaded with the solute is then transferred to the stripping section and is mixed with stripping aqueous solution containing a suitable reagent that provides the driving force required to recover (back extract) the solute. The organic phase obtained after stripping is called lean organic phase and is recycled back for extraction and the aqueous phase containing metal now goes to final metal recovery.

1.8.2. Extractants for the metal ion recovery

The extractants used for the separation of valuable materials in solvent extraction are high viscous organic ligands. In all solvent extraction procedures, the ligands are dissolved in an “inert” second organic medium in which the ligands are completely miscible [44]. The inert organic medium is called as diluent. The diluent role in solvent extraction procedure is to obtain desirable hydrodynamic properties for solvent extraction and to improve the selectivity of extraction. Several advantages such as improved mass transfer, improved phase separation, decreased solubility of the extractant into the aqueous phase are obtained as a result of the addition of diluents. Sometimes, other components such as phase modifiers and synergists are also added to alter physicochemical characteristics of the organic phase and also to enhance extraction. The liquid phase containing the extractant, diluent, modifier and synergist is called the solvent phase. Following are the characteristic features of a ligand to be used as extractant [45].

a. High solubility in paraffinic solvents (non-polar solvents),
b. Low solubility in the aqueous phase,
c. Non-volatility, non-toxicity and non-inflammability,
d. High complexation ability with the metal ions of interest,
e. High solubility of the metal-ligand complex in the organic phase, i.e. high metal loading capacity in the organic phase,
f. Ease of stripping of metal ions from the organic phase,
g. Reasonably high selectivity for the metal ion of interest over the other metal ions present in the aqueous solution,
h. Optimum viscosity for ease of flow and optimum inter facial tension (IFT) to enable a faster rate of phase disengagement,
i. Ease of regeneration of the extractant for recycling,
j. High resistance to radiolytic and chemical degradation during operation, and ease of synthesis / availability at a reasonable cost.

1.8.3. Types of extractants

Extraction (also known as metal ion recovery from aqueous phase) involves the transfer of metal ion from aqueous phase to organic phase. Typically, the organic phase contains the extractant ligand which coordinates to the metal ion. Metal ion transfer requires the charge neutralization of the metal species and replacement of some or all of its water of hydration by extractants. The transportation of a neutral complex from the polar to the nonpolar solvent results in extraction from an aqueous phase to an organic phase. The metal ion transfer, therefore, depends up on the complexation characteristics of the extractant. Extraction mainly depends upon the stability of metal complexes formed by different mechanisms, such as by coordination, ion association, chelation and by the formation of solvated complexes. Based on the nature of complexation mechanisms involved, the extractant can be classified as (a) Acidic extractants (b) Basic (anion) extractants (c) Neutral extractants (solvating agents) and (d) Chelating extractants [43].

1.8.3.1. Acidic extractants

Acidic extractants form complex with metal ion by cation-exchange mechanism. A general reaction of an acidic extractant with a metal follows the equation 1.2.

$$M^{n+}_{(aq)} + n\,HA_{(org)} \Leftrightarrow M(A)_{n(org)} + n\,H^{+}_{(aq)} \qquad (1.2)$$

Here n provides the number of protons exchanged between phases and the stoichiometry of the extracted molecule, and is based on the charge of the metal cation. The extraction of metal ion takes place with the release of hydrogen ions. At lower acidity, the extractant dissociates and form metal complex solvates easily. So the extraction of metal ions is favorable at lower acidity. For these systems, pH is an important consideration since it can drive the reaction equilibrium. Back extraction of metal ions is carried out at higher acidity. In the presence of higher acidity, the metal complex is not stable in organic phase and transferred to aqueous phase. Generally, acidic extractants have functional groups such as -COOH, >P(O)OH and -SO_3H. Bis(2-ethylhexyl)phosphoric acid (HDEHP) is one of many acidic organophosphorus based extractant molecules that have been studied for the purpose of actinide and lanthanide separations [46]. The phosphoric, phosphonic and phosphinic acids and similar compounds containing polyfunctional groups, alkylphosphoric acids are the most promising acidic extractants.

1.8.3.2. Basic (anionic) extractants

In anion extractant based separations, the metal ion is existed in the form of an anionic species and it get exchanged with an anion present in the extractant. The basic extractants extract the metal ion by anion exchange mechanism [43]. The Long chain primary (RNH_2), secondary (R_2NH), tertiary (R_3N) amines and quaternary ammonium salts ($(R_4N)^+ X^-$) belong to this category. The anionic metal species (MY^-) present in the aqueous phase is exchanged with the anion of the quaternary amine salt. The metal extraction reaction by anion exchange is shown in equations 1.3 and 1.4.

$$R_3N_{(org)} + HX_{(aq)} \Leftrightarrow R_3NH^+X^-_{(org)} \qquad (1.3)$$

$$R_3NH^+X^-_{(org)} + MY^-_{(aq)} \Leftrightarrow R_3NH^+MY^-_{(org)} + X^-_{(aq)} \qquad (1.4)$$

Several quaternary ammonium salts also have been explored for various anion exchange applications. For eg., tri-n-octylamine (Alamine 336) and tri-octylmethylammonium chloride (Aliquat 336) [47] are the two important basic extractants. Another major nuclear application of plutonium purification from nitric acid medium by anion exchange mehanism. It is based on the selective extraction of the anionic plutonium(IV) nitrate species of the type $[Pu(NO_3)_5]^-$and $[Pu(NO_3)_6]^{2-}$ formed at high concentrations of nitric acid [48] by anion exchange resins. The main advantage of anion exchange method for plutonium purification is due to the fact that plutonium forms anionic species at high nitric acid concentrations, whereas the other interfering elements and fission products do not form such anionic complexes.

1.8.3.3. Neutral Extractants

Neutral extractants are reagents containing donor atoms with lone pair of electrons for the solvation of neutral inorganic species. The metal ions combines with anions form a neutral metal complex. Neutral extractants only extract the electrically neutral metal complex. Stoichiometric amount of anions must be present to form the neutral complex. The extraction of metal ion involves the formation of an adduct between the neutral species of the metal ion and the extractant. Extraction of a metal ion (M^+) by a neu

$$M^+X^- + L \Leftrightarrow (M^+X^-)L \quad (1.5)$$

Neutral extractants generally posses functional groups such as P=O, C=O, N-H etc as the lone pair electrons donating sites. The lone pair electrons are charge-polarized in acidic medium, donates its electron density to the vacant orbitals of the metal ions. The solvating power depends strongly on the basicity of the reagent. Several neutral extractants such as phosphates, phosphinates, phosphonates, amides, diamides, diglycolamides etc., have been reported in literature. Since the adduct is soluble in the organic phase, the metal ion undergoes extraction. Tri-*n*-butyl phosphate is the most widely used neutral extractant for reprocessing of spent nuclear fuels [29]. Another example of a solvating extractant used in nuclear reprocessing is CMPO octyl(phenyl)N,N-diisobutylcarbamoylmethylphosphine oxide. Both of these solvating extractants, as well as many others, coordinate with the metal through the phosphoryl oxygen.

1.8.3.4. Chelating extractants

Chelating extractants extract metal ions by chelation i.e. the formation of ring structures with the metal ions by the extractant molecule. Some examples of these types of extractants are hydroxyoximes and diketones especially. 5,8-diethyl-7-hydroxy-6-dodecanone oxime (LIX 63) [49], 2-hydroxy-5-dodecylbenzophenone oxime (LIX 64) [50], thenoyltrifluoro acetone (TTA) etc., belong to this family of extractants [51].

1.8.4. Two-cycle separation of minor actinides from HLLW

1.8.4.1. Lanthanide-Actinide (III) co-extraction (Group separation)

Several extraction systems have been proposed and studied for the co-extraction of An(III) and Ln(III) from HLLW and number of flow-sheets based on those reagents have been developed world wide. TRans Uranium element EXtraction (TRUEX) process developed in USA involves *n*-octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) as extractant in combination with tributyl phosphate (TBP) [52, 53], TriAlkyl Phosphine Oxides (TRPO) developed by Chinese TRPO process [54, 55], Di-IsoDecyl-Phosphoric Acid (DIDPA) in combination with TBP used in Japanese DIDPA process [56, 57]. As an alternative to the organo phosphorous reagents mentioned in the above processes, which do not stick to the CHON principle, the malonamides *N,N′*-DiMethyl-*N,N′*-DiButylTetraDecylMalonAmide (DMDBTDMA), *N,N′*-DiMethyl-*N,N′*-DiOctyl-2-HexylEthoxyMalonAmide (DMDOHEMA) and diamides [58, 59] have been developed in France. Recently, the family of diglycolamide extractants, Octyl derivatives of diglycolamides (DGAs) have been extensively studied [60-62]. Branching of the alkyl chain attached to the acyl nitrogen atom of diglycolamide is reported to suppress the co-extraction of fission products. Therefore, a branched isomer of N, N, N′, N′-Tetraoctyl diglycolamide (TODGA) , namely, N, N, N′, N′-tetra (2-ethylhexyl) diglycolamide (TEHDGA) [62] has been used for studies so as to reduce the co-extraction of fission products. The symmetrical diglycolamide (TEHDGA, TODGA) forms third phase with HLLW. So phase modifier is added to the extractant phase. In order to avoid the drawbacks of symmetrical diglycolamide, several unsymmetrical diglycolamides (UDGA) were developed and studied for the extraction of trivalent metal ions from nitric acid medium [63]. Among the various UDGAs studied, the *N*,*N*,-didodecyl-*N*',*N*'-dioctyl-3-oxapentane-1,5-diamide, trivially called as didodecyl-dioctyl-diglycolamide (D3DODGA) is a promising reagent for trivalent actinide partitioning. Along with these, another class of extractants, namely *N,N,N',N'*-tetraalkyl-3,6-dioxaoctane diamide (DOODA), DOODA-C_8 and DOODA-C_{12} have been studied [64].

1.8.4.2. Mutual separation of lanthanides and actinides

Both trivalent actinides and lanthanides, co-extracted in the first cycle from HLLW are further mutually separated from each other in the second cycle. This mutual separation is necessary for the effective transmutation of actinides because lanthanides act as neutron poisons and reduces the neutron economy during transmutation process. Further, lanthanides might also interfere in the glass formation process with the HLLW, as they do not form solid solution with the raw materials of glass and segregate in separate phase with the tendency to grow under thermal treatments. However, the separation of Ln(III) from An(III) is a challenging task due to their similarities in chemical and extraction properties. The methods developed so far for the Ln-An separation usually exploit the finer differences in the chemical behavior of lanthanides and actinides towards various ligands. A marginal size difference between Ln(III) and An(III) plays an important role for their mutual separations. According to Pearson's hard-soft acid base theory [65], both An (III) and Ln(III) are classified as hard acids. But the An(III) have slightly softer nature than the Ln(III). In addition, the valence 5f-orbitals of actinides are spatially extended more as compared to the 4f-orbitals of lanthanides and thus the trivalent actinides have a greater tendency to form covalent bonding as compared to the lanthanides [66, 67]. Being lighter ions, Ln(III) act as relatively hard acids and form complexes preferably with oxygen atom based ligands over nitrogen based ones. On the other hand, An(III) being relatively larger in size prefers nitrogen based soft donor ligands over oxygen based ligands [67]. However, neither nitrogen based ligands nor oxygen based ligands can extract either An(III) or Ln(III) preferably. Therefore, the An(III) can be held in aqueous phase using suitable complexing agents and the Ln(III) are extracted using a suitable extractant or vice versa.

Several methods and materials have been reported in literature for lanthanide-actinide separation. For example a TALSPEAK (Trivalent Actinide Lanthanide Separation with Phosphorus-Reagent Extraction from Aqueous Komplexes) process has been demonstrated successfully for lanthanide actinide separation. This process involves the selective separation of An(III) from lactate buffered diethylenetriaminepentaaceticacid (DTPA) solution using bis-(2-ethylhexyl)phosphoric acid (HDEHP) in 1,4-diisopropylbenzene [46, 68]. Suneesh *et al.,* [69] developed a completely incinerable acidic extractant, *N,N*-di-2-ethyl hexyl diglycolamic acid (HDEHDGA) and studied for the Ln(III)–An(III) separations. This extractant has shown promising nature for the efficient separation of Ln(III) from An(III).

1.8.5. Single-cycle separation of minor actinides from HLLW

In the recent past, single-cycle methods [70-79] for the separation of trivalent actinides are receiving increased attention. There are a couple of approaches reported in literature. The first one is the direct separation of trivalent actinides from HLLW. The methods such as Selective ActiNide Extraction (i-SANEX) concept, Actinide reCycling by SEParation and Transmutation (ACSEPT) and 1-cycle SANEX concept [70-72] were developed for direct separation of actinides from HLLW. In contrast to this, the second approach involves the extraction of both the trivalent actinides and lanthanides together in organic phase followed by selective stripping of actinides alone from the loaded organic phase [73-79]. Based on this approach, both TRUEX and TALSPEAK process solvents were combined to form TRUSPEAK process [74], and by combining DIAMEX and TALSPEAK process solvents to form Partition of Actinides and Lanthanides with Acidic extractant, Diamide, and INcinerable complexants (PALADIN) process [76] were developed.

1.8.5.1. Direct separation of trivalent actinides from lanthanides

The direct separation of actinides from HLLW is possible using actinide selective extractants as compared to trivalent lanthanides. Actinides are softer acid as compared to lanthanides. Extractant having multiple soft donor atoms can be used for the selective separation of actinides. Some processes are discussed below.

1.8.5.1.1. BTP process

Kolarik *et al.* developed 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines (named BTPs, Bis Triazine Pyridine) for the trivalent actinide – lanthanide separation

[72]. Very efficient separations have been obtained with 2,6-bis(5,6-n-propyl-1,2,4-triazin-3-yl)pyridine (nPr-BTP), which is considered as the reference molecule of the bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines. The BTP extractants are CHON molecules and capable to extract actinides selectively from moderate nitric acid concentration.

The radiation stability of the nPr-TBP extractant is less. Its synthesis is tedious. It has a low solubility in organic diluents and slow extraction kinetics. The extraction kinetics of nPr-BTP is too slow for practical applications. Several attempts have been made to accelerate the extraction kinetics by using co-extractants, such as TBP or DMDOHEMA. These modifiers, however, lower the selectivity towards An(III).

1.8.5.1.2. BTBP process

New Bis Triazine Bis Pyridine (BTBP) ligands, which are structurally related to the BTP family, have been prepared and extraction behavior of actinides was studied in Europe. 2,6-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazy-3-yl)-[2,2']bipyridine, which is called CyMe4-BTBP is reported to be very effective for the actinide - lanthanide separation [70]. The problem of $CyMe_4BTBP$ is due to very low kinetics of metal extraction. In order to enhance the kinetics, the malonamide DMDOHEMA or TODGA has been used as phase transfer catalyst. The limitation of these extractants are poor hydrolytic and radiolytic stability, slow extraction kinetics, low back extraction of An(III) from the loaded organic phase etc.

1.8.5.2. Single-cycle separation using a combination of solvents

In two-cycle process, both neutral and acidic extractants are used in individual cycle. But the combination of neutral extractant and acidic extractant may facilitate the direct An(III) separation in a single-cycle. The pictorial representation of single cycle is shown in figure 1.5. In single-cycle process, the trivalent actinides and lanthanides are co-extracted from HLLW using combined solvent formulation and recovery of actinides alone from the loaded solvent phase was carried out by aqueous soluble and actinide selective diethyltriamminepentaaceticacid (DTPA)-citric acid (CA) solution. This strategy reduces the waste generation, the human efforts and be more economical. Lumetta *et al.* introduced the concept of combining the neutral and acidic extractants for the separation of Ln(III) from the transuranic elements [73]. The authors indicate the promising nature of combining neutral and acidic extractants to achieve a single-cycle separation of trivalent actinides alone from HLLW. Some single-cycle process for minor actinide partitioning is described here.

1.8.5.2.1. TRUSPEAK process

The TRUSPEAK process is a combination of TRUEX and TALSPEAK process. The solvent used in individual process is combined here. The solvent is CMPO - HDEHP in n-dodecane. Dhami *et al.* studied the extraction and stripping behavior of Am(III) and Eu(III) using a solution composed of HDEHP - CMPO dissolved in *n*-paraffinic diluents [74]. The extracted metal ion was stripped using a unique solution composed of 0.4 M hydrazine hydrate, 0.4 M formic acid + 0.05 M DTPA and achieved a separation factor of ~3 for americium over europium. However, these separation factors are very low to achieve the complete separation of lanthanides from actinides.

1.8.5.2.2. PALADIN process

A new process, namely Partition of Actinides and Lanthanides with Acidic extractant, Diamide, and INcinerable complexants (PALADIN) process was developed in France to produce a single solvent for separating lanthanides from actinides based on the reagents diamides and HDEHP [76]. Some undesirable metal ions such as Mo, Zr, Fe, Pd and to some extent Ru were also extracted due to the presence of both diamide and HDEHP which make it essential to scrub the loaded organic phase for removing those metal ions prior to the stripping of actinides. In addition, the extractants used are also not completely incinerable due to the presence of phosphorous based reagent, HDEHP. The combination of neutral and acidic extractants facilitates the extraction of An(III) and Ln(III) from 3-4 M nitric acid medium, and also favors the selective stripping of An(III) into aqueous phase containing DTPA by retaining the Ln(III) in organic phase.

Similarly, Gannaz *et al.* studied the extraction of Eu(III) and Am(III) by a mixture of extractants consisting of a malonamide (DMDOHEMA) and di-n-hexylphosphoric acid (HDHP) [75]. During extraction from nitric acid medium, the solvent behaves primarily like a malonamide that extracts both trivalent actinides and lanthanides. However, selective stripping of trivalent actinides from the loaded organic phase was controlled by HDHP present in organic phase as well as the aqueous complexing formulation developed by the authors. This process has the drawback that two different extractants are used in the organic phase, which will complicate the solvent clean-up and that the pH of the aqueous phase must be carefully adjusted. Furthermore, numerous ions are co-extracted to the solvent phase.

Using the UDGA, *N*,*N*,-didodecyl-*N*',*N*'-dioctyl-3-oxapentane-1,5-diamide (D^3DODGA) and di-2-ethylhexyl diglycolamic acid (HDEGDGA) reagents, a novel approach namely, SMART (Single-cycle process for Minor Actinide partitioning using completely incinerable ReagenTs), was developed by Ravi *et al*, for the separation of trivalent actinides in a single processing step [77]. Prasant *et al*, developed single cycle separation methods for minor actinide partitioning by using the combination of extractants include tetra-bis(2-ethylhexyl)diglycolamide (TEHDGA) and bis(2-ethylhexyl)phosphoric acid (HDEHP), teraoctyldiglycolammide (TODGA) and HDEHP Among these extractants, higher separation factor of Am(III) over Eu(III) was obtained by using TEHDGA and HDEHP. Synergistic extraction of Am(III) and Eu(III) was observed over a range of nitric acid concentrations (0.1 M to 4 M) [78]. The study also indicated the possibility of separating Am(III) from simulated high level liquid waste in a single processing cycle by using 0.1M TEHDGA-0.25 MHDEHP/*n*-DD as solvent and 0.05 M DTPA-0.5 M citric acid at pH 3 as stripping formulation [78, 79].

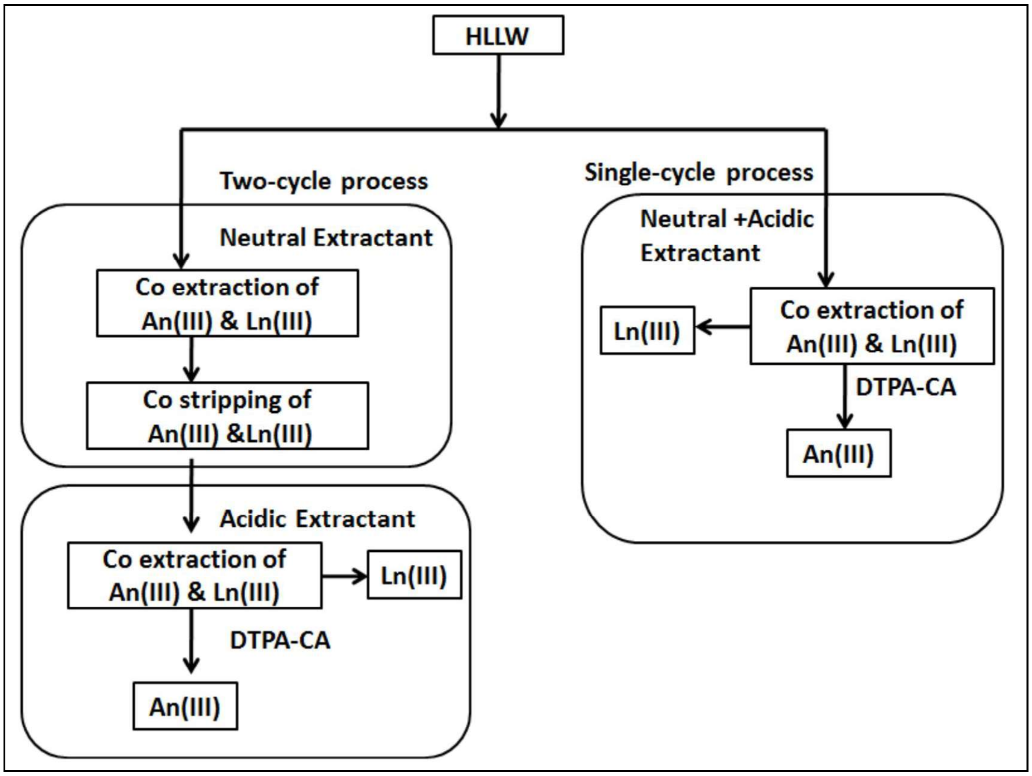


Figure 1.5. Graphical representation of two cycle and single cycle process.

1.9. Solid phase separations for minor actinide partitioning

1.9.1. Solid phase extraction

The term solid-phase extraction generally refers to macro porous polymers that hold an organic complexing compound or extractant within the pore structure of the polymer. These materials can be called as extraction chromatography resins, solvent-loaded resins, ligand-immobilized resins or solvent-impregnated resins. The word ‘‘impregnation” was originally introduced in the ion exchange literature by Lederer et al. [80] in a series of published papers entitled ‘‘Chromatography on paper impregnated with ion-exchange resins”. It is often said that solid-phase extraction resins combine the metal selectivity of liquid-liquid solvent extraction with the operational benefits of packed bed ion exchange into the conventional polymeric adsorbent material. They combine not only the advantages of resin ion exchange for processing dilute solutions but also with the simplicity of equipment and operation characteristics of solid ion-exchange technology [81]. Separations based on solid phase extractants (SPE) are promising because of the following advantages (a) any ligand can be immobilized into the form of a solid phase extractant (b) no issue of third phase formation (c) less waste generation (d) disposal of the extractant is relatively easier as compared to solvent extraction techniques [82, 83]. Warshawsky [84] and Grinstead [85] were the two principal pioneers responsible for introducing the concept, synthesis and applications of ‘‘solvent-impregnated resins” for metal removal to the open literature in 1971. Warshawsky tested α and β-diphenylglyoximes impregnated onto macro reticular polystyrene beads (XAD-2) as an adsorptive reagent [86]. The concept provides a possibility to obtain a range of chelating sorbents using simple impregnation technique. The impregnated materials bridge the gap between liquid-liquid extraction and conventional ion exchange [87]. An important advantage is the possibility of performing many cyclic operations without significant losses of the extraction capacity. Solid-phase extraction has wide applications in pharmaceutical and analytical organic chemistry. Extractant molecules are adsorbed through interactions between the resin surface and hydrophobic regions of the extractant molecules (van der Waal's interactions). A solid-phase extraction material comprises three major components: a solid support or substrate (typically inert polymer), a stationary extractant phase, and a mobile fluid phase (e.g., conditioning, feed, wash, or strip solution). The three phses of a solid-phase extraction resin are depicted in figure 1.6.

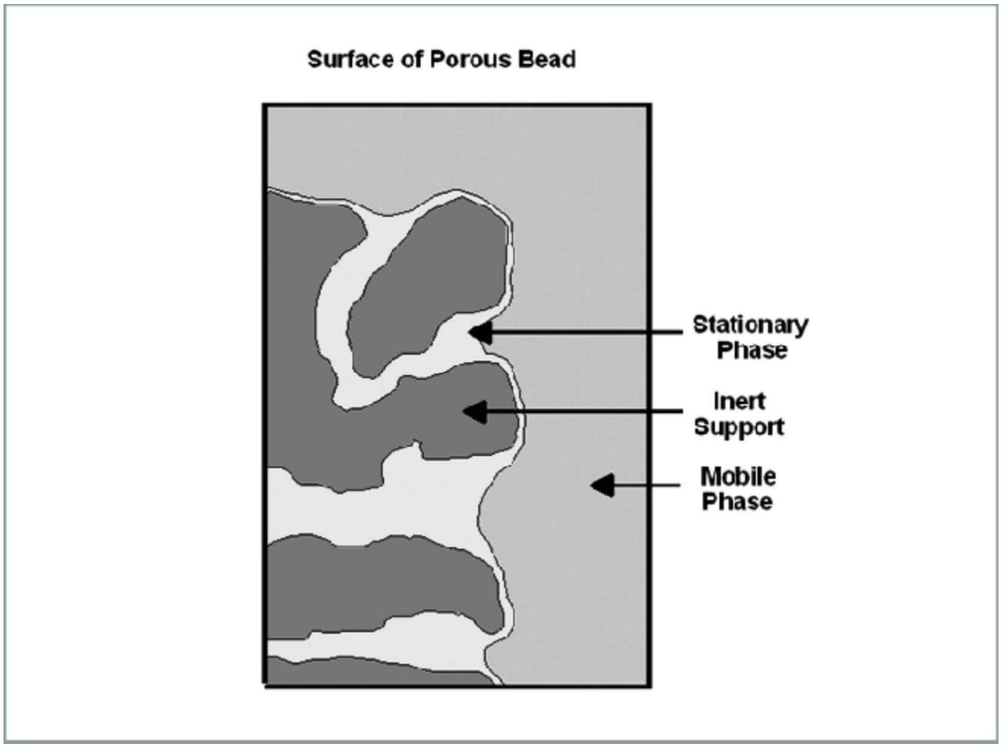


Figure 1.6. Solvent impregnated resin bead [88].

An ideal SIR must have the following features (Warshawsky, 1981) [89]:

1. The extractant should be a liquid or retained in the liquid state by the addition of an appropriate diluent.
2. The extractant should have a very minimal solubility in the aqueous solution containing the solute to be extracted.
3. The polymeric support should be fully expanded and remain so during the impregnation process–macroporous polymers exhibit minimum volume variations during impregnation.
4. The impregnation process should not have a deleterious effect on the properties of the extractant or polymer.

These impregnated resins are roughly classified into two groups: extractant-impregnated sorbents and Levextrel resins [90] as shown in figure 1.7.

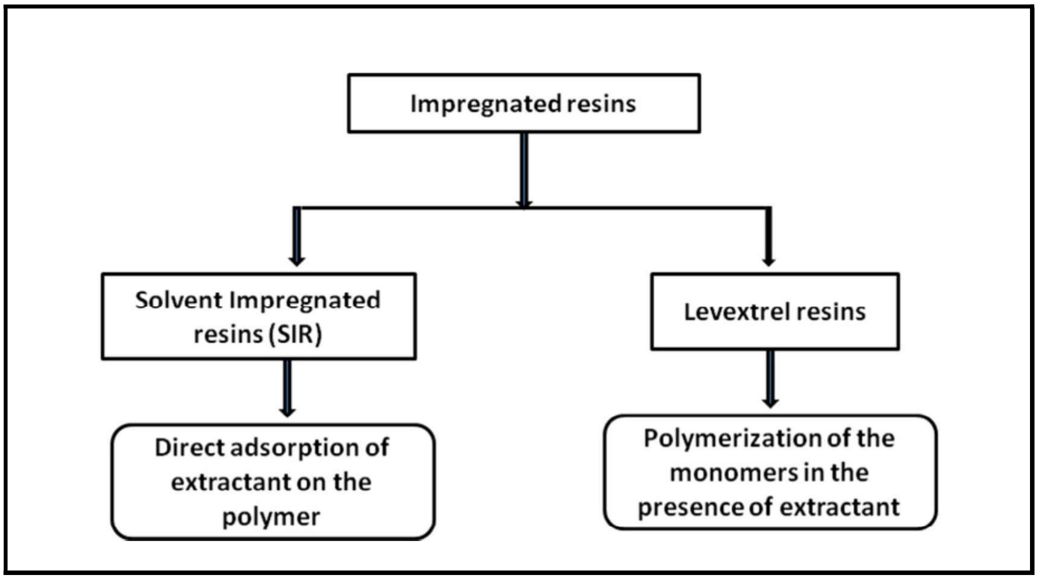


Figure 1.7. Classification of impregnated resins.

1.9.1.1. Methods for the preparation of solvent impregnated resins

The most widely used techniques are based on the physical adsorption of the extractant into the pores of the support material. The preferred method for incorporating the chosen extractant into the support is often dependent upon the type of extractant-metal complex. Following are the methods for producing extractant impregnated resins [91].

Dry impregnation – this is the most often used method wherein the extractant, or extractant diluted with an appropriate organic diluent, is contacted with the polymer in batch mode for a period of time necessary to obtain maximum saturation of the extractant within the polymer pores. The diluent is then removed via vacuum evaporation resulting in a two-component, polymer-extractant material. This method is most successful in the impregnation of hydrophilic extractants, such as amines, ethers, ketones, esters, etc

Wet impregnation – The extractant, dissolved in a pre calculated amount of diluent, is placed in contact with the polymer until all the liquid phase is absorbed by the polymer. The beads are then immersed in aqueous metal salt solution. After completion of the formation of the metal-extractant complex, the resin is washed with water, the metal is eluted using acid, and the resin is rewashed with water. The resulting SIRs are then ready for application. Alternatively, the metal-extractant complex is formed first in the liquid phase and then directly impregnated as above.

Modifier addition method – a modifier is added to the extractant-diluent and the mixture is adsorbed into the polymer as described in the above methods. The diluent is then removed by evaporation, leaving a polymer extractant-modifier resin. In which a mixture of the extractant with a modifier agent promotes water penetration into the polymer network used. Then the obtained SIR is a three-component system: polymer-extractant-modifier. The chosen modifier is typically more polar than the extractant and is added to enhance water penetration into the porous network of the polymer.

1.9.1.2. Methods for the preparation of Levextrel resins

Levextrel resins are macro porous styrene/divenyl benzene copolymers containing a metal –selective extractant which has been added directly to the mixture of the monomers during the bead polymerization process. The polymerization conditions depend on the extractant properties, such as its acidity, viscosity and water solubility. Liquid phosphoric esters, aliphatic amines, and aliphatic and aromatic oximes have appropriate characteristics to be used in Levextrel resin synthesis. The Levextrel resin is one product of encapsulation technology, is carried out by adding the metal complex to a mixture of monomers during bead polymerization followed by stripping the metal ion by treating resin with an acid solution [90].

1.9.1.3. Solid-phase extraction sorbents

The essential requirements for a solid sorbent are (i) the possibility to extract selectively a large number of trace elements over a wide pH range. (ii) quantitative sorption and elution (iii) kinetically faster sorption and desorption mechanism (iv) regenerability (v) high retention capacity (vi) accessibility (viii) mechanical and chemical strength. Based on the inert support used for immobilizing the extractant, solid phase extractants can be broadly classified as SPE with organic (natural and synthetic polymers) support and SPE with inorganic (inorganic oxides) support.

SPE with organic support

Organic support is a cross-linked polymer matrix, made up of hydrocarbon chains, such as styrene and divinyl benzene [92]. Generally, the polymer matrix of the resins is hydrophobic. The result of cross-linking and control of other experimental parameters results in spherical beads which are suitable for SPE. The high degree of hydrophobicity of these polymeric materials is the reason for their large capacity. The proper choice of the main monomer and/or cross linking agent can moderate the overall hydrophobicity of the complete organic sorbent. Furthermore, the aromatic rings of the matrix network permit electron-donor interactions between the sorbent and π bonds of the solute, which may further increase analyte-sorbent interactions, which increases the energy of sorption [82, 83]. The retention properties of poly (styrene-divinylbenzene) polymers can also be increased by light surface modification with polar functional groups, such as acetyl, benzoyl, hydroxyl methyl or sulfonate [93]. The polar substituents reduce the interfacial tension between the polymer surface and aqueous sample, increasing contact between the analyte and polymeric sorbent. The macro porous (macro reticular) polymeric resins, having a rigid three-dimensional structure, are most suitable to incorporate large amounts of extractants due to the high specific surface area, high mechanical strength, and rather low solvent swelling during the impregnation process. In general, they have a specific surface area of 150-900 $m^2.g^{-1}$, a porosity of 0.4-0.6, an average pore diameter of 4-9 nm, and a pore volume of 0.6-1.1 $cm^3.g^{-1}$ [91].

SPE with inorganic support

Inorganic adsorbents are extremely proven candidates for the selective separation of toxic and radiotoxic metal ions [94, 95]. The most important inorganic oxide adsorbents for SPE are silica gel, alumina, Florisil (synthetic magnesium silicate) and diatomaceous earth which is a flux calcined silica with a low surface area. Silica gel is a granular, vitreous, porous form of silicon dioxide made synthetically from sodium silicate. They offer a high selectivity towards a given metal ion. In addition, chelating agents can be easily loaded on silica gel with high stability. The attraction over this material is further improved by the surface modification of inorganic matrix with organic complexing moieties. The driving force for this development of organo-functionalized adsorbents (OFS) stems from the fact that it can be tuned to task specific adsorbent by proper selection of complexing moieties. These inorganic materials possess the desirable properties such as high selectivity, chemical and radiation stability for treating radioactive wastes. Moreover, these spent inorganic adsorbents can be immobilized in the form of glass or ceramic for final disposal [96]. Among the various OFS, organo functionalized silica gel based adsorbents have been studied extensively for the separation of metal ions from various feeds. Surface hydroxyl (SOH) groups present on hydrous silicon dioxide are responsible for the surface modification of the adsorbent. Inorganic oxide supports such as Acidic oxides ($Si0_2$) are expected to adsorb only cations, basic oxides (such as magnesia MgO) should adsorb only anions. Consequently, amphoteric oxides (namely titania TiO_2, alumina $A1_2O_3$, zirconia ZrO_2), adsorb cations under basic conditions, while anions are adsorbed under acidic conditions [97]. The adsorption properties of many oxides strongly depend on the characteristics of the solid, namely crystal structure, morphology, defects. Adsorption on inorganic oxides may also be influenced by the presence of neutral electrolytes in the matrix.

1.9.1.4. Solid-phase extraction sorbents for actinides and lanthanides separations

Currently, most commercial or proposed processes for actinide separation from spent nuclear fuel are performed using solvent extraction techniques, which are explained in Sections 1.8.4 and 1.8.5. However, the use of solid sorbent materials as an alternative to solvent extraction, as explained in section 1.9.1 has many advantages. These include the avoidance of organic solvents (which removes problems associated with chemical and radiolytic degradation of the diluent such as reduced performance and secondary waste generation) [98], faster kinetics in many cases [99], the fact that the extractant molecule does not need to be designed to be soluble in an organic phase or obey the CHON principle, a phase modifier is never required and there is no possibility of third phase formation. Thus, using solid sorbent materials reduces the complexity of actinide separations relative to solvent extraction, which in turn reduces the time and cost required. In addition, the complexity necessarily introduced when designing a solvent extraction process can sometimes have negative consequences to the separation performance. For example, adding long chain alkyl groups to extractants in order to increase their solubility in organic diluents can reduce their extraction efficiency [100] or cause undesirable aggregation at the solvent interface during extraction. One advantage of inorganic solid phase materials used as sorbents for nuclear separations is that after loading with radionuclides the material can be potentially used as a waste form precursor or transmutation matrix. Thus the time and cost associated with the extra processing steps of stripping and oxide conversion can be avoided. A number of extractants for partitioning An and/or Ln elements from dissolved nuclear fuel solutions or accompanying waste streams have been developed. In order to develop a sorbent material for nuclear (actinide) separations, several factors must be considered. For example, sorbents for selective separation of targeted elements from highly acidic aqueous solutions of irradiated nuclear fuel should preferably exhibit favorable hydrolytic and radiolytic stability, as well as chemical stability. It is considered preferable for solid phase sorbents to have open, porous structures in order to provide high surface areas which result in more active sites per gram of material (high capacity) and facilitate rapid mass transport (fast kinetics). The solid phase sorbent should have a granular physical form with a particle size large enough to made practically usefull in a flow-through column setup. The extractant ligand is impregnated or coated onto solid support structures such as polymer resins, porous silica, polymer membranes, metal oxide particles, clays, carbon-based materials or magnetic nano-particles [101]. However, there are very few examples of solid phase materials used for nuclear separations at industrial or pilot scales [102].

1.9.1.4.1. Polymer based solvent impregnated resins for actinide and lanthanide extraction studies

Solvent impregnated resins prepared by immobilization of extractant molecules in non-reactive macro porous polymer supports have been widely developed for actinide separations [102], although they are more commonly used for analytical purposes than full scale processing due to their chemical instability [53]. The adsorption and extraction behavior of U(VI), Pu(IV), Am(III) from 4 M HNO3 was reported with TBP impregnated in Amberlite XAD-7. The extraction of U(VI) from dilute aqueous solutions by polyurethane foam impregnated with 5,8-diethyl-7-hydroxy-6-dodecanone oxime (LIX 63) [103] and TBP have been reported, respectively. Van Hecke and Modolo [104] investigated the uptake of several actinides, i.e., U(VI), Th(IV), Am(III) and Cm(III), by two novel extraction chromatographic sorbents which contain 2-(2-hexyloxyethyl)-N,N’-dimethyl-N,N’-dioctylmalonamide (DMDOHEMA) and N,N,N’,N’-tetraoctyl-3-oxapentane-1,5-diamide (TODGA), and proved that the actinides and lanthanides can be separated from the bulk of other fission products using impregnated sorbents. The actinides in acidic solutions (^{233}U, ^{239}Pu, ^{241}Am, ^{244}Cm, and fission products ^{90}Sr/^{90}Y) can also be separated by the resins containing mixing extractants, CMPO in TBP [105]. XAD-2 impregnated with Cyanex 272 proved to be reliable in isolation of U(VI) from synthetic mixture, uranium microlite (leachates) ore tailings, and industrial effluents [106]. By using TOPO-impregnated XAD-4 extraction chromatographic resins, bulk Pu(IV) present in a sample can be removed to the required level at which it does not interfere in the impurities analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES) [107]. A transuranic specific (TRU Spec) resin composed of CMPO and TBP impregnated in Amberchrom CG-71 acrylic ester resin beads has been demonstrated for the extraction of Pu(IV), Np(IV) and Am(III) from 1 to 4 M nitric acid [108]. CMPO has also been impregnated into several other polymer matrices including polyacrylonitrile, poly-acrylate and polystyrene and the sorption performance of the resulting materials was investigated. The differing extraction efficiencies and sorption kinetics of these various CMPO impregnated materials demonstrated that the choice of polymer matrix can have a significant impact on sorption performance, which can be attributed to differences in the porosity and functionality of the polymer frameworks. Karve and Rajgor [109] compared the sorption of U(VI), Th(IV), Nd(III), and La(III) on XAD-2 resins impregnated with Cyanex 272 and Cyanex 302, respectively. Separation of these elements was then possible using various eluents. Extraction of lanthanides were achieved at pH 3.5 by D2EHPA impregnated on Amberlite XAD-7 resin. TODGA impregnated into Amberchrom CG-71 resin beads demonstrated extraction of Pu(IV), Th(IV), Am(III)and Ln(III) from 1–4 M nitric acid.

1.9.1.4.2. Silica based solvent impregnated resins for actinide and lanthanide extraction studies

Many examples exist of organic extractant molecules from solvent extraction processes being incorporated into silica based solid sorbent materials. Extractants, such as BTP, TODGA, CMPO, DTPA have been impregnated into a styrene-divinyl benzene polymer which is in turn embedded into porous silica particles to make sorbent materials (SiO_2-P) for selective minor actinide extraction or separation of Ln and An from simulated high level waste. iBu-BTP impregnated SiO_2-P was used to study the extraction behavior of Am(III) from 3M nitric acid [102]. A novel hybrid silica-based adsorbents with new N-donor ligand, 2, 6-bis(5,6-dialkyl-1,2,4–triazine-3-yl)-pyridine (R-BTP) molecules impregnated into a macroreticular styrene–divinylbenzene copolymer, immobilized in porous silica particles were studied [110]. CMPO/SiO_2-P, was synthesized by impregnating and immobilizing CMPO into the pores of SiO_2-P particles support to separate long-lived minor actinide elements such as Am(III) and Cm(III) from highly active liquid waste. DMDBTDMA is the first amide based ligand proposed for the recovery of trivalent actinides and lanthanides from HLW [111]. The DMDBTDMA resin was prepared by impregnating 50% w/w ligand on Chromosorb-W (dimethyl dichlorosilane treated acid washed celitediatomaceous silica). The distribution behavior of several actinides and fission product elements such as UO_2^{2+} ,Pu^{4+} ,Am^{3+} , Eu^{3+} , Cs^{+} and Sr^{2+} from nitric acid solution was investigated. Nogami et al. [112] investigated the U(VI) adsorption from nitrate media by porous silica impregnated with 1,1,3,5,5-pentaphenyl-1,3,5-triphosphapentane trioxide (PPTPT) and 1,1,5,5,2',2'-hexaphenyl-1,3,5,2'-tetraphospha-3-ethylpentane tetra oxide (HPTEPT), respectively. More sophisticated solid phase materials for separations can be synthesized by functionalization of silica based framework materials via covalent silane anchor groups. Several carboxylate and phosphonate functionalized disordered porous silica materials have been shown to extract Ln from pH 3–6 aqueous solutions.

1.10. Adsorption isotherms

Adsorption isotherms describe the relationship between the equilibrium concentration of metal ions in solution and the amount of metal ions adsorbed on a specific adsorbent at a constant temperature. The variation in the loading behavior of metal ions in the SIR can be described by adsorption isotherms. Several isotherm models such as, Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherms are available for analyzing experimental data. Each adsorption model provides an insight into the nature of adsorption and the interaction happening between the adsorbent and adsorbate.

1.10.1. Langmuir isotherm

The Langmuir adsorption isotherm model is widely used to describe the adsorption of an adsorbate on a homogeneous, flat surface [113]. The Langmuir isotherm assumes (1) a finite number of surface sites (2) no electrostatic or chemical interactions (3) constant binding energy for all surface sites (4) that binding energy is independent of the adsorption density and (5) that maximum amount of adsorption is limited to a monolayer coverage of the surface sites.

The Langmuir isotherm can be written as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{1.6}$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent(mg.g^{-1}),

C_e is the the equilibrium concentration of adsorbate (mg.mL^{-1})

q_m is the maximum adsorption capacity of the adsorbent (monolayer coverage)

K_L is Langmuir isotherm constant that determines the affinity of the adsorbent towards the adsorbate (mL.mg^{-1}).

1.10.2. Freundlich isotherm

The Freundlich isotherm is an empirical expression, which assumes that the sorbent surface sites have binding energies with an exponential distribution. The Freundlich model is particularly suitable for describing processes involving heterogeneous sorbents [114] having broad ranges of sorption site energies. This model has the form [115]

$$q_e = K_f C_e^{1/n} \qquad (1.7)$$

where q_e is the amount of the solute sorbed per unit weight of the sorbent (mg.g^{-1}),

C_e is the equilibrium concentration of solute in the bulk solution (mg.mL^{-1}),

K_f is the Freundlich adsorption constant indicative of the relative sorption capacity of the sorbent (mL.g^{-1}) and

1/n is the constant indicative of the intensity of the sorption processes.

The exponent n is related to the energy of sorption and to site heterogeneity.

The value of n approaches unity for homogeneous sorbents of uniform site energy.

1.10.3. Temkin isotherm

This isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. It is based on the assumption that due to the adsorbate- adsorbate repulsions the heat of adsorption of all the molecules in the layer decreases linearly with the coverage of molecules and the adsorption of adsorbate is uniformly distributed [116]. The expression of the Temkin model is given by Eq. (1.8)

$$q_e = \left(\frac{RT}{b}\right)\ln\alpha + \left(\frac{RT}{b}\right)\ln C_e \qquad (1.8)$$

where α is the Temkin isotherm equilibrium binding constant ($mL.g^{-1}$)

b is the Temkin isotherm constant ($kJ.mol^{-1}$) related to heat of sorption

R is the universal gas constant (8.314 $J.mol^{-1}.K^{-1}$)

T is the Temperature at 298 K.

C_e is the equilibrium concentration of adsorbate ($mg.mL^{-1}$)

q_e is the amount of metal adsorbed per gram of the adsorbent at equilibrium($mg.g^{-1}$).

1.10.4. Dubinin- Radushkevich isotherm

The physical or chemical nature of adsorption over the adsorbent can be determined from the D-R adsorption model. The non-linear form of D-R model is represented in equation1.9.

D–R model [117, 118] is to determine the type of sorption (physical or chemical).

$$q_e = q_m \exp\left(-K_{DR}\left[RT\ln\left(1+\frac{1}{C_e}\right)\right]^2\right)$$

$$q_e = q_m \exp\left(-K_{DR}\varepsilon^2\right) \qquad (1.10)$$

where K_{DR} is the D-R constant, is related to the mean free energy of adsorption E (in kJ/mole)

ε is known as the Polanyi potential,

R is the universal gas constant and

T is the temperature in Kelvin

q_e is the amount of metal adsorbed per gram of the adsorbent at equilibrium(mg.g^{-1}).

1.11. Radiolytic stability of solvent impregnated resins

Radiation stability of the solvent impregnated resins is one of the most important aspects while developing these for the extraction of radioactive metal ions, particularly those involving high level radioactive waste. Extractants with higher radiation stability are preferred. Owing to high dose of radiation encountered during the extraction process, these solvent impregnated resins are exposed to the huge quantities of ionizing radiations. For this reason it is important that these extractant impregnated resins are stable to radiolysis. As a result, the cleavage of chemical bonds in the solvent happens and forms chemically active species such as free radicals and ions. Some of these species may recombine or react with other molecules depending on the energy and type of radiation [119, 120]. The chemically active species such as free radicals, ions, and other neutral molecules which are produced as a result of interaction of radiation with solvent are collectively called as degradation products. These degradation products alter the physical, chemical and extraction properties of the reagents and may interfere in the complex formation of extractants with the metal ions to a significant extent. Therefore, the extraction and stripping properties of metal ions may vary. Thus, the degradation of solvent not only reduces the extraction efficiency, but also alters the separation factors, physical and chemical properties. In addition, the reusability of its solvent strongly depends on the radiolytic stability. Therefore, the components of the solvent formulation to be employed in the nuclear solvent extraction process must have adequate radiolytic stability. In this context, it is very important to understand radiation chemistry and evaluation of radiation stability of a solvent proposed for the extraction of actinides from HLLW.

1.12. Scope of the present study

The safe management of HLLW, which is generated during reprocessing of the spent nuclear fuels, is one of the challenging tasks in nuclear industry. The so called minor actinides, americium, curium and neptunium, as well as a small amount of residual plutonium are the most important ling-lived radionuclides, which are responsible for the long-term radiation hazards of high-level liquid waste (HLLW). For the remediation of HLLW, the strategy of P&T(Partitioning and Transmutation) is being explored, which proposes the separation of minor actinides such as Am, Np, Cm from lanthanides in HLLW and their subsequent incineration in high flux reactors/accelerator driven subcritical systems . The success of P&T strategy depends on efficient separation of minor actinides. Partitioning of trivalent actinides from HLLW is complicated owing to the similarity in the coordination chemistry of lanthanides with disadvantageous ratio present in it.

The present study aims at exploring the feasibility of developing the single-cycle method for the separation of actinides directly from HLLW by solid phase extraction mode. Here solid phase extraction was achieved by solvent impregnated resins. The solvent formulation in this approach is composed of neutral and acidic extractant. Liquid-liquid extraction method is widely used in nuclear industry. However, the major disadvantage associated with this technique includes third phase formation, generation of large volumes of secondary waste and handling of large volumes of volatile organic compounds. In contrast to the liquid-liquid extraction methods, the solid phase separation studies using solvent impregnated resin (extraction chromatographic resins) offers following advantages, (a) any ligand can be immobilized into the form of a solid phase extractant (b) no issue of third phase formation(c) less waste generation (d) disposal of the extractant is relatively easier as compared to solvent extraction techniques. In fact, solid phase extraction is suitable for the separation of micro-quantities of radionuclides present in a large volume of feed solution, as in the present case. It is a promising technique for the separation of metal ions from aqueous solution owing to its simplicity, robustness, regenerating ability and can be easily engineered into plant scale levels and technologically demonstrated.

In this context, the present study is, to prepare the wide variety of solvent impregnated resins containing different neutral and acidic extractants. In connection with this octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyl-phosphine oxide (CMPO), tetra-bis(2-ethylhexyl)diglycolamide (TEHDGA) or bis-(2-ethylhexyl)phosphoric acid (HDEHP) or mixture of extractants (CMPO+HDEHP)and (TEHDGA+HDEHP) in an acrylic polymer matrix was prepared and studied for the extraction of Am(III) and Eu(III) over a range of nitric acid concentration. Studies were also carried out for the separation of trivalent lanthanides and actinides from fast reactor simulated high-level liquid waste (FR-SHLLW) solution by TEHDHA+HDEHP combined resin. An attempt was made to develop a procedure for the mutual separation of Am(III) and Eu(III) by using these impregnated resins and citrate-buffered DTPA solution.

The present investigation also encompasses the radiolytic degradation of solvent impregnated resins containing CMPO, TEHDGA and HDEHP extractants.

Since these impregnated resins used for actinide partitioning are continuously exposed to high radiation, therefore, understanding of radiolytic stability of these resins process is extremely important for complete process development. In this context, the solvent impregnated resins containing both neutral and acidic extractants were irradiated to various dose levels by γ-radiation and the distribution ratio of Am(III) and Eu(III) was measured as a function of absorbed dose.

This study also deals with adsorption behavior of Europium (III) on solvent impregnated resins (SIR) containing CMPO, TEHDGA &HDEHP extractants. In this work sorption capacity of solvent impregnated resins (SIR) with respect to Eu(III) metal ion has been investigated. The extraction isotherm of Eu(III) in various SIRs (irradiated and un irradiated) have been fitted using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) adsorption models.

1.13. References

1. http://www.world-nuclear.org/focus/climate-change-and-nuclear-energy/sustainable-energy.aspx
2. S. A. Bhardwaj, Indian nuclear power programme - Past, present and future, Sadhana, 38 (2013) 775-794.
3. “Blue print for Power Sector Development”, Ministry of Power, Govt. of India, (2001).
4. A. Mohan, The Future of Nuclear energy in India, ORF occasional paper, (2016).
5. B. Raj, H. S. Kamath, R. Natarajan and P. R. Vasudeva Rao, A perspective on fast reactor fuel cycle in India, Prog. Nucl. Energy, 47 (2005) 369-379.
6. R. B. Grover, S. Chandra, Scenario for growth of electricity in India, Energy Policy, 34 (2006) 2834-2847.

7. S. David, Future Scenarios of fission based reactors, Nucl. Phys. A, 751 (2005) 429–441.
8. C. Pal, Environmental pollution and Development, Mittal Publications, 1st Edition (1999).
9. http://www.world-nuclear.org/focus/climate-change-and-nuclear-energy/nuclear-must-be-part-of-the-international-response.aspx
10. International atomic energy agency website:www.iaea.org
11. S. Glasstone, Source book on atomic energy, Krieger Publishing Company, (1979).
12. India energy outlook, world energy outlook special report, International energy agency (2015).
13. R. G. Cochran, E. E. Lewis, N. Tsoulfanidis, W. F. Miller, The nuclear fuel cycle: analysis and management, American Nuclear Society (1990).
14. J. Bruno, R. C. Ewing, Spent nuclear fuel, Elements, 2 (2006) 343-349.
15. M. Bunn, J. P. Holdren, S. Fetter, B. Van Der Zwaan, The economics of reprocessing versus direct disposal of spent nuclear fuel, Nucl. Technol., 150 (2005) 209-230.
16. J. M. Gras, R. D. Quang, H. Masson, T. Lieven, C. Ferry, C. Poinssot, M. Debes, J. M. Delbecq, Perspectives on the closed fuel cycle–Implications for high-level waste matrices, J. Nucl. Mater., 362 (2007) 383-394.
17. R. Chidambaram, R. K. Sinha, Importance of closing the nuclear fuel cycle, Nuclear energy, (2006) 90.
18. International Atomic Energy Agency, Thorium fuel cycle-Potential benefits and challenges, IAEA-TECDOC-1450, (2005) 45.

19. H. J. Bhabha, The role of atomic power in India and its immediate possibilities. Proc. of the international conference on the peaceful uses of atomic energy held in Geneva, 1 (1955) 103.
20. P. Sengupta, C. P. Kaushik, G. K. Dey, M. Ramkumar (ed.), On a sustainable future of the earth's natural resources, Springer Earth System Sciences, DOI 10.1007/978-3-64232917-3_2, Springer-Verlag Berlin Heidelberg (2013).
21. http://www.npcil.nic.in/content/302_1_AllPlants.aspx
22. B. Raj, S. L. Mannan, P. R. Vasudeva Rao, M. D. Mathew, Development of fuels and structural materials for fast breeder reactors, Sadhana, 27 (2002) 527–558.
23. http://barc.gov.in/reactor/tfc.html
24. S. Usha, R. R. Ramanarayanan, P. Mohanakrishnan, R. P. Kapoor, Research reactor KAMINI, Nucl. Eng. Des., 236 (2006) 872-880.
25. B. Bhattacharjee, An overview of R and D in fuel cycle activities of AHWR, Nuclear fuel cycle technologies: closing the fuel cycle (2003).
26. P. K. Dey, N. K. Bansal, Spent fuel reprocessing: A vital link in Indian nuclear power program, Nuclear Engineering and Design, 236 (2006) 723.
27. J. P. Ackerman, Chemical basis for pyrochemical reprocessing of nuclear fuel, Ind. Eng. Chem. Res., 30 (1991) 141-145.
28. A. V. Bychkov, O. V. Skiba, Review of non-aqueous nuclear fuel reprocessing and separation methods, Chemical separation technologies and related methods of nuclear waste management, Eds. G. R. Choppin, M. Kh.Khankhasayev, Kluwer academic publishers, Netherlands, (1999) 71-98.

29. H. A. C. Mckay, J. H. Miles, J. L. Swanson, The PUREX Process, In Science and Technology of tributyl phosphate (Applications of Tributyl Phosphate in Nuclear Fuel Reprocessing); W.W. Schulz, J.D. Navratil, K.P. Bender, Eds., CRC Press, Inc: Boca Raton Florida, U.S.A., Vol. III (1990) 1.
30. D. D. Sood, S. K. Patil, Chemistry of nuclear fuel reprocessing: current status, J. Radioanal. Nucl. Chem., 203 (1996) 547-573.
31. K. Van Hecke, P. Goethals, Research on advanced aqueous reprocessing of spent nuclear fuel: literature study, Open report of the Belgian nuclear research centre, (2006).
32. Status and Trends of Spent Fuel reprocessing, IAEA TECDOC-1103, (1999).
33. http://www.neuton.kth.se/publications/library/kamlPh.D.pdf.
34. C. Mc Combie, Nuclear waste management worldwide, Physics Today, 50 (1997) 56-62.
35. K. Raj, K. K. Prasad, N. K. Bansal, Radioactive waste management practices in India, Nucl. Eng. Des., 236 (2006) 914-930.
36. L. H. Baestle, Burning of Actinides: A complementary waste management option?, IAEA Bulletin, 34 (1992) 32.
37. Actinide and Fission Product Partitioning and Transmutation-Status and Assessment report, OECD/NEA, (1999).
38. C. Madic N. Ouvrier, EUROPART: EUROpean research program for the PARTitioning of minor actinides from high active wastes arising from the reprocessing of spent nuclear fuels, Radiochim. Acta, 96 (2008) 183-185.
39. L. Koch, J. P. Glatz, R. J. M.Konings, J. Magill. Partitioning and transmutation studies at ITU, ITU annual report 1999-(EUR 19054) 34-49.

40. V. Anastasov, M. Betti, F. Boisson, F. Depisch, F. Houlbreque, R. Jeffree, I. Khamis, S. Lattemann, J. C. Miquel, S. Nisan, P. K. Tewari, Status of minor actinide fuel development, IAEA Nuclear energy series No. NF-T-4.6. (2009).
41. K. L. Nash, A review of the basic chemistry and recent developments in trivalent F-Elements separations, Solvent Extr. Ion Exch., 11 (1993) 729–768
42. Y. Marcus, A. S. Kertes, Ion Exchange and Solvent Extraction of Metal Complexes, Wiley Interscience, (1969) 707-906.
43. M. Cox, J. Rydberg, Introduction to solvent extraction, In: Solvent Extraction principles and practice revised and expanded extraction, J. Rydberg, M. Cox., C. Musikas, G. R. Choppin, (Eds), CRC press, (2004).
44. M. Cox, Solvent extraction in hydrometallurgy, In: principles and practice of solvent extraction, J. Rydberg, C. Musikas, G.R. Choppin, (Eds), Marcel Dekkar, Inc., USA, (1992) 357.
45. A. Suresh, T. G. Srinivasan, P. R. Vasudeva Rao, Parameters influencing third phase Formation in the Extraction of $Th(NO_3)_4$ by some trialkyl phosphates, Solvent Extr. Ion Exch., 27 (2009) 132-158.
46. K. L. Nash, The chemistry of TALSPEAK: a review of the science, Solvent Extr. Ion Exch., 33 (2015) 1-55.
47. N. Kabay, M. Arda, B. Saha, M. Streat, Removal of Cr(VI) by solvent impregnated resins (SIR) containing aliquat 336, React. Funct. Polym., 54 (2003) 103-115.

48. R. Kumaresan, K. N. Sabharwal, T. G. Srinivasan, P. R. Vasudeva Rao, G. Dhekane, Synthesis, characterization, and evaluation of gel-type poly(4-vinylpyridine) resins for plutonium sorption, Solvent Extr. Ion Exch., 25 (2007) 515–528.
49. P. Zhang, K. Inoue, K. Yoshizuka, H. Tsuyama, Extraction and selective stripping of molybdenum (VI) and vanadium (IV) from sulfuric acid solution containing aluminum (III), cobalt (II), nickel (II) and iron (III) by LIX 63 in Exxsol D80, Hydrometallurgy, 41 (1996) 45-53.
50. A. W. Ashbrook, Commercial chelating solvent extraction reagents: I. Purification and isomer separation of 2-hydroxyoximes, J. Chromat. A., 105 (1975) 141-150.
51. R. A. Day Jr, R. M. Powers, Extraction of uranyl ion from some aqueous salt solutions with 2-thenoyltrifluoroacetone, J. Am. Chem. Soc., 15 (1954) 3895-3897.
52. W. W. Schulz, E. Philip Horwitz, The truex process and the management of liquid tru waste, Sep. Sci. Technol., 23 (1988) 1191.
53. J. N. Mathur, M. S. Murali, K. L. Nash, Actinide partitioning–a review, Solvent Extr. Ion Exch., 19 (2001) 357
54. Y. Zhu, R. Jiao, Chinese experience in the removal of actinides from highly active waste by trialkylphosphine oxide extraction, Nucl. Technol., 108 (1994) 361–369.
55. M. S. Murali, J. N. Mathur, Use of mixture of TRPO and TBP for the partitioning of actinides from high level waste solutions of PUREX origin and its comparison with CMPO and other phosphorous based extractants, Solvent Extr. Ion Exch., 19 (2001) 61–77.

56. S. Tachimori, H. Nakamura, Extraction of some elements by mixture of DIDPA-TBP and application to actinoid partitioning process, J. Nucl. Sci. Technol., 19 (1982) 326–333.
57. Y. Morita, J. P. Glatz, M. Kubota, L. Koch, G. Pagliosa, K. Roemer, A. Nicholl, Actinide partitioning from HLW in a continuous DIDPA extraction process by means of centrifugal extractors, Solvent Extr. Ion Exch., 14 (1996) 385–400.
58. C. Cuillerdier, C. Musikas, P. Hoel, L. Nigond, X. Vitart, Malonamides as new extractants for nuclear waste solutions, Sep. Sci. Technol., 26 (1991) 1229.
59. G. Modolo, L. Amato, G. Modolo, R. Nannicini, C. Madic, P. Baron, DIAMEX counter-current extraction process for recovery of trivalent actinides from simulated high active concentrate, Sep. Sci. Technol., 42 (2007) 439-452.
60. Y. Sasaki, S. Sujuki, S. Tachimori, The novel extractants, diglycolamides, for the extraction of lanthanides and actinides in HNO_3-n-dodecane system, Solvent Extr. Ion Exch., 19 (2001) 91.
61. G. Modolo, H. Asp, H. Vijgen, R. Malmbeck, D. Magnusson, C. Sorel, Demonstration of a TODGA based continuous counter current extraction process for the partitioning of actinides from a simulated PUREX raffinate Part-II: Centrifugal contactor runs, Solvent Extr. Ion Exch., 19 (2008) 62-76.
62. R. B. Gujar, S. A. Ansari, P. K. Mohapatra, V. K. Manchanda, Development of T2EHDGA based process for actinide partitioning. Part I: batch studies for process optimization, Solvent Extr. Ion Exch., 28 (2010) 350–366.
63. J. Ravi, K. A. Venkatesan, M. P. Antony, T. G. Srinivasan, P. R. Vasudeva Rao. New unsymmetrical digycolamide ligands for trivalent actinide separation, Radiochim. Acta, 102 (2014) 609-617.

64. Y. Sasaki, Y. Morita, Y. Kitatsuji, T. Kimura, Extraction Behavior of Actinides and Metal Ions by the Promising Extractant, N,N,N',N'-Tetraoctyl-3,6-dioxaoctanediamide (DOODA), Solvent Extr. Ion Exch., 28 (2010) 335-349.
65. R. G. Pearson, Hard and Soft acids and bases, J. Am. Chem. Soc., 85 (1963) 3533-3539.
66. H. C. Aspinall, Chemistry of the f-Block Elements, CRC Press, (2001).
67. R. M. Diamond, K. Street Jr., G. T. Seaborg, An Ion-exchange Study of Possible Hybridized 5f Bonding in the Actinides, J. Am. Chem. Soc., 76 (1954) 1461.
68. M. Nilsson, K. L. Nash, A review of the development and operational characteristics of the TALSPEAK process, Solvent Extr. Ion Exch., 25 (2007) 665–701.
69. A. S. Suneesh, K. A. Venkatesan, K. V. Syamala, M. P. Antony, P. R. Vasudeva Rao, Mutual separation of americium(III) and europium(III) using glycolamic acid and thioglycolamic acid, Radiochim. Acta, 100 (2012) 425–430.
70. A. Wilden, C. Chreinemachers, M. Sypula, G. Modolo, Direct selective extraction of actinides (III) from purex raffinate using a mixture of CyMe4BTBP and TODGA as 1-cycle sanex solvent, Solvent Extr. Ion Exch., 29 (2011) 190-212.
71. A. Wilden, G. Modolo, P. Kaufholz, F. Sadowski, S. Lange, M. Sypula, D. Magnusson, U. Mullich, A. Geist, D. Bosbach, Laboratory-scale counter-current centrifugal contactor demonstration of an innovative-SANEX process using a water soluble BTP, Solvent Extr. Ion Exch., 33 (2015) 91–108.
72. Z. Kolarik, U. Mullich, F. Gassner, Selective extraction of Am(III) over Eu(III) by 2,6-ditriazolyl- and 2,6-ditriazinylpyridines, Solvent Extr. Ion Exch., 17 (1999) 23-32.

73. G. J. Lumetta, A. V. Gelis, F. Vandegrift, Solvent systems combining neutral and acidic extractants for separating trivalent lanthanides from the transuranic elements, Solvent Extr. Ion Exch., 28 (2010) 287–312.
74. P. S. Dhami, R. R. Chitnis, V. Gopalakrishnan, P. K, Wattal, A. Ramanujam. A. K. Bauri, Studies on the partitioning of actinides from high level waste using a mixture of HDEHP and CMPO as extractant, Sep. Sci. Technol., 42 (2007) 439-452.
75. B. Gannaz, R. Chiarizia, R. K. Antonio, C. Hill, G. Cote, Extraction of lanthanides(III) and Am(III) by mixtures of malonamide and dialkylphosphoric acid, solvent Extr. Ion Exch., 25 (2007) 313-337.
76. X. Hérès, C. Nicol, I. Bisel, P. Baron, L. Ramain, PALADIN: A One Step Process for Actinides(III)/Fission Products Separation, GLOBAL '99: Nuclear Technology – Bridging the Millennia, Jackson Hole, WY, August 29-September 3, 1999, American Nuclear Society, La Grange Park, Illinois; pp. 585–591.
77. J. Ravi, K. A. Venkatesan, M. P. Antony, T. G. Srinivasan, PR Vasudeva Rao, Single-cycle method for partitioning of trivalent actinides using completely incinerable reagents from nitric acid medium, Radiochim. Acta, 102 (2014) 599-607.
78. P. K. Nayak, R. Kumaresan, K. A. Venkatesan, M. P. Antony, P. R. Vasudeva Rao, A new method for partitioning of trivalent actinides from high-level liquid waste, Sep. Sci. Technol., 48 (2013) 1409.

79. P. K. Nayak, R. Kumaresan, K. A. Venkatesan, S. Rajeswari, G. G. S. Subramanian, M. P. Antony, P. R. Vasudeva Rao, Single-cycle separation of americium (III) from simulated high level liquid waste using tetra-bis (2-ethylhexyl) diglycolamide and bis (2-ethylhexyl) phosphoric acid solution, J. Environ. Chem. Eng., 1 (2013) 559.
80. M. Lederer, V. Moscatelli, C. Padiglione, Chromatography of paper impregnated with ion-exchange resins: VII. Ion exchange with organic solvents, J. Chromatogr. A, 10 (1963) 82-92.
81. E. Philip Horwitz, R. Chiarizia, M. L. Dietz, A novel strontium-selective extraction chromatographic resin, Solvent Ext. Ion Exch., 10 (1992) 313-336.
82. N. J. Simpson, Solid-phase extraction: principles, techniques, and applications, CRC Press, (2000).
83. E. M. Thurman, M. S. Mills, Solid-phase extraction: principles and practice, New York: Wiley; (1998).
84. A. Warshawsky, South African Patent Application 71/5637, (1971).
85. R. R. Grinstead, Report by the Dow Chemical Co., On Contract No. 14-12-808 to the Water Quality Office of US Environmental Protection Administration, January (1971).
86. A. Warshawsky, Polystyrene impregnated with β-diphenylglyoxime, a selective reagent for palladium, Talanta, 21 (1974) 624–626.
87. A. Warshawsky, J.A. Marinsky, Y. Marcus, Ion Exchange and Solvent Extraction, Marcel Dekker, New York, 18 (1981) 229.

88. E. Philip Horwitz, Extraction chromatography of actinides and selected fission products: principle and achievements of selectivity, International Workshop on the Application of Extraction Chromatography in Radionuclide Measurement, IRMM, Belgium (1996) HP199.
89. A. Warshawsky, Extraction with solvent-impregnated resins, In: Ion Exchange and Solvent Extraction, 8 (1981) 229-310.
90. J. L. Cortina, A. Warshawskay, Developments in solid-liquid extraction by solvent impregnated resins, eds., J. A. Marinsky, Y. Marcus, in: Ion Exchange and Solvent Extraction, Marcel Dekker, Inc., New York, 13 (1997).
91. R. S. Juang, Preparation, Properties and Sorption Behavior of Impregnated Resins Containing Acidic organo phosphorus extractants, proc. Natl. Sci. Counc. ROC (A), 23 (1999) 353-364.
92. A. Warshawaky, Chelating Ion Exchangers, in Ion Exchange and Sorption Processes, In: Hydrometallurgy, M. Streat, D. Naden (eds), Critical Reports on Applied Chemistry, Vol. 19, John Wiley & Sons, (1987) 166.
93. M. E. Leon-Gonzalez, L. V. Perez-Arribas, Chemically modified polymeric sorbents for sample preconcentration, J. Chrornatogr. A, 902 (2000) 3-16.
94. A. A. Zagorodni, Ion exchange materials: properties and applications: properties and applications, Elsevier, (2006).
95. R. Chiarizia, E. Philip Horwitz, K. A. D'Arcy, S. D. Alexandratos, A. W. Trochimzuk, Uptake of Actinides and other Ions by Dipiosil, a New Silica based Chelating Ion Exchange Resin, In: Ion Exchnge Developments and Applications, J.A. Greig (ed). Proceedings of IEX, The Royal Society of Chemistry, UK, 90 (1996) 321.

96. W. Lutze, R. C. Ewing, Radioactive waste forms for future, North-Holland, Oxford, (1988).

97. E. Vassileva, I. Proinova, K. Hadjiivanov, Solid-phase extraction of heavy metal ions on a high surface area titanium dioxide (anatase), Analyst, 121 (1996) 607-612.

98. A. Y. Zhang, Q. H. Hu, W. H. Wang, E. Kuraoka, Application of a macroporous silica-based CMPO-impregnated polymeric composite in group partitioningof long-lived minor actinides from highly active liquid by extraction chromatography, Ind. Eng. Chem. Res., 47 (2008) 6158–6165.

99. V. Hubscher-Bruder, J. Haddaoui, S. Bouhroum, F. Arnaud-Neu, Recognition of some lanthanides, actinides, and transition- and heavy-metal cations by N-donor ligands: thermodynamic and kinetic aspects, Inorg. Chem., 49 (2010) 1363–1371

100. K. Matloka, A. Gelis, M. Regalbuto, G. Vandegrift, M. J. Scott, C-3-symmetrictripodal thio/diglycolamide-based ligands for trivalent f-element separations, Sep. Sci. Technol., 41 (2006) 2129–2146.

101. O. B. M. Mokhodoeva, G. V. Myasoedova, E. A. Zakharchenko, Solid-Phase extractants for radionuclide preconcentration and separation, New Possibilities, Radiochemistry, 53 (2011) 35–43.

102. T. J. Tranter, Solid-phase extraction technology for actinide and lanthanide separations in nuclear fuel reprocessing, in: K. L. Nash, G. J. Lumetta (Eds.), Advanced Separation Techniques for Nuclear Fuel Reprocessing and Radioactive Waste Treatment, Woodhead Publishing Limited, Cambridge (2011).

103. K. Akiba, H. Hashimoto, Recovery of uranium by polyurethane foam impregnated with 5, 8-diethyl-7-hydroxy-6-dodecanone oxime, J. Radioanal. Nucl. Chem., 130 (1989) 13-20.

104. K. Van Hecke, G. Modolo, Separation of actinides from low level liquid wastes (LLLW) by extraction chromatography using novel DMDOHEMA and TODGA impregnated resins, J. Radioanal. Nucl. Chem., 261 (2004) 269–275.

105. J. E. Roane, T. A. DeVol, Simultaneous separation and detection of actinides in acidic solutions using an extractive scintillating resin, Anal. Chem., 74 (2002) 5629–5634.

106. M. Karve, K. Pandey, Cyanex272 impregnated on Amberlite XAD-2 for separation and preconcentration of U(VI) from uranmicrolite (leachates) ore tailings, J. Radioanal. Nucl. Chem., 285 (2010) 627–633.

107. C. Krishnakumar, P. Revathi, K. K. Nandy, K. S. Kumar, T. Kumar, J. K. Gayen, B. Shreekumar, P. K. Dey, ICP-AES analysis of impurities in PuO_2 after separation of Pu by TOPO impregnated XAD-4, J. Radioanal. Nucl. Chem., 295 (2013) 1019–1022.

108. E. Philip Horwitz, R. Chiarizia, M. L. Dietz, H. Diamond, Separation and pre-concentration of actinides from acidic media by extraction chromatography, Anal. Chim. Acta, 281 (1993) 361–372.

109. M. Karve, R. V. Rajgor, Amberlite XAD-2 impregnated organophosphinic acid extractant for separation of uranium (VI) from rare earth elements, Desalination, 232 (2008) 191–197.

110. H. Hoshi, Y.Z. Wei, M. Kumagai, T. Asakura, Y. Morita, Separation of trivalent actinides from lanthanides by using R-BTP resins and stability of R-BTP resin, J. Alloys Compd., 408 (2006) 1274–1277.

111. K. L. Nash, C. Madic, J. N. Mathur, J. Lacquement, Actinide separation and technology, in: L.R. Morss, N.M. Edelstein, J. Fuger, J.J. Katz (Eds.), The Chemistry of the Actinide and Trans-actinide Elements, 4, 3rd ed., Springer, The Netherlands, (2006) 2622.

112. M. Nogami, Y. Sugiyama, Y. Ikeda, Adsorptivity of silica-supported adsorbents impregnated with polyphosphine polyoxides to U (VI) and some other metal ions in nitric acid media, J. Radioanal. Nucl. Chem., 284 (2010) 195–199.

113. K. R. Hall, L. C. Eagleton, A. Acrivos, T. Vermeulen, Pore- and Solid-Diffusion Kinetics in Fixed-Bed Adsorption under Constant-Pattern Conditions, Ind. Eng. Chem. Fund., 5 (1966) 212–223.

114. N. D. Hutson and R. T. Yang, A Dynamic Approach to Brownian Coagulation of Electrostatically Stabilized Colloid Particles, Adsorption J. Colloid Interf. Sci. (2000), pp 189

115. S. Bilgili, Adsorption of 4-chlorophenol from aqueous solutions by xad-4 resin: Isotherm, kinetic, and thermodynamic analysis, J. Hazard. Mater., 137 (2006) 157−164.

116. M. I. Tempkin, V. Pyzhev, Kinetics of ammonia synthesis on promoted iron catalyst, Acta Phys. Chim., USSR 12 (1940), 327–356.

117. A. Gunay, E. Arslankaya, I. Tosun, Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics, J. Hazard. Mater., 146 (2007) 362–371.

118. A. Dabrowski, Adsorption—from theory to practice, Adv. Colloid Interface Sci., 93 (2001) 135–224.

119. Y. Sugo, Y. Sasaki, S. Tachimori, Studies on hydrolysis and radiolysis of N,N,N′,N′-tetraoctyl-3-oxapentane-1,5-diamide, Radiochim. Acta, 90 (2002) 161-165.

120. R. B. Gujar, S.A. Ansari, A. Bhattacharyya, P.K. Mohapatra, A.S. Kanekar, P.N. Pathak, V.K. Manchanda, Studies on the radiolytic stability of N,N,N',N'-tetra-2-ethylhexyl diglycolamide in n-dodecane solution containing different phase modifiers, J. Radioanal. Nucl. Chem., 288 (2011) 621-627.

CHAPTER 2

Chapter 2: Experimental

This chapter describes in detail about the preparation of solvent impregnated resins employed for the extraction of Am(III) and Eu(III). Different types of neutral extractants and acidic extractants were utilized in the present study. Neutral extractants such as octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) and Tetra-bis(2-ethylhexyl) diglycolamide (TEHDGA) and acidic extractant, bis-(2-ethylhexyl) phosphoric acid (HDEHP) were used as extractants in the preparation of solvent impregnated resin (Extraction chromatographic resin). Single extractant and combined neutral, acidic extractants both were prepared for extraction studies at all nitric acid concentrations. Tulsion ADS 400 was used as a solid support for the impregnation of the extractants. Purity of all the procured compounds has been ascertained by analytical techniques, such as FT-IR, ^{1}H & ^{13}C-NMR and by distribution coefficient measurements. Experimental procedures such as liquid-liquid extraction and solid-phase extraction of Am(III) and other metal ions, adsorption studies and irradiation studies were discussed in detail. Methods and materials employed for the analysis of radioactive and nonradioactive samples have been discussed. Details of instruments such as NaI(Tl) detector, inductively coupled plasma - optically emission spectrometry (ICP-OES) etc., employed for the above mentioned studies have been explained in detail in this chapter.

2.1. Chemicals and reagents

All the chemicals and reagents used in this study were of analytical grade and they were used as received unless otherwise mentioned.

2.1.1. Radioactive tracers

The radioisotope $^{(152+154)}$Eu tracer was procured from Board of Radiation and Isotope Technology (BRIT), Mumbai, India. Initially the radioisotope was in hydrochloric acid medium. The medium (HCl) of the radioactive tracer was changed by evaporating it to dryness under IR lamp, followed by its makeup with dilute nitric acid (HNO_3) to a known volume.

^{241}Am tracer was received from Oak Ridge National Laboratory (ORNL) as Am_2O_3 and dissolved in nitric acid. This ^{241}Am tracer was also diluted using dilute nitric acid. Both radioactive tracers were in dilute nitric acid medium. The purity of $^{(152+154)}$Eu and ^{241}Am was ascertained by gamma spectrometry and alpha spectrometry respectively.

2.1.2. Organic materials and solvents

Dichloromethane (DCM)

Dichloromethane was obtained from M/s Fischer Inorganics and Aromatics Limited, Chennai, India.

Diglycolic anhydride and dialkyl amines

Diglycolic anhydride (technical grade, 90%), dioctylamine, and di-2-ethylhexylamine of A.R. grade were procured from M/s Sigma Aldrich Chemie GmbH, Germany.

Dicyclohexylcarbodiimide (DCC)

Dicyclohexylcarbodiimide (DCC, 90%) was procured from M/s Spectrochem, Mumbai, India.

Tri-*n*-butyl phosphate (TBP)

Tri-*n*-butyl phosphate (TBP) was obtained from M/s Fluka Chemie GmbH, Buche, Switzerland. It was washed with dilute sodium carbonate solution (~ 0.2M) followed by distilled water and then dried under vacuum.

***n*-Dodecane (*n*-DD)**

n-Dodecane (99%) was obtained from M/s Spectrochem Private Limited, Mumbai, India and used as such.

Methanol

AR grade methanol was obtained from M/s Ranbaxy Fine Chemicals Limited, New Delhi, India and used as such.

***n*-Hexane**

n-Hexane (AR grade) was obtained from M/s Ranbaxy Fine Chemicals Limited, New Delhi, India and used as such.

Ethylacetate

Ethylacetate was obtained from M/s Fischer Inorganics and Aromatics Limited, Chennai, India.

Acetone

Acetone of AR grade was procured from M/s Merck Specialties Private Limited, Mumbai, India.

Silica-gel

Silica-gel (100-200 mesh) for column chromatography was obtained from M/s Sisco Research Lab Private Limited, Mumbai, India and dried at 373 K for one hour prior to use.

Alumina

Alumina (AR grade) was procured from M/s Merck Specialties Private Limited, Mumbai, India.

Thin Layer Paper Chromatographic Paper Plate

Thin layer paper chromatographic paper plate was procured from M/s Sigma Aldrich, India.

Resins used for the studies

Tulsion ADS 400 resin was used for the impregnation of CMPO, TEHDGA and HDEHP. It is a macroporous acrylic copolymer, obtained from M/s Thermax Pvt. Ltd, Pune, India. It's properties and purification procedure were given in section 2.6.2.1.

2.1.3. Aqueous solutions and complexing agents

Acid solutions

The acid solutions (HNO_3, GR grade, Merck Specialties Private Limited, Mumbai, India) were prepared by the dilution of concentrated acids and the solutions were standardized by standard acid-base titration methods using standard NaOH solution and phenolphthalein as indicator.

pH buffer solutions

Buffer 1

A solution of 0.05 M potassium hydrogen phthalate (dried at 110°C) was prepared in double distilled water. pH of this solution was 4.01 at 298K.

Buffer 2

A solution of 0.01M Borax ($Na_2B_4O_7.10H_2O$) was prepared in double distilled water. pH of this solution was 10 at 298K.

Phenolphthalein

Phenolpthalein (M/s Merck Specialities Private Limited, Mumbai, India) solution was prepared by dissolving ~ 500 mg of phenolpthalein in 100 mL of 1:1 mixture of distilled water and ethanol.

Sodium Nitrate

Sodium Nitrate was obtained from M/s S.D. Fine Chemicals, Mumbai, India.

Sodium Nitrite

Sodium Nitrite (AR grade) was obtained from M/s S.D. Fine Chemicals, Mumbai, India and used as such.

Diethylenetriaminepentaaceticacid (DTPA)

Diethylenetriaminepentaacetic acid was procured from M/s Acros Organics, Geel, Germany.

Citric acid

Citric acid, anhydrous was obtained from M/s LOBA Chemicals, Mumbai, India.

CyDTA

Trans-1, 2-diaminocyclohexane-*N,N,N'N'*-tetraacetic acid (CyDTA) was obtained from M/s Sigma Aldrich Chemie GmbH, Steinheim, Germany.

Europium nitrate

Europium nitrate hexahydrate ($Eu(NO_3)_3.6H_2O$) was purchased from M/s Sigma Aldrich, India.

EDTA

AR grade EDTA [bis(ethylenediaminetetraacetic acid)] was obtained from M/s Sigma Aldrich Chemie GmbH, Steinheim, Germany and used as such.

Methyl Thymol Blue

AR grade methyl thymol blue was obtained from M/s S.D. Fine Chemicals, Mumbai, India. The solution of methyl blue was prepared by dissolving ~25 mg in 10 mL of distilled water for using as indicator for the standardization of europium solution.

Europium oxide

AR grade europium oxide, Eu_2O_3 (purity: 99.9%) procured from M/s S.D. Fine Chemicals, Mumbai and used for the preparation of the solution of europium nitrate.

2.2. Extractants used in distribution studies

2.2.1. Octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO)

Octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide was synthesised by the procedure (given in Appendix) described elsewhere [1] and supplied by National Chemical Laboratory, Pune. Further purification was carried out by column chromatography using neutral alumina as stationary phase and *n*-hexane as mobile phase prior to impregnation to remove the acidic impurities. The purity of the product was ascertained by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy. The purity was further tested by extraction of americium(III) from 0.01 M and 3.0 M nitric acids using a TRUEX solvent composition. The distribution values of Am(III) obtained at these nitric acids were comparable with the reported values [2].

2.2.2. Tetra-bis(2-ethylhexyl) diglycolamide (TEHDGA)

The tetraalkyldiglycolamides (TEHDGA) were synthesized by reaction of diglycolic anhydride with dialkylamines and dicyclohexylcarbodiimide (DCC) in dichloromethane as described elsewhere [3, 4]. The general reaction scheme is shown in figure 2.1. The characterization details of TEHDGA by NMR and IR are given below.

TEHDGA: ^{1}HNMR ($CDCl_3$, δ relative to TMS): 4.330 (s, 4 H); 3.370 (m, 4 H); 3.043 (d, 4 H, J=7.0 Hz); 1.669 (m, 3 H); 1.560 (m, 3 H); 1.250 (m, 30 H); 0.880 (m, 24 H). ^{13}C NMR ($CDCl_3$, δ relative to TMS): 169.52, 68.72, 49.94, 47.89, 37.91, 36.63, 30.52, 28.81, 28.79, 23.81, 23.06, 14.07, 14.03, 10.90, 10.61. IR (neat, ν cm^{-1}): 2958 (C-H stretch), 2924(C-H stretch), 2874(weak, C-H stretch), 1651(C=O stretch), 1464 (-CH_2-bend), 1380 (C-N stretch) and 1116 (C-O-C stretch). Yield was >94 %.

The crude product obtained was purified by column chromatography using silica gel and 5% ethyl acetate/ petroleum ether as eluent. The purity of these extractants was ascertained by IR and NMR techniques. TEHDGA is a brown viscous light brown liquid. Its density was measured as 0.91074 g cm^{-3} and viscosity was 449-451 cP at 303K. Its refractive index (n_D^{30}) was determined to be 1.46809, while its surface tension was estimated as 27.18 mN/m at 303 K.

2.2.3. Bis-(2-ethylhexyl) phosphoric acid (HDEHP)

Bis (2-ethylhexyl) phosphoric acid (HDEHP) was purchased from M/s Sigma Aldrich, Chemie GmbH, Germany.

The chemical structures of the extractants used in impregnation for distribution studies are shown in figure 2.2.

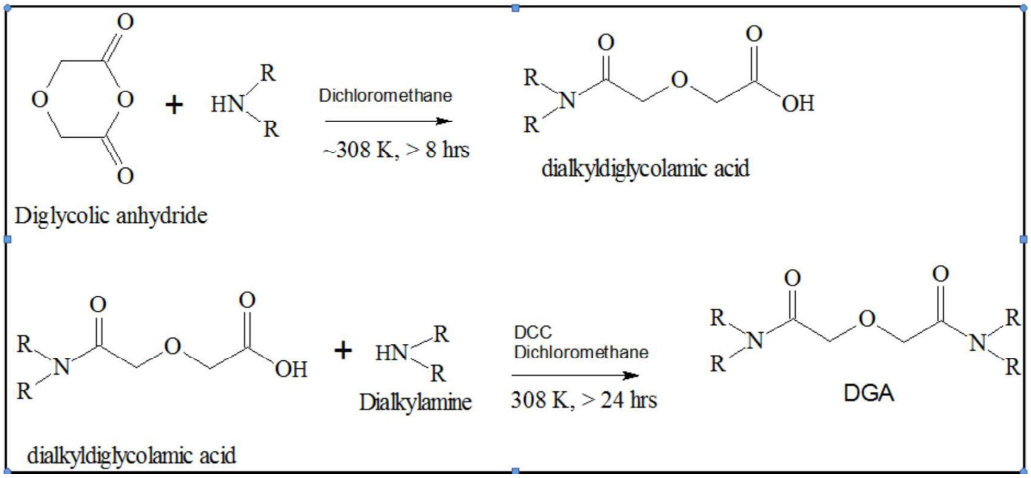


Figure 2.1. Reaction scheme for the synthesis of diglycolamides.

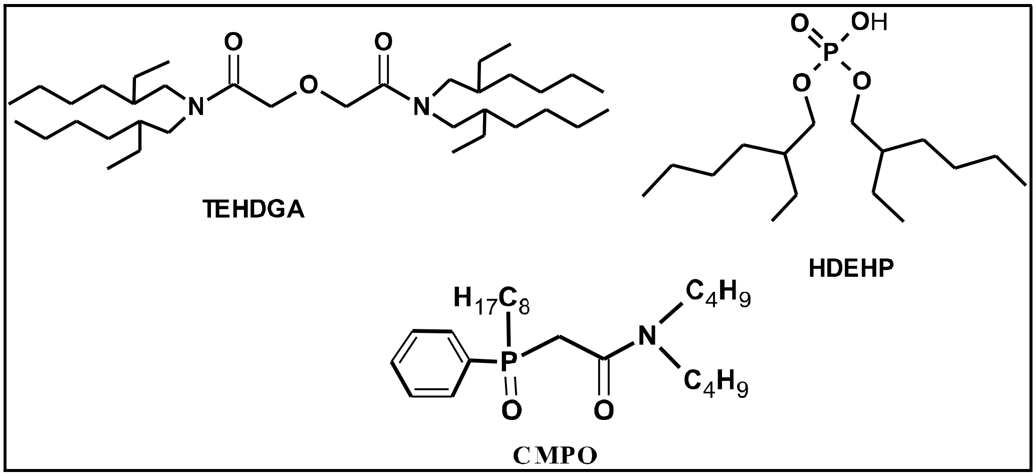


Figure 2.2. Structure of extractants.

2.3. Instrumentation

2.3.1. Gamma counter

The radioactivity of ^{241}Am, $^{(152+154)}$Eu was measured independently using a gamma counter (NaI(Tl) detector). The gamma detector which constitutes a well type NaI(Tl) scintillation detector associated with photomultiplier tube (PMT) unit, single channel analyzer (SCA) and a timer-scaler unit. The NaI(Tl)-photomultiplier integral assembly along with other associated electronic modules were procured from Electronic Corporation of India Limited (ECIL), Hyderabad, India.

Sodium iodide activated with 0.1–0.2% of thallium, NaI(Tl) is by far the most widely used inorganic scintillator for the assay of gamma emitting radionuclides. Salient features of the detectors are the low cost, ease of operation and ruggedness [5, 6]. The band gap in NaI crystal is of the order of 5-6 eV. When gamma rays fall on the detector its energy is used up either for excitation of electrons from valence band to conduction band or for the ionization of atom. De-excitation of electrons from conduction band to valance band leads to the emission of photons in UV region as the band gap is large. To shift the emitted photons in visible region, which is requisite of PMT, NaI crystal is doped with activator impurity like Tl which forms the intermediate level conduction band. The resolution of NaI(Tl) detector is about 7% at 662 keV. Nearly 100% detection efficiency for moderate energy photons in a well type NaI(Tl) detector offers great advantages for counting of low activity samples. A suitable aliquot of the desired analyte solution was taken in glass counting tubes which was then placed in the cavity of detector coupled with PMT and associated electronics. Each sample was counted for sufficient time so as to get more than 10,000 counts to restrict the statistical counting error within ±1%.

2.3.2. Gamma chamber for irradiation

A compact, self-shielded (Gamma Chamber 5000, BRIT) gamma chamber was used in the present study. The radiation field was provided by a set of stationary cobalt-60 gamma source placed in a cylindrical cage. The samples were placed in an irradiation chamber located in the vertical drawer inside the lead flask. The volume of irradiation chamber was about 5 L. The gamma chamber was calibrated using Fricke dosimeter.

2.3.3. Rotary evaporator

A rotary evaporator (Model R-3000 from M/s Buchi Laboratory Technique AG, Switzerland) was used for distilling off volatile solvents from the reaction mixture and from fractions collected during the column chromatography. It was used for removing the solvents during impregnation of extractants on solid adsorbents (Tulsion ADS 400).

2.3.4. Thermostatted rotary water bath shaker

A JULABO (F33-HE) refrigerated circulator with a temperature controlling accuracy of ± 0.010 K and a heating immersion circulator with a temperature controlling accuracy of ± 0.010 K were also used for the experiments.

2.3.5. pH meter

All pH measurements were made with M/s Cyberscan 500 pH, Metrohm. The meter was calibrated at 298 K with standard buffers of pH 4, 7 and 10.

2.3.6. Inductively coupled plasma-optical emission spectrometer

In this study, Ultima C spectroanalyser (M/s HORIBA, France) equipped with Inductively Coupled Plasma excitation source covering the wavelength range of 200-800nm was used for elemental analysis. Its high specificity, multi-element capability, good detection ability to perform rapid analysis and free from chemical interference, make this technique suitable for wide variety of applications [8]. The solution under analysis is nebulised and the aerosol thus formed is transported to a high-frequency plasma (8,000–10,000°C) in which the constituents of the sample solution are atomized, ionized and excited to higher energy states. The excited states of the atoms or ions return to their ground state by emitting photons of a particular wavelength which is characteristic to the element present. The characteristic emission lines of the atoms and ions are dispersed by a monochromator (sequential) or polychromator (simultaneous) and the intensity of the lines is recorded in a photo multiplier tube (PMT) detector. Here, the sequential, simultaneous spectrometer provides a resolution of 0.005 nm and 0.011nm, respectively. RF generator of 40.68 MHz with a maximum output power of 1550 W was used for plasma generation. When calibrated against standards the technique provides a quantitative analysis of the original. The wavelengths are selected in accordance with the required limit of detection and the possibility of interference by other elements present in the sample solution. The block diagram of a typical ICP-OES is shown in figure 2.3 and table 2.1 provides the conditions for the measurement.

2.3.7. NMR spectrometer

A Brucker Avance III 500 MHz (AV 500) multi nuclei solution NMR spectrometer was used for recording the NMR pattern of the synthesized diglycolamic acids and diglycolamides. $CDCl_3$ was used as the solvent.

2.3.8. FT-IR spectrometer

A BOMEM MB-100 FT-IR spectrometer with a range 4000-650 cm^{-1} and a resolution of 4 cm^{-1} was used for recording IR pattern of the samples. The synthesized diglycolamide samples were placed in between two zinc-selenide windows.

2.3.9. Electronic single pan balance

A calibrated electronic single pan balance with a sensitivity of 0.01 mg was used for weighing.

Table 2.1. Operating conditions and description of ICP-OES instrument

RF generator type	**Crystal controlled, water cooled**
Sequential Spectrometer-optical design	Czerny Turner mounting
Simultaneous Spectrometer-optical design	Paschen-Range mounting
Forward power	1000 W
Reflected Power	<5 W
Plasma gas flow rate	12 $L.min^{-1}$
Sheath gas flow rate	0.1 $L.min^{-1}$
Auxillary gas flow rate	0 $L.min^{-1}$
Sample intake	1 $mL.min^{-1}$

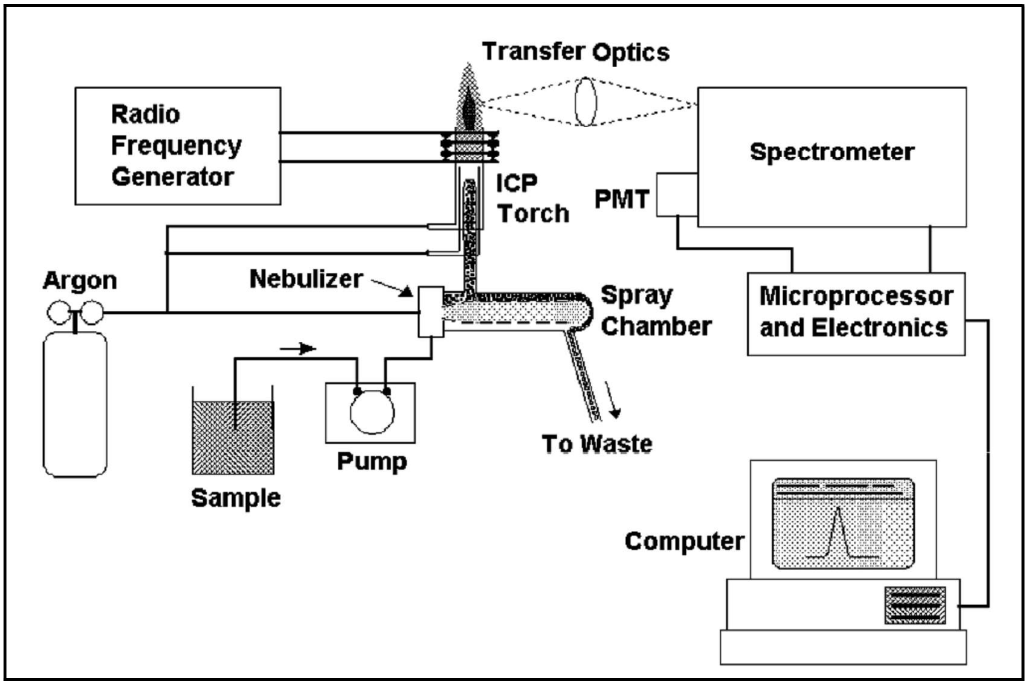


Figure 2.3. Block diagram of a typical ICP – OES instrument [7].

2.3.10. Column chromatography

The crude product obtained after the reaction contains both reactants, products intermediate compounds, bi-products and solvents. This complex mixer was purified using column chromatography to get the pure product. The column (60 cm length and 5 cm diameter) was packed with silica gel of mesh size 100-200 with the help of petroleum ether. The crude product was loaded on the top of the column. The products were eluted from the column using hexane or petroleum ether as the mobile phase. The eluted fraction was collected in conical flask. The mobility of the compound was checked by TLC. The eluted final product was dried completely using rotary evaporator for 2-3 hour continuously under reduced pressure.

2.3.11. Thin Layer Chromatography

Thin-Layer Chromatography (TLC) of reactants and reaction mixture was performed using TLC Aluminum Silica-gel 60 F254 Sheets (Merck) cut into small pieces of approx. 4 × 10 cm size. Fine capillaries were used to spot the compounds or reaction mixture and the TLC was performed in solvent containing 15-30% of ethyl acetate in petroleum ether or hexane. The sheets were subsequently air-dried and placed in an iodine chamber for spot visualization.

2.4. Preparation of Fast Reactor Simulated High-Level Liquid Waste (FR-SHLLW)

The composition of simulated FR-HLLW was based on the waste arising from reprocessing of spent fuel from a fast reactor spent nuclear fuel with a burn-up of 80,000 MWd/t [9]. Table 2.2 shows the composition of simulated FR-HLLW. A series of stock solutions were prepared for various metal ions which are used to prepare the SHLLW. The nitrate or oxide salt of individual metal ion was dissolved in nitric acid ($\leq$ 1 M) to prepare their stock solutions. The concentration of metal ion in its stock solution was estimated using ICP-OES and complexometric titration. Simulated HLLW was prepared by adding the appropriate volume of stock solution of each metal ion together in nitric acid. 0.05 M CyDTA was added to simulated FR-SHLLW to avoid the extraction of palladium(II) and zirconium(IV) [10]. Finally the nitric acid concentration was adjusted to 3 M using nitric acid. The final free acidity was determined by standard acid-base titrations using standard NaOH and phenolphthalein indicator. During titration saturated potassium oxalate solution was added as a masking agent to prevent interference from hydrolysable ions.

2.5. Standard europium nitrate solution for adsorption studies

Europium nitrate solution was prepared by dissolving Eu_2O_3 in the concentrated nitric acid followed by drying under an IR lamp. The nitric acid was evaporated to dryness and the europium nitrate was redissolved in 3 M HNO_3. The free acidity of $Eu(NO_3)_3$ solution was measured by acid-base titration using saturated potassium oxalate solution as a masking agent for Eu(III). The concentration of europium was estimated by a standard EDTA solution (0.05 M) with methylthymol blue as indicator. From this stock solution, different concentration of Eu(III) solution was prepared as per the experimental requirement.

Table 2.2. The simulated composition of fast reactor high-level liquid waste (FR-SHLLW). The composition is based on the HLLW arising from reprocessing of spent fast reactor fuel with a burn-up of 80,000 MWd/Te and 2 year cooling

Element	Concentration [g.L^{-1}]	Element	Concentration [g.L^{-1}]	Element	Concentration [g.L^{-1}]
La	0.342	Mo	1.092	Cs	1.125
Ce	0.684	Cr	0.101	Rb	0.055
Pr	0.339	Te	0.163	Se*	0.002
Nd	1.125	Cd	0.038	Na	3.000
Sm	0.306	Ni	0.1	Ag	0.109
Pm*	0.053	Sr	0.147	Tc*	0.262
Eu	0.032	Ba	0.414	Sb*	0.007
Gd	0.065	Ru	0.813	^{241}Am	0.218
Tb*	0.011	Pd	0.600	$^{(152+154)}$Eu	Tracer
Dy	0.006	Zr	0.822	[HNO_3]	~ 3 M
Y	0.074	Rh	0.262		
Fe	0.5	Sn*	0.163		

* Sb, Sn, Se – were not added as they are sparingly soluble. La was added for Tb, and Pm. Mo was added for Tc.

2.5.1. Potassium oxalate solution

Saturated potassium oxalate solution was prepared by dissolving potassium oxalate salt in double distilled water to saturation and adjusting the pH to 7 by adding NaOH solution or dilute nitric acid. This solution was used to complex the metal ions present in the sample solution, to be investigated for the estimation of free acidity by titration against NaOH solution.

2.5.2. Standard EDTA solution

The solution of EDTA was prepared by dissolving required quantity of disodium dihydrogenethylenediaminetetraacetate by weight in distilled water to get the desired concentration solution. This solution standardisation was done by titration of nearly neutralised zinc chloride or zinc sulphate solution.

2.6. Experimental procedures

2.6.1. Liquid - liquid extraction studies for checking the purity of extractants

All the extraction studies were carried out in duplicate at 298 K unless otherwise mentioned. The distribution ratio of a species in a biphasic system is defined as the ratio of the concentration of the species in organic phase to that of in aqueous phase at equilibrium [11]. The equilibration was carried out in a constant temperature water bath. A small equilibration tube (10 mL capacity), equipped with a stopper was used for extraction studies. The organic phase was pre-equilibrated with desired concentration of nitric acid prior to metal ion extraction. The extraction experiments involved equilibration of equal volumes of organic phase (extractant with diluent) and aqueous phase (metal solutions) for about one hour in a constant temperature water bath. Extraction of americium(III) as a function of nitric acid was studied by equilibrating the organic phase with nitric acid solution spiked with ^{241}Am(III) tracer (20 mg/L in all experiments). After equilibration the radioactivity present in both organic and aqueous phases was measured. The γ-radioactivity for ^{241}Am(III) isotope was measured using a well-type NaI(Tl) scintillation detector coupled with single channel analyzer. The distribution ratio of metal ion (D_{M}) in a biphasic system was determined as the ratio of the concentration of metal ion in organic phase to that in the aqueous phase. The distribution ratio (D_{M}) of the metal ion was determined by using the equation 2.1.

$$D_{\text{M}} = \frac{[M]_{org}}{[M]_{aq}} \tag{2.1}$$

where, M_{org} and M_{aq} are the radioactivity (or concentration) of radionuclide (or metal ion) in organic and aqueous phases respectively.

2.6.2. Solid-liquid extraction studies for the uptake of Am(III) and Eu(III) ions

2.6.2.1. Preparation of solvent impregnated (extraction chromatographic) resins

Tulsion ADS 400 was used as a solid polymeric support for the solvent impregnation. Tulsion ADS 400 is a macroporous acrylic polymer with a particle size ranging from 0.4 to 1.2 mm. The surface area of the dry beads is about 400 $m^2.g^{-1}$. The monomers present in the Tulsion ADS 400 was removed by washing with water, methanol and acetone sequentially and dried at 353 K under vacuum. The required quantity of CMPO or THEDGA or HDEHP or CMPO+HDEHP or TEHDGA+HDEHP was dissolved in dichloromethane and equilibrated with Tulsion ADS 400 taken in dichloromethane. The equilibration was carried out using a vortex shaker for about 8 hours. After mixing, dichloromethane was evaporated slowly using rotary evaporator at 353 K. The resin beads were weighed after drying. From the amount of extractant incorporated in the resin, the percentage of impregnation (wt./wt.) was calculated.

2.6.2.2. Distribution coefficient measurements

The distribution coefficient of Am(III) and Eu(III) was determined by batch equilibration procedure. About 0.05 g of CMPO or THEDGA or HDEHP or CMPO+HDEHP or TEHDGA+ HDEHP was equilibrated with 5 mL of aqueous phase containing desired concentration of nitric acid spiked with $^{(152+154)}$Eu(III) or ^{241}Am(III) tracer in duplicate. The mixture was taken in a 15 mL capacity ground glass stoppered tubes and equilibrated at a constant temperature water bath of 298 K using a roto-spin. After 3 h, the equilibration was stopped and an aliquot was taken from the aqueous phase. The radioactivity of ^{241}Am(III) or $^{(152+154)}$Eu(III) in aqueous phase was measured using well-type NaI(Tl) detector. The distribution coefficient (K_d) of radionuclides was determined by using an equation 2.2. The separation factor (SF) was determined using equation 2.3. The radioactivity in resin phase was determined indirectly by computing the difference between initial and final radioactivity of ^{241}Am(III) or $^{(152+154)}$Eu(III) in aqueous phase.

$$K_d \;(\text{mL.g}^{-1}) = \left(\frac{\text{A}_0 - \text{A}_f}{\text{A}_\text{f}}\right) \times \left(\frac{\text{v}}{\text{m}}\right) \tag{2.2}$$

$$\text{S.F} = \frac{\text{K}_\text{d} \text{ of Eu(III)}}{\text{K}_\text{d} \text{ of Am(III)}} \tag{2.3}$$

where A_0 and A_f are the initial and final radioactivity of aqueous phase. v is the volume of aqueous sample (5 mL), and m is the mass (0.05 g) of the sorbent. To understand the extraction behavior of metal ions in the walls of the test-tube (for blank correction), experiments were conducted by equilibrating 10 mL of the 0.01 M nitric acid solution (or 0.001 M) spiked with $^{(152+154)}$Eu(III) (or ^{241}Am(III)) tracer for about 4-6 hours (depending upon the adsorbent). After four hours (sometimes six hours depending up on the type of adsorbent) of equilibration, the radioactivity of the aqueous solution was measured. The results indicated that the changes in the radioactivities before and after equilibration were negligible. This indicates that there was no sorption of Eu(III) and Am(III) by the equilibration tube.

The relative standard deviation (RSD) associated with the measurement of distribution ratio is about ± 5 % in the range of distribution ratio values 1 to 10^5 in radiometric technique. At high distribution ratio ($K_d > 10^5$), aqueous phase contains background level radioactivity. Similarly, at low distribution ratio ($K_d < 1$), aqueous phase contains higher level of radioactivity as similar to the initial activity. Therefore, the above two cases lead to the error in measurements of distribution ratios using radiometric method.

About one gram of 10% HDEHP+ 30% TEHDGA impregnated resin was equilibrated with 5 mL of FR-SHLLW for 3 hours at 298 K. The elemental composition of FR-SHLLW before and after equilibration was analyzed using ICP-OES. Based on initial and final concentration of metal ions, the percentage of extraction of metal ions in the impregnated resin was calculated.

2.6.2.3. Kinetic studies

The kinetics of extraction of Am(III) (or Eu(III)) in 10% HDEHP + 30 % TEHDGA- impregnated resin was studied by equilibrating 0.05 g of impregnated resin with 5 mL of nitric acid solution (1M) spiked with ^{241}Am(III) or $^{(152+154)}$Eu(III) tracer at various intervals of time. Experiments were performed for 5 minutes to 180 minutes. After the stipulated time of equilibration, samples were taken from the aqueous phase. The radioactivity of ^{241}Am(III) or $^{(152+154)}$Eu(III) was measured by using a well-type NaI(Tl) detector. The percentage of extraction of Am(III) or Eu(III) was calculated from the initial and final radioactivity of the aqueous phase.

The rate of extraction of the metal ion in the resin phase (mmol.g^{-1}) is directly proportional to the concentration of "free" sites, q_{free}, available for extraction.

$$\frac{dq_t}{dt} = k_1\, q_{free} \tag{2.4}$$

or

$$\frac{dq_t}{dt} = k_2\, q_{free}^2 \tag{2.5}$$

where, q_t is the amount of metal ion extracted at time t (in mmol.g^{-1}), q_{free} is the "free sites"available for extraction (in mmol.g^{-1}), k_1 and k_2 are the pseudo-first order and pseudo second order rate constants respectively. The q_{free} can be tacitly related to the amount of metal ions extracted at equilibrium by equation 2.6.

$$q_{free} = q_e - q_t \tag{2.6}$$

where, q_e is the amount of metal ion extracted at equilibrium (in mmol/g). Substituting the equation 2.6 in equation 2.4, results in equation 2.7.

$$\frac{dq_t}{dt} = k_1\left(\mathrm{q_e} - \mathrm{q_t}\right) \tag{2.7}$$

Integrating the equation 2.7 between the limits = 0 to t q_t = 0 to q_t results in the Lagregren equation of the form shown in equation 2.8

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{2.8}$$

Similarly, q_{free} substituting in equation 2.5 and upon integration results in the pseudo second order equation of the form shown in equation 2.9.

$$q_t = \frac{q_e^2 \mathrm{k}_2 \mathrm{t}}{1+\mathrm{q}_e \mathrm{k}_2 \mathrm{t}} \qquad (2.9)$$

2.6.2.4. Studies on selective separation of Am(III)

Batch studies were conducted to determine a suitable stripping regent to separate Eu(III) from Am(III). For this purpose 0.05g of impregnated resin was equilibrated with the aqueous phase containing complexing agents, such as diethylenetriaminepentaacetic acid (DTPA) and citric acid (CA) along with Am(III). It was reported that DTPA selectively hold americium(III) in aqueous phase to enable the separation of Eu (III) over Am(III) [12]. Addition of these reagents to aqueous phase facilitates the retention of trivalent actinides much more than lanthanides that facilitates the mutual separation of lanthanides from actinides.

2.7. Irradiation experiments

Irradiation was done at the Gamma chamber GC-5000 with cobalt-60 γ -irradiation facility supplied by BRIT, India. The dose rate of gamma chamber was 2 kGy.hr^{-1}. The dose rate was calibrated by Fricke dosimeter. Resins in a stoppered reagent bottle (100 mL) was placed inside the γ -chamber for various periods from 2 to 300 h at an exposure dose rate of 2 kGy.hr^{-1}. Different types of resins, such as CMPO, TEHDGA, HDEHP, CMPO+HDEHP and TEHDGA+HDEHP/ADS 400 were subjected to the cumulative absorbed dose of 5, 10, 25, 50, 100, 200 and 550 kGy. All the resins were irradiated under similar conditions. The effect of irradiation was ascertained by measurement of distribution coefficients at irradiated and unirradiated conditions. The distribution coefficient of Am(III) and Eu(III) was determined by adding the requisite quantity of tracers ^{241}Am and $^{(152+154)}$Eu to the irradiated samples and following the procedure as mentioned in section 2.6.2.2.

2.8. Adsorption Isotherms

Sorption isotherm studies were performed by equilibrating known weight of impregnated resins (0.05 g) with 3 M nitric acid containing various initial concentrations of europium(III) (20 to 500 mg.L^{-1}) for three hours in a thermostated waterbath. The aqueous phase was spiked with $^{(152+154)}$Eu(III) tracer. After equilibration, suitable aliquots of the aqueous phase were taken for measuring the radioactivity of $^{(152+154)}$Eu using a well type NaI(Tl) scintillation counter. The concentration of Eu(III) in the resin phase was calculated by the difference in the initial and final radioactivity of $^{(152+154)}$Eu in the aqueous phase. The adsorbed europium at equilibrium (q_e) was calculated using equation 2.10.

$$q_e = (C_o - C_e) \times \left(\frac{\mathrm{v}}{\mathrm{m}} \right) \qquad (2.10)$$

where, C_0 and C_e are the initial and equilibrium Eu(III) concentration in aqueous phase. v is the volume of aqueous sample (5 mL), and m is the mass (0.05 g) of the sorbent.

The variation in the loading of Eu(III) as a function of equilibrium concentration of Eu(III) in aqueous phase for the irradiated and un-irradiated SIRs can be described by adsorption isotherms. The adsorption behavior of Eu(III) can be further evaluated by fitting the isothermal adsorption data into various models such as Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms[12-15].

The results of all the experiments described here are discussed in the subsequent chapters.

2.9. References

1. J. N. Mathur, M. S. Murali, P. R. Natarajan, L. P. Badheka, A. Banerji, Extraction of actinides and fission products by octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl-phosphine oxide from nitric acid media, Talanta, 39 (1992) 493-498.
2. W. W. Schulz, E. Philip Horwitz, The Truex Process and the Management of Liquid TRU uwaste, Sep. Sci. Technol., 23 (1988) 1191-1210.
3. Y. Sasaki, Y. Sugo, S. Suzuki, S. Tachimori, The novel extractants, diglycolamides, for the extraction of lanthanides and actinides in HNO_3–n-dodecane system, Solvent Extr. Ion Exch., 19 (2001) 91-103.
4. G. Modolo, H. Asp, C. Schreinemachers, V. Vijgen, Development of a TODGA based Process for Partitioning of Actinides from a PUREX Raffinate Part I: Batch Extraction Optimization Studies and Stability Tests, Solvent Extr. Ion Exch., 25 (2007) 703-721.
5. G. F. Knoll, Radiation detectors for X-ray and gamma-ray spectroscopy, J. Radioanal. Nucl. Chem., 243 (2000) 125-131.
6. D. D. Sood, A. V. R. Reddy and N. Ramamoorthy, "Fundamentals of Radiochemistry", 2nd ed., IANCAS publication, BARC, Mumbai (2004), 115.
7. Moore, G.L., Introduction to Inductively Coupled Plasma – Atomic Emission spectroscopy, Elsevier Science, Amsterdam, The Netherlands, 3rd Edition, (1988) 121.
8. Boss, C.B., Fredeen, K.J., Concepts, instrumentation and techniques in

inductively coupled plasma optical emission spectrometry, Perkin Elmer, 2nd Edition (1997) 36.

9. J. N. Mathur, M. S. Murali, M. V. Balarama Krishna, R. H. Iyer, R. R. Chitnis, P. K. Wattal, A. K. Bauri, A. Banerji, Recovery of neptunium from highly radioactive waste solutions of PUREX origin using CMPO, J. Radioanal. Nucl. Chem., 213 (1996) 419–429.
10. P. K. Nayak, R. Kumaresan, K. A. Venkatesan, S. Rajeswari, G. G. S. Subramanian, M. P. Antony, P. R. Vasudeva Rao, Single-cycle separation of americium (III) from simulated high levelliquid waste using tetra-bis (2-ethylhexyl) diglycolamide and bis (2-ethylhexyl) phosphoric acid solution, J. Environ. Chem. Eng., 1 (2013) 559.
11. M. Cox, J. Rydberg, Introduction to solvent extraction, In: Solvent Extraction principles and practice revised and expanded extraction, J. Rydberg, M.Cox., C. Musikas, G.R. Choppin, (Eds), CRC press, (2004).
12. Langmuir, Irving. "The condensation and evaporation of gas molecules." Proceedings of the National Academy of Sciences 3, no. 3 (1917) 141-147.
13. H. Freundlich, Uber die adsorption in losungen (adsorption in solution), Z. Phys. Chem. 57 (1906) 384–470.
14. M. J. Temkin, V. Pyzhev, Recent modifications to Langmuir isotherms, Acta Physiochim., URSS 12 (1940) 217–222.
15. M. M. Dubinin, E. D. Zaverina, L. V. Radushkevich, Sorption and structure ofactive carbons. I. Adsorption of organic vapors, Zh. Fiz. Khim., 21 (1947) 1351–1362.

CHAPTER 3

Chapter 3: Extraction behavior of Am(III) and Eu(III) from nitric acid medium in CMPO-HDEHP impregnated resins

3.1. Introduction

Nuclear reactors employ natural or enriched uranium as the fuel [1]. The spent nuclear fuel discharged from the nuclear reactor contains fissile elements such as plutonium, depleted uranium and several other elements formed by fission reaction, known as fission products. PUREX process is being adapted worldwide, for the recovery of uranium and plutonium from the spent nuclear fuel [2]. PUREX process basically consists of solvent extraction of U(VI) and Pu(IV) from nitric acid medium by a solution of 1.1 M tri-*n*-butylphosphate (TBP) in *n*-dodecane. The raffinate rejected after extraction of U(VI) and Pu(IV) during PUREX process is known as high-level liquid waste (HLLW), which contains long-lived minor actinides such as ^{237}Np, ^{241}Am, ^{243}Am, and ^{244}Cm and fission product nuclides such as ^{90}Sr, ^{91}Zr, ^{95}Mo, ^{99}Tc, ^{101}Ru, ^{135}Cs, ^{137}Cs along with the rare earth elements (lanthanides) and platinum group metals [3]. For the remediation of HLLW, P&T (Partitioning and Transmutation) strategy is being explored by several countries worldwide. The method involves the separation of minor actinides such as Am, Np, Cm from HLLW and subsequent incineration of minor actinides in high flux reactors/accelerator driven subcritical systems [4, 5]. Since lanthanides act as neutron poisons that reduce the efficacy of transmutation process, the separation of lanthanide from minor actinides or vice-versa is necessary prior to transmutation. Therefore, P&T option converts all long-lived radionuclides into short-lived (or stable) species.

At present, partitioning of minor actinides from HLLW is a two-cycle process [6]. In the first cycle, the trivalent lanthanides (Ln(III)) and actinides (An(III)) are extracted from HLLW into the organic phase composed of a neutral extractant present in *n*-dodecane followed by the recovery of both lanthanides and actinides from the loaded organic phase using dilute nitric acid. In the second cycle, mutual separation of actinides from lanthanides is performed by using acidic extractant. In this cycle, both trivalent lanthanides and actinides obtained as the aqueous product in the first cycle are extracted by using an acidic extractant, and the selective stripping of actinides alone from the organic phase is carried out by using aqueous soluble complexing agents such as, diethylenetriamminepenta acetic acid (DTPA) and citric acid (CA). Several neutral extractants such as carbamoylorganophoshorous compounds (TRUEX process), trialkylphosphine oxides (TRPO process), diisodecylphosphoric acid (DIDPA process) have been explored for the separation of trivalent actinides and lanthanides in first cycle [6, 7]. As an alternative to the organo phosphorous reagents mentioned in the above processes, which do not stick to the CHON principle, the malonamides and diglycolamide derivates have been extensively studied for the extraction of trivalent actinides and lanthanides, in first cycle. Recently, unsymmetrical diglycolamides (UDGA) were also developed and studied for the extraction of trivalent metal ions from nitric acid medium [8, 9]. Along with these, another class of extractants, namely *N,N,N',N'*-tetraalkyl-3,6-dioxaoctane diamide (DOODA), DOODA-C_8 and DOODA-C_{12} have been studied [10].

The mutual separation of lanthanides (Ln) and actinides (An) is a challenging task owing to the similarities in chemical and extraction properties of lanthanides and actinides. The methods developed so far for the Ln-An separation usually exploits the finer differences in the chemical behavior of lanthanides and actinides towards the various ligands. According to Pearson's hard-soft acid base theory [11, 12] An(III) preferred to form complexes with nitrogen based soft donor ligands over oxygen based ligands. Therefore, the An(III) can be held in aqueous phase using suitable complexing agents and the Ln(III) are extracted using a suitable extractant or vice versa. Several methods and materials have been reported in literature for lanthanide-actinide separation. For example, TALSPEAK (Trivalent Actinide – Lanthanide Separation by Phosphorus reagent Extraction from Aqueous Komplexes) process has been demonstrated successfully for lanthanide actinide separation. This process involves the selective separation of An(III) from lactate buffered diethylenetriaminepentaacetic acid (DTPA) solution using bis-(2-ethylhexyl)phosphoric acid (HDEHP) in 1,4-diisopropyl benzene [13]. The completely incenerable extractant Bis(2-ethylhexyl)diglycolamic acid (HDEHDGA) was studied for the extraction of Eu(III) and Am(III) from nitric acid medium by Suneesh *et al.* [14].

In contrast to the two-cycle approach, single-cycle methods have been receiving much attention in the recent past, for the separation of trivalent actinides directly from HLLW. The literature showed that there are two approaches available for the single cycle process. In one approach, actinides(III) can be directly extracted from PUREX raffinate by using the extractant consisting of soft donor ligands. For example, Kolarik *et al.* developed 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl) pyridines (named BTPs, Bis Triazine Pyridine) for the trivalent actinide – lanthanide separation [15]. Wilden *et al.* studied and demonstrated the 1-cycle SANEX process for direct selective separation of actinides(III) from PUREX raffinate by using a mixture of tetramethyl-5,6,7,8-tetrahydro-benzo-[1,2,4]–triazin-3-yl-[2,2']-bipyridine ($CyMe_4$ BTBP) and tetraoctyl-diglycolamide (TODGA) in a TPH/1-octanol solution [16].

Another approach deals with the extraction of both An(III) + Ln(III) from nitric acid medium by a suitable solvent. The selective separation of actinides(III) alone from the loaded organic phase can be achieved using a soft donor stripping agents [17, 18]. In this context, Lumetta *et al.* studied the extraction behavior of Am(III) and Eu(III) in a TRUSPEAK solvent formulation consisting of 0.1 M *n*-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) + 1 M bis(2-ethylhexyl)-phosphoric acid (HDEHP) in *n*-DD, from 1 M nitric acid medium [19]. The authors showed the selective stripping of actinides (III) from the loaded organic phase using an aqueous formulation composed of 0.05 M diethylenetriaminepentaacetic acid (DTPA) and 1.5 M citrate at pH 3.5. Similarly, Gannaz *et al.* studied the extraction of Eu(III) and Am(III) by a mixture of extractants consisting of a malonamide (DMDOHEMA) and di-*n*-hexylphosphoric acid (HDHP) [20]. Using the UDGA, *N*,*N*,-didodecyl-*N'*,*N'*-dioctyl-3-oxapentane-1,5-diamide (D^3DODGA) and di-2-ethylhexyl diglycolamic acid (HDEGDGA) reagents, a novel approach namely, SMART (Single-cycle process for Minor Actinide partitioning using completely incinerable ReagenTs), was developed by Ravi *et al.* for the separation of trivalent actinides in a single cycle method [21, 22]. Here, the recovery of Am(III) from the loaded organic phase was carried out by the optimized aqueous formulation composed of 0.01 M diethylenetriaminepentaacetic acid (DTPA) + 0.5 M citricacid (CA) at pH 1.5 [22]. Prasant *et al.* developed single cycle separation method by using the extractants such as tetra-bis(2-ethylhexyl)diglycolamide (TEHDGA) and bis(2-ethylhexyl)phosphoric acid (HDEHP); teraoctyl-diglycolammide (TODGA) and

HDEHP for minor actinide partitioning. Among these extractants, higher separation factor of Am(III) over Eu(III) was obtained by using TEHDGA and HDEHP. Synergistic extraction of Am(III) and Eu(III) was observed over a range of nitric acid concentrations (0.1 M to 4 M). The study also indicated the possibility of separating Am(III) from simulated high level liquid waste in a single processing cycle by using 0.1M TEHDGA-0.25M HDEHP/*n*-DD as solvent and 0.05 M DTPA-0.5 M citric acid at pH 3 as stripping formulation [23].

Industrially, the separations methods are being widely used in actinide partitioning are based on solvent extraction. Though the solvent extraction is a promising technique, it has some limitations such as, third phase formation and high solvent inventory [24]. To minimize these limitations solid phase extraction method was developed. In fact the solid phase extraction method (SPE) is an apt method for the separation of small quantities of trivalent actinides from a large volume of HLLW. Solid-phase extraction technique is a simple, rapid and low solvent inventory method, combines the selectivity of solvent extraction with the operational benefits of column chromatography [25]. Solid-phase extraction technique has been widely applied to the separation and pre-concentration of radionuclides from various matrices including biological and environmental samples [26, 27]. Horwitz *et al.* developed several extraction chromatographic resins and applied for the separation of actinides, fission products etc., from acidic media [28, 29]. It was showed that individual separation of tri-, tetra- and hexavalent actinides using CMPO-TBP impregnated resins from nitric and hydrochloric acid media. Similarly, Mathur *et al.* studied the extraction behavior of trivalent lanthanides and actinides using CMPO impregnated on chromosorb-102. The studies reported the separation of Am(III) + Ln(III), Pu(IV) and U(VI) from synthetic and actual PUREX raffinate using CMPO impregnated polymer [30]. The recovery of minor actinides from sulphate bearing actual high active waste was carried out by both solvent extraction and extraction chromatographic techniques using CMPO as extractant [31]. Diglycolamide (DGA) impregnated resins were also studied for the separation and pre-concentration of actinides from nitric acid medium [32]. Wei *et al.* and Zhang *et al.* studied the silica based extraction resins for the separation of minor actinides from high-level waste. The study involved the preparation of extraction chromatographic resins such as CMPO/SiO_2-P, HDEHP/SiO_2-P, Cyanex 301/SiO_2-P for the selective separation of Am(III) from Ln(III) [33, 34]. However, limited studies have been reported so far, for the single-cycle separation of actinides by solid-phase extraction technique.

In the present chapter, the extraction behavior of Am(III) and Eu(III) from nitric acid medium in a solvent impregnated resins containing either octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) or bis-(2-ethylhexyl)phosphoricacid HDEHP and a combination of CMPO and HDEHP extractants was studied. The distribution coefficient of Am(III) and Eu(III) was measured in various impregnated resins from different nitric acid concentrations and the mechanistic aspects of extraction was derived by using slope analysis of the extraction data. An attempt was made to develop a procedure for the mutual separation of Am(III) and Eu(III) by using the CMPO-HDEHP impregnated resins and citrate-buffered DTPA solution.

3.2. Extraction of Am(III) in HDEHP impregnated resins

The extraction behavior of Am(III) in 30% CMPO +10% HDEHP (named as combined resin) from nitric acid medium in the impregnated resin is shown in figure 3.1. To understand the role of these extractants in the combined resin, the extraction of behavior of Am(III) in the individual solvent impregnated resins namely 30% CMPO-impregnated resin or 10% HDEHP-impregnated resin was studied and the results are also shown in figure 3.1. It can be seen that the distribution coefficient of Am(III) in 10% HDEHP-impregnated resin decreased with increase in the concentration of nitric acid, as expected. The linear regression of the extraction data results in the slope of ~ 3, indicating that three H^+ ions are released for the extraction of a trivalent metal ion, Am(III), from nitric acid medium by the reaction represented in equation 3.1. This equation was also validated by measuring the distribution coefficient of Am(III) as a function of HDEHP concentration of the resin at 0.01 M nitric acid concentration. The results are presented in figure 3.2. It can be seen that the distribution coefficient of Am(III) increases with increase in the amount of HDEHP present in the resin. Linear regression analysis of the extraction data results in a slope of $\approx$ 3, indicating that 3 molecules of HDEHP are involved in the extraction of Am(III).

$$M^{3+}_{aq} + 3\overline{HDEHP} \Leftrightarrow \overline{M(DEHP)_3} + 3H^+_{aq} \qquad (3.1)$$

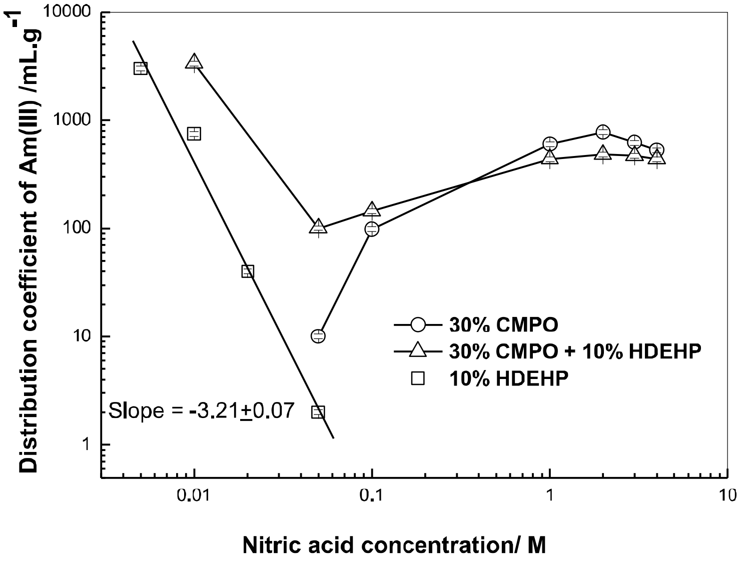


Figure 3.1. Variation of distribution coefficient of Am(III) as a function of nitric acid concentration. Resin = 30% CMPO/ADS 400 or 10% HDEHP/ADS 400 or 30%CMPO+10%HDEHP/ADS 400. Aqueous phase = HNO_3 from 0.01 M to 4 M.

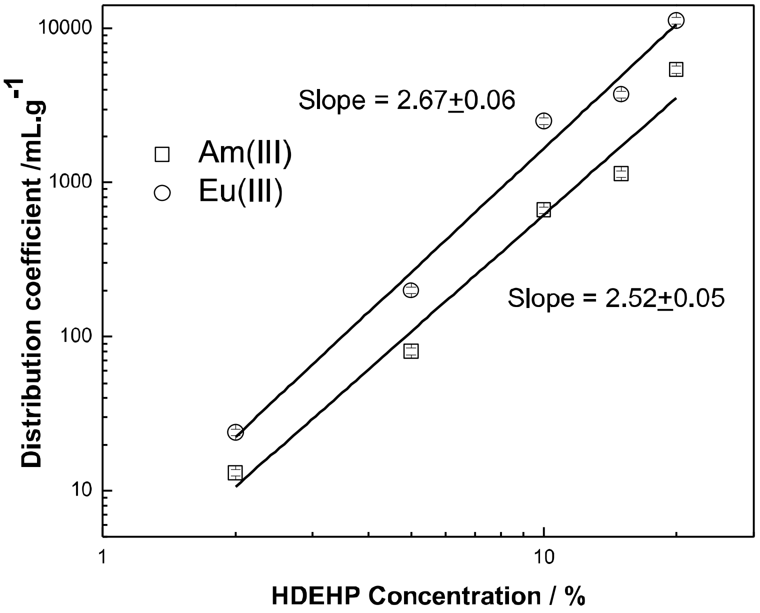


Figure 3.2. Dependence of distribution coefficient on the concentration of HDEHP in resin phase for the extraction of Am(III) and Eu(III) at 0.01 M HNO_3.

3.3. Extraction of Am(III) in CMPO impregnated resins

The extraction behavior of Am(III) in 30% CMPO impregnated resin is shown in figure 3.1. It can be seen that the distribution coefficient of Am(III) in the resin increases with increase in the concentration of nitric acid as expected for the extraction of trivalent metal ion in a solvent phase composed of a neutral extractant namely CMPO [6]. The distribution coefficient of Am(III) increases from 12 at 0.05 M nitric acid reaches the maximum value of ~ 900 at 2 M nitric acid. To obtain the number molecules of CMPO present in resin phase involved in the extraction of Am(III), the variation in the distribution coefficient of Am(III) was studied as a function of CMPO concentration in resin phase at 2 M nitric acid. The results are presented in figure 3.3.

It can be seen that the distribution coefficient of Am(III) increases with increase in concentration of CMPO. Linear regression of the extraction data results in a slope of 2, which is in good agreement with the results reported by others [35, 36]. This indicates that two molecules of CMPO are involved in the extraction of Am(III) from nitric acid medium, as shown in equation 3.2. However, the literature also indicates that the number of CMPO molecules involved in the complexation of trivalent metal ions could vary from 1 to 4 [37, 38].

$$\mathrm{M^{3+}_{aq} + 3NO^{-}_{3aq} + 2\overline{CMPO} \Leftrightarrow \overline{M(NO_3)_3(CMPO)_2}} \qquad (3.2)$$

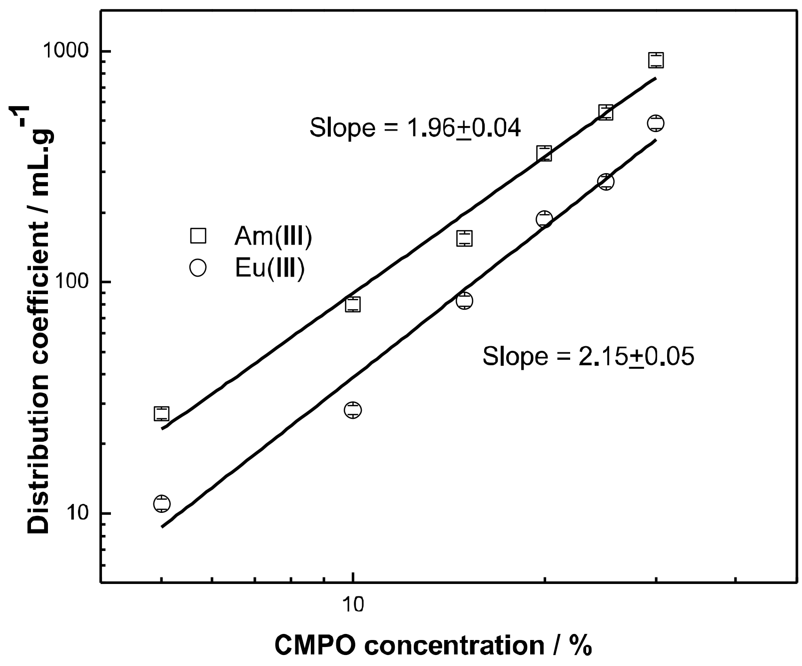


Figure 3.3. Dependence of distribution coefficient on the concentration of CMPO in resin phase for the extraction of Am(III) and Eu(III) at 2 M HNO_3.

3.4. Extraction of Am(III) in combined resin

The variation in the distribution coefficient of Am(III) in 30% CMPO+10% HDEHP impregnated resin is also shown in figure 3.1. It can be seen that the distribution coefficient of Am(III) decreases with increase in the concentration of nitric acid, results in a minimum value at 0.05 M nitric acid followed by increase in distribution coefficient. It is noted that the distribution coefficient of Am(III) in 30% CMPO + 10% HDEHP resin is much higher than those observed in 10% HDEHP resin at all acidities. In addition, the distribution coefficient of Am(III) observed in the combined resin (30% CMPO + 10% HDEHP) is higher than those observed in 30% CMPO resin at acidities lower than 0.5 M nitric acid. Above 0.5 M nitric acid, the distribution coefficient of Am(III) in the 30% CMPO + 10% HDEHP resin is lower than those observed in 30% CMPO resin. This indicates that extraction of Am(III) at lower nitric acid concentration (< 0.5 M) is governed by synergistic extraction and above 0.5 M the extraction is governed by antagonism. The synergistic extraction of metal ions in solvent extraction system containing both neutral and acidic extractants has been reported by others also [19, 23]. However, the antagonism observed in the present case is not common in the literature. Tkac *et al.* [37] reported that the addition of HDEHP to CMPO phase results in the formation of HDEHP-CMPO adduct and lowers the concentration of free-CMPO molecules available for extraction of metal ion. In view of this, the distribution ratio of Am(III) was reported to decrease to a significant extent especially at higher acidities and at higher HDEHP concentrations. Therefore, the antagonism observed in the present case could be due to the formation of HDEHP-CMPO adduct which seems to lower the concentration of free CMPO available for complexation of trivalent metal ion.

3.5. Extraction of Eu(III) in individual and combined resins

A similar synergistic extraction of Eu(III) is also observed in 30% CMPO +10% HDEHP impregnated resin, as shown in figure 3.4. Similar to Am(III) extraction, the extraction of Eu(III) in 10% HDEHP resin at various acidities results in a slope of -3 and the variation of HDEHP concentration at 0.01M nitric acid yields the slope value of ≈ 3 (Figure 3.2). About two molecules of CMPO are involved in the extraction of Eu(III) in 30% CMPO impregnated resin at 2 M nitric acid (Figure 3.3). Therefore, the mechanism of extraction indicated in equation 3.1 and 3.2 are also valid for Eu(III) extraction. Above 0.5 M nitric acid the extraction of Eu(III) in 30% CMPO + 10% HDEHP-impregnated resin is governed by antagonism.

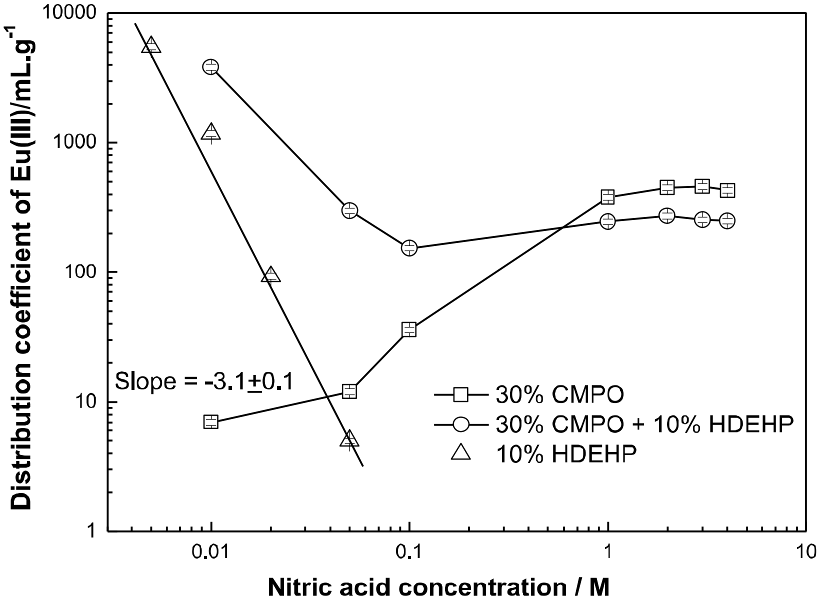


Figure 3.4. Variation of distribution coefficient of Eu(III) as a function of nitric acid concentration. Resin = 30% CMPO/ADS 400 or 10% HDEHP/ADS 400 or 30%CMPO+10%HDEHP/ADS 400. Aqueous phase = HNO_3 from 0.01 M to 4 M.

3.6. Extraction mechanism at 0.01 M nitric acid

To understand the behavior of Am(III) and Eu(III) extraction in the combined system namely 30% CMPO + 10% HDEHP impregnated resin, the variation of either CMPO or HDEHP in the combined resin was studied and the results are discussed below. The synergistic extraction of Am(III) and Eu(III) observed in 30%CMPO + 10% HDEHP resin at lower acidities shows that both CMPO and HDEHP could be participating in extraction. Therefore, the effect of loading of CMPO in CMPO + 10% HDEHP impregnated resin was studied at 0.01 M nitric acid and the results are shown in figure 3.5. It can be seen that increasing the loading of CMPO (in wt. %) increases the extraction of both Am(III) and Eu(III). Linear regression analysis of the extraction data results in a slope of 0.5. This indicates the participation of the neutral extractant CMPO even at lower nitric acid concentrations. Similarly, the dependence of HDEHP concentration in the extraction of Am(III) and Eu(III) at lower acid concentration in the 30% CMPO + HDEHP resin was studied and the results are shown in figure 3.6. The resin in this case contained a fixed concentration of CMPO (30 wt%) and different loading of HDEHP.

The results indicate that the distribution coefficient of Am(III) and Eu(III) increases with increase in the concentration of HDEHP. Linear regression of the extraction data results in a slope of 2.4 for Am(III) and 2.1 for Eu(III). It is important to note that the magnitude of slope obtained in this case (combined extraction system) is slightly lower than the slope (~ 2.5) reported in case of HDEHP impregnated resin (figure 3.2). This shows that the participation of HDEHP in the extraction of trivalent metal ion is lowered upon impregnation of CMPO along with HDEHP.

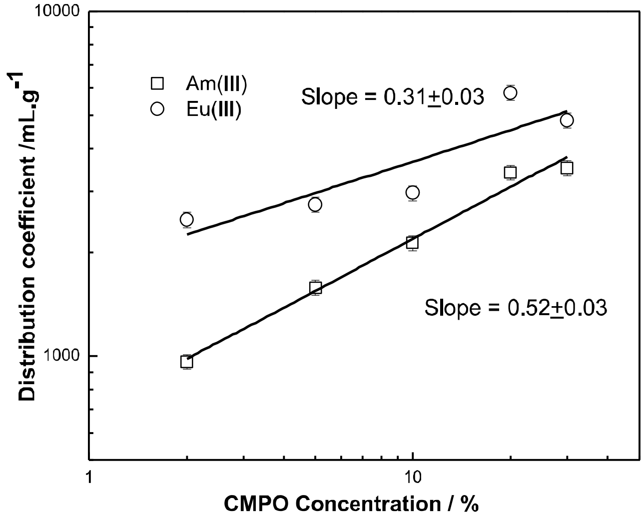


Figure 3.5. Dependence of distribution coefficient on the concentration of CMPO in resin phase for the extraction of Am(III) and Eu(III). Resin = CMPO + 10% HDEHP/ ADS 400. Aqueous phase = 0.01 M HNO_3.

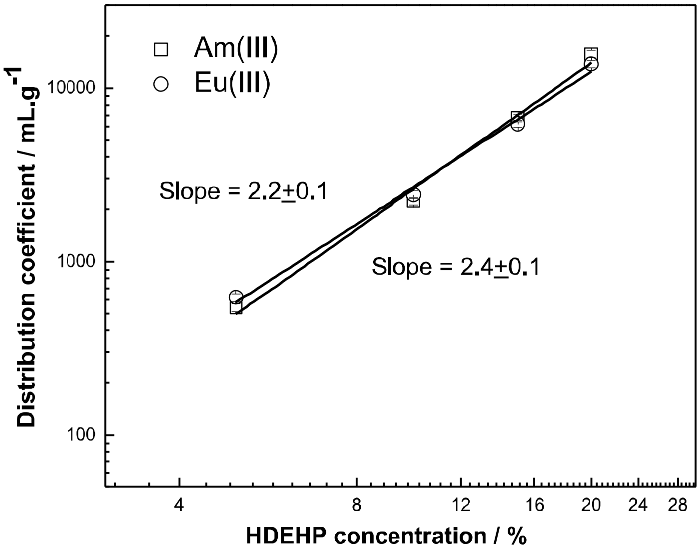


Figure 3.6. Dependence of distribution coefficient on the concentration of HDEHP in resin phase for the extraction of Am(III) and Eu(III). Resin= HDEHP + 30% CMPO/ ADS 400. Aqueous phase = 0.01 M nitric acid.

Perhaps this could be due to the participation of CMPO in the extraction of trivalent metal ions at lower acidities also. Therefore, the studies at lower acidities indicate that both CMPO and HDEHP participates in the extraction of Am(III) and Eu(III) resulting in synergistic extraction of these metal ions in the combined extractant impregnated resin.

3.7. Extraction mechanism at 2 M nitric acid

To understand the role of CMPO and HDEHP at higher nitric acid concentration where antagonism (~ 2 M HNO3) is observed, the effect of CMPO concentration on the extraction of Am(III) and Eu(III) in the CMPO + 10% HDEHP impregnated resin was studied. The concentration of CMPO in the resin was varied from 2wt.% to 20 wt.% at a constant loading of 10 wt% HDEHP in the resin. The results on the variation of the distribution coefficient of Am(III) and Eu(III) as a function of concentration of CMPO is shown in figure 3.7. It can be seen that the distribution coefficient of Am(III) and Eu(III) increases with increase in the concentration of CMPO. Linear regression of the extraction data results in a slope of ~ 2. This value compares well with the slope obtained in case CMPO alone impregnated resin (Figure 3.3). This shows that two molecules of CMPO are involved in the extraction of trivalent metal ion similar to the mechanism shown in equation (3.2).

Similarly the dependency of HDEHP concentration on the extraction of Am(III) and Eu(III) in the combined extractant impregnated resin was studied and the results on the variation of distribution coefficient of Am(III) and Eu(III) as a function of HDEHP concentration is shown in figure 3.8. The concentration of HDEHP was varied from 5 wt.% to 20 wt.% in the resin at a fixed loading of 30 wt% CMPO. It is interesting to note that the distribution coefficient of both Am(III) and Eu(III) decreases with increase in the concentration of HDEHP in resin. This indicates that HDEHP exhibits the role of antagonism in the combined extractant impregnated resin. Based on the above studies, the mechanism of trivalent metal ion extraction in the combined extractant impregnated resin at lower acidities (< 0.5M) can be given by equation 3.3.

$$\mathrm{M^{3+}_{aq}} + (3-\mathrm{x})\mathrm{NO^{-}_{3aq}} + \mathrm{x}\overline{\mathrm{HDEHP}} + (2-\mathrm{y})\overline{\mathrm{CMPO}} \Leftrightarrow \overline{\mathrm{M(NO_3)_{3-x}(DEHP)_x(CMPO)_{2-y}}} + \mathrm{xH^{+}_{aq}} \quad (3.3)$$

where x=0 to 3 and y=0 to 2

It should be noted that this equation is applicable only below 0.5M nitric acid where synergic extraction of Am(III) and Eu(III) is observed (see figures 3.1 and 3.4). Above synergic region (above 0.5M nitric acid), the extraction is governed by antagonism and HDEHP does not participate in the extraction. Under such condition only CMPO is responsible for extraction and the mechanism shown in eqation 3.2 is applicable.

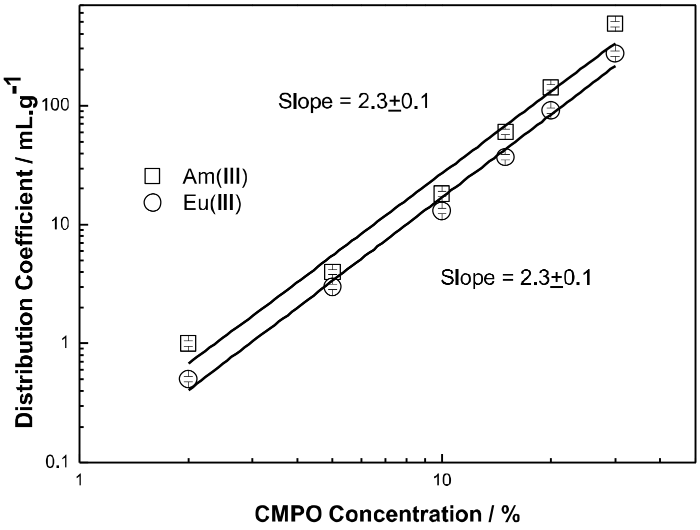


Figure 3.7. Dependence of distribution coefficient on the concentration of CMPO in resin phase for the extraction of Am(III) and Eu(III). Resin = CMPO + 10% HDEHP/ ADS 400. Aqueous phase = 2 M HNO$_3$

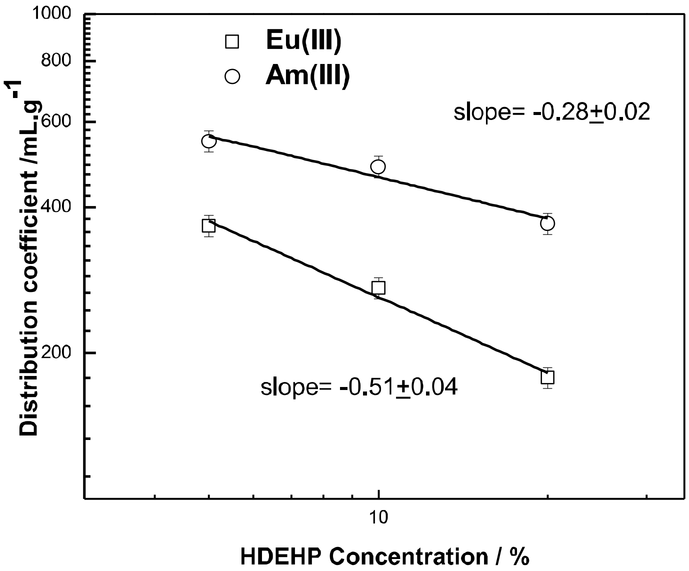


Figure 3.8. Dependence of distribution coefficient on the concentration of HDEHP in resin phase for the extraction of Am(III) and Eu(III). Resin= HDEHP + 30% CMPO/ ADS 400. Aqueous phase = 2 M nitric acid.

It is clear from the above discussion that the extraction of Am(III) from nitric acid medium is accompanied by the co-extraction of Eu(III), if present along with Am(III) in aqueous waste. The high-level liquid waste contains not only Eu(III) but also other trivalent lanthanides coexisting together with Am(III). Therefore, it is quite likely that the lanthanides are also extracted along with Am(III). However, it was necessary to separate the lanthanides from actinides prior to transmutation, since the lanthanides act as neutron poisons that reduces the efficiency of transmutation. Therefore, an attempt was made to separate these lanthanides from actinides by using aqueous soluble complexing agents, such as diethylenetriaminepentaacetic acid (DTPA) and citric acid (CA). These reagents are well known in literature as they are employed for the mutual separation of lanthanides and actinides.

Addition of these reagents to aqueous phase facilitates the retention of trivalent actinides much more than lanthanides facilitating the extraction of lanthanides in organic phase. The results on the extraction of Am(III) and Eu(III) from the aqueous solution containing various concentration of DTPA and citric acid are shown in table 3.1. It can be seen that the distribution coefficient of Am(III) and Eu(III) decreases with increase in pH of aqueous phase, perhaps due to the retention of both Am(III) and Eu(III) in aqueous phase. However, the separation factor (SF) remains nearly constant ranging from 3 to 5 in the pH range 2 to 3. A SF of 4 is obtained at pH 3 condition that employs 0.001 M DTPA+0.1 M CA in aqueous phase. Previously, Prasant et al. reported a separation factor of ~ 10 for the selective recovery of Am(III) from the loaded organic phase in SMART approach [22]. Lumetta et al. [17] reported a separation factor of ~ 30 for the selective recovery of Am(III) in ALSEP process. Even though the separation factor achieved in the present case is less, the study shows the possibility of separating Am(III) from Eu(III) from nitric acid medium by column chromatographic mode.

Table 3.1. Extraction of Am(III) and Eu(III) from the aqueous solution containing various concentration of DTPA and citric acid

pH	10% HDEHP+30% CMPO stripping with 0.005 M DTPA+0.1 M CA			10% HDEHP+ 30% CMPO stripping with 0.001 M DTPA+0.1 M CA			20% HDEHP+ 30% CMPO stripping with 0.001 M DTPA+ 0.1 M CA		
	$D_{Am(III)}$	$D_{Eu(III)}$	S.F.= $D_{Eu(III)}/D_{Am(III)}$	$D_{Am(III)}$	$D_{Eu(III)}$	S.F.= $D_{Eu(III)}/D_{Am(III)}$	$D_{Am(III)}$	$D_{Eu(III)}$	S.F.= $D_{Eu(III)}/D_{Am(III)}$
1.5	81	127	1.56	113	185	1.63	383	731	1.90
2	12	48	4	41	132	3.21	192	746	3.88
2.5	2	7	3.5	6	29	4.83	42	173	4.11
3	1	5	5	2	8	4	17	63	3.70

3.9. Conclusion

Solvent impregnated resins containing extractants such as CMPO or HDEHP or mixture of extractants CMPO + HDEHP in an acrylic polymer matrix was prepared and studied for the extraction of Am(III) and Eu(III) over a range of nitric acid concentration. The effect of various parameters such as concentration of nitric acid in aqueous phase and the concentration of CMPO and HDEHP in the resin phase was studied. The distribution coefficient of Am(III) and Eu(III) in HDEHP-impregnated resin decreased with increase in the concentration of nitric acid. The distribution coefficient of Am(III) and Eu(III) in CMPO-impregnated resin increased with increase in the concentration of nitric acid as expected for the extraction of trivalent metal ion in a solvent phase composed of a neutral extractant. The effect of loading of CMPO and HDEHP in CMPO + HDEHP impregnated resin was studied at 0.01 M and 2 M nitric acid. Slope analysis of the extraction data indicates that extraction is predominantly governed by HDEHP at low nitric acid concentrations and by CMPO at higher acidities with the involvement of two CMPO and three HDEHP molecules during extraction

In a combine system, synergistic extraction was observed at lower nitric acid concentration and antagonism at higher nitric acid concentration. The dependence of concentration of HDEHP decreased and that of CMPO increased with increase in the concentration of nitric acid. The antagonism observed in the present case could be due to the formation of HDEHP-CMPO adduct that seems to lower the concentration of free CMPO available for complexation of trivalent metal ion. The studies confirmed the involvement of both the CMPO and HDEHP in extraction at all acidities investigated in the present study. Separation of Eu(III) over Am(III) was studied with aqueous soluble complexing agents, such as diethylenetriaminepentaacetic acid (DTPA) and citric acid (CA). Various concentrations of DTPA and citric acid were studied for the extraction of Am(III) and Eu(III). The separation factor increased with increase of pH of stripping solution. A SF of 4 is obtained at pH 3 condition that employs the 0.001 M DTPA+0.1 M CA composition.

3.10. References

1. A. A. Kakodkar, Nuclear power in India: An inevitable option for sustainable development of as sixth humanity, World Nuclear Association Annual Symposium, London (2002).
2. J. L. Swanson, "PUREX Process Flowsheets". In: Science and Technology of Tributyl phosphate, Eds. W. W. Schulz, L. L. Burger, J. D. Navratil, K. P. Bender, CRC Press Inc. Boca Raton (1984) 55.
3. P. A. Baisden, G. R. Choppin, Nuclear waste management and the nuclear fuel cycle, Radiochemistry and Nuclear Chemistry, Encyclopedia of Life Support Systems (EOLSS), (S. Nagyl, ed.) Eolss Publishers, Oxford, UK (2007).
4. S. Bourg, C. Hill, C. Caravaca, C. Rhodes, C. Ekberg, R. Taylor, A. Geist, G. Modolo, L. Cassayre, R. Malmbeck, M. Harrison, G. Angelis, A. Espartero, S. Bouvet, N. Ouvrier, ACSEPT—Partitioning technologies and actinide science: towards pilot facilities in Europe, Nucl.Eng. Des., 241 (2011) 3427.
5. J. Magill, V. Berthou, D. Haas, J. Galy, R. Schenkel, H. Wiese, G. Heusener, J. Tommasi, G. Youinou, Impact limits of partitioning and transmutation scenarios on the radiotoxicity of actinides in radioactive waste, Nucl. Energy, 42 (2003) 263.
6. J. N. Mathur, M. S. Murali, K. L. Nash, Actinide partitioning – a review, Solvent Extr. Ion Exch., 19 (2001) 357-390.
7. S. A. Ansari, P. N. Pathak, P. K. Mohapatra, V. K. Manchanda, Aqueous partitioning of minor actinides by different processes, Sep. Purif. Rev., 40 (2011) 43-76.

8. R. B. Gujar, S. A. Ansari, P. K. Mohapatra, V. K. Manchanda, Development of T2EHDGA based process for actinide partitioning. Part I: batch studies for process optimization, Solvent Extr. Ion Exch., 28 (2010) 350–366.
9. J. Ravi, K. A. Venkatesan, M. P. Antony, T. G. Srinivasan, P. R. Vasudeva Rao, New unsymmetrical digycolamide ligands for trivalent actinide separation, Radiochim. Acta, 102 (2014) 609-617.
10. Y. Sasaki, Y. Morita, Y. Kitatsuji, T. Kimura, Extraction Behavior of Actinides and Metal Ions by the Promising Extractant, N,N,N',N'-Tetraoctyl-3,6-dioxaoctanediamide (DOODA), Solvent Extr. Ion Exch., 28 (2010) 335-349.
11. R. G. Pearson, Hard and Soft acids and bases, J. Am. Chem. Soc., 85 (1963) 3533-3539.
12. G. R. Choppin, M. P. Jensen, Actinides in Solution: Complexation and Kinetics, In The Chemistry of the Actinides and Trans actinide Elements, 3rd Ed.; L.R. Morss, N.M. Edelstein, and J. Fuger, eds., Springer, Dordrecht, 23 (2006) 2561-2563.
13. M. Nilsson, K. L. Nash, A review of the development and operational characteristics of the TALSPEAK process, Solvent Extr. Ion Exch., 25 (2007) 665–701.
14. A. S. Suneesh, K. A. Venkatesan, K. V. Syamala, M. P. Antony and P. R. Vasudeva Rao, Mutual separation of americium(III) and europium(III) using glycolamic acid and thioglycolamic acid, Radiochim. Acta, 100 (2012) 425-430.

15. Z. Kolarik, U. Mullich, F. Gassner, Selective extraction of Am(III) over Eu(III) by 2,6-ditriazolyl- and 2,6-ditriazinylpyridines, Solvent Extr. Ion Exch., 17 (1999) 23-32.
16. A. Wilden, G. Modolo, C. Schreinemachers, F. Sadowski, S. Lange, M. Sypula, D. Magnusson, A. Geist, F. W. Lewis, L. M. Harwood, M. J. Hudson, Direct selective extraction of actinides(III) from PUREX raffinate using a mixture of CyMe4BTBP and TODGA as 1-cycle SANEX solvent Part III: Demonstration of a laboratory-scale counter-current centrifugal contactor process, Solvent Extr. Ion Exch., 31 (2013) 519–537.
17. G. J. Lumetta, A. V. Gelis, F. Vandegrift, Solvent systems combining neutral and acidic extractants for separating trivalent lanthanides from the transuranic elements, Solvent Extr. Ion Exch., 28 (2010) 287–312.
18. P. K. Nayak, R. Kumaresan, K. A. Venkatesan, M. P. Antony, P. R. Vasudeva Rao, A new method for partitioning of trivalent actinides from high-level liquid waste, Sep. Sci. Technol., 48 (2013) 1409–1416.
19. G. J. Lumetta, J. C. Carter, A. V. Gelis, G. F. Vandegrift, Combining octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide and bis-(2-ethylhexyl)phosphoric acid extractants for recovering transuranic elements from irradiated nuclear fuel, In: C. M. Wai, B. J. Mincher (Eds.), Nuclear Energy and the Environment, ACS Symposium Series 1046 (2010), American Chemical Society, Washington, DC, 107.
20. B. Gannaz, R. Chiarizia, R. K. Antonio, C. Hill, G. Cote, Extraction of lanthanides(III) and Am(III) by mixtures of malonamide and dialkylphosphoric acid, solvent Extr. Ion Exch., 25 (2007) 313-337.

21. J. Ravi, K. A. Venkatesan, M. P. Antony, T. G. Srinivasan, and P. R. Vasudeva Rao, Single-cycle method for partitioning of trivalent actinides using completely incinerable reagents from nitric acid medium, Radiochim. Acta, 102 (2014) 599-607.
22. P. K. Nayak, R. Kumaresan, S. Chaurasia, K. A. Venkatesan, G. G. S. Subramanian, T. Prathibha, K. V. Syamala, B. Robert Selvan, S. Rajeswari, M. P. Antony, P. R. Vasudeva Rao, Studies on the feasibility of using completely incinerable reagents for the single-cycle separation of americium(III) from simulated high-level liquid waste, Radiochim. Acta, 103 (2015) 265–275.
23. P. K. Nayak, R. Kumaresan, K. A. Venkatesan, S. Rajeswari, G. G. S. Subramanian, M. P. Antony, P. R. Vasudeva Rao, Single-cycle separation of americium (III) from simulated high level liquid waste using tetra-bis (2-ethylhexyl) diglycolamide and bis (2-ethylhexyl) phosphoric acid solution, J. Environ. Chem. Eng., 1 (2013) 559.
24. P. R. Vasudeva Rao, Z. Kolarik, A review of third phase formationin extraction of actinides by neutral organo-phosphorus extractants, Solvent Extr. Ion Exch., 14 (1996) 955–993.
25. E. Philip Horwitz, D. R. McAlister, M. L. Dietz, Extraction chromatography versus solvent extraction: how similar are they, Sep. Sci. Technol., 41 (2006) 2163–2182.
26. R. Rodriguez, J. Avivar, L. O. Leal, V. Cerda, L. Ferrer, Strategies for automating solid-phase extraction and liquid-liquid extraction in radiochemical analysis, TrAC Trend. Analyt. Chem., 76 (2016) 145.

27. E. Philip Horwitz, R. Chiarizia, M. L. Dietz, H. Diamond, D. M. Nelson, Separation and preconcentration of actinides from acidic media by extraction chromatography, Anal. Chem. Acta, 281 (1993) 361.
28. M. L. Dietz, E. Philip Horwitz, A. H. Bond, Extraction Chromatography: progress and opportunities. In: Metal Ion Separation and Preconcentration: Progress and Opportunities, A. H. Bond, M. L. Dietz, R. D. Rogers, Eds., American Chemical Society:Washington, DC (1999) 234–250.
29. E. Philip Horwitz, R. Chiarizia, M. L. Dietz, A novel strontium-selective extraction chromatographic resin, Solvent Ext. Ion Exch., 10 (1992) 313-336.
30. J. N. Mathur, M. S. Murali, R. H. Iyer, A. Ramanujam, P. S. Dhami, V. Gopalakrishnan, M. K. Rao, L. P. Badheka, A. Banerji, Extraction chromatographic separation of minor actinides from PUREX high-level wastes using CMPO, Nuclear Technol., 109 (1995) 216–225.
31. V. Gopalakrishnan, P. Dhami, A. Ramanujam, M. Krishna, M. Murali, J. N. Mathur, R. Iyer, A. Bauri, A. Banerji, Extraction and extraction chromatographic separation of minor actinides from sulphate bearing high level waste solutions using CMPO, J. Radioanal. Nucl. Chem., 191 (1995) 279–289.
32. E. Philip Horwitz, D. R. McAlister, A. H. Bond, R. E. Barrans, Novel extraction of chromatographic resins based on tetraalkyldiglycolamides: Characterization and Potential Applications, Solvent Extra. Ion Exch., 23 (2005) 319-344.

33. A. Zhang, Q. Hu, W. Wang, E. Kuraok, Application of a macroporous silica-based CMPO-impregnated polymeric composite in group partitioning of long-lived minor actinides from highly active liquid by extraction chromatography, Ind. Eng. Chem. Res., 47 (2008) 6158–6165.

34. Y. Wei, M. Kumagai, Y. Takashima, G. Modolo, R. Odoj, Studies on the separation of minor actinides from high-level wastes by extraction chromatography using novel silica-based extraction resins, Nuclear Technol., 132 (2000) 413-423.

35. C. Z. Wang, W. Q. Shi, J. H. Lan, Y. L. Zhao, Y. Z. Wei, Z. F. Chai, Complexation behavior of Eu(III) and Am(III) with CMPO and Ph_2CMPO ligands: insights from density functional theory, Inorg. Chem., 52 (2013) 10904–10911.
36. L. Rao, Y. Xia, B. M. Rapko, P. F. Martin, Synergistic extraction of Eu(III) and Am(III) by thenoyltrifluoroacetone and neutral donor extractants: (Carbamoylmethyl) phosphine oxide and 2,6-bis((diphenylphosphino)methyl) pyridine N,P,PTrioxide, Solvent Extr. Ion Exch., 16 (1998) 913–929.
37. P. Tkac, G. F. Vandegrift, G. J. Lumetta, A. V. Gelis, Study of the interaction between HDEHP and CMPO and its effect on the extraction of selected lanthanides, Ind. Eng. Chem. Res., 51 (2012) 10433-10444.

38. S. Belair, A. Labet, C. Mariet, P. Dannus, Modeling of the extraction of nitric acid and neodymium nitrate from aqueous solutions over a wide range of activities by CMPO, Solvent Extr. Ion Exch., 23 (2005) 481–499.

CHAPTER 4

Chapter 4: Extraction behavior of Am(III) and Eu(III) from nitric acid medium in TEHDGA-HDEHP impregnated resins

4.1. Introduction

The current approach for partitioning of trivalent actinides from High-Level Liquid Waste (HLLW) is a two-cycle approach [1, 2], namely, the group separation i.e., the separation of trivalent actinides along with lanthanides from HLLW, followed by the mutual separation of lanthanides and actinides. Thus, the extractants such as CMPO, DGA and malonamides have been proposed for group separation (i.e. step 1) [3-11] and extractants such as bis(2-ethylhexyl)phosphoric acid (HDEHP), bis-triazinylpyridine (BTP) have been proposed for lanthanide-actinide separation (i.e. step -2) [12, 13]. In the recent past, a single-cycle process has been developed by combining two or more extractants in a single solvent formulation to achieve extraordinary extraction as well as to develop a simple processing method for minor actinide partitioning [14-20]. The details were discussed in the previous chapter. The methods most of them explained in literature are based on solvent extraction. However, the use of solid sorbent materials as an alternative to solvent extraction. Applications and advantages [21-27] of solid phase extraction were given in previous chapter in detail.

The alkyl derivatives of diglycolamides (DGAs) are being regarded as promising reagents for the separation of trivalent actinides and lanthanides from nitric acid medium [28-31]. The exceptional feature in DGA responsible for efficient extraction of trivalents is the etheric oxygen present between the two amidic moieties. This feature facilitates the DGA molecule to form a stable tridentate coordination with metal ions during extraction [32]. Therefore, it is quite likely that substituting DGAs in place of CMPO in a single cycle method could improve the extraction of Am(III) and Eu(III).

In view of this, the present chapter deals with the extraction behavior of Am(III) and Eu(III) from nitric acid medium in the solvent impregnated resins consisting of either tetra-bis(2-ethylhexyl)diglycolamide (TEHDGA) or bis(2-ethylhexyl)-phosphoric acid (HDEHP), or a combination of both TEHDGA + HDEHP extractants. The distribution coefficient of Am(III) and Eu(III) was measured in these resins over a range of nitric acid concentration. The rate of extraction of Am(III) and Eu(III) in the TEHDGA + HDEHP impregnated resin was studied. The mechanistic aspect of extraction was probed from the slope analysis of the extraction data. Studies were also carried out for the separation of trivalent lanthanides and actinides from fast reactor simulated high-level liquid waste (FR-SHLLW) solution. The feasibility of adopting the single-cycle separation was examined by determining the separation factor of Am(III) over Eu(III) by using a stripping formulation containing diethylenetriaminepentaacetic acid (DTPA) and citric acid (CA) at pH 3.

4.2. Kinetics of extraction

The rate of uptake of Am(III) and Eu(III) in the 30% TEHDGA +10% HDEHP impregnated resin was studied at 1 M nitric acid concentration. The results are shown in figures 4.1 and 4.2.

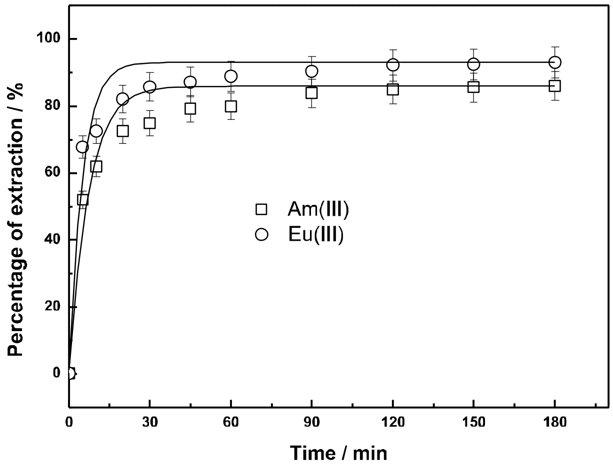


Figure 4.1. Variation in the percentage extraction of Eu(III) and Am(III) as a function of time, fitted by using pseudo-first order rate equation. Resin phase= 10% HDEHP + 30% TEHDGA – impregnated resin (0.05 g), Aqueous Phase= 1 M HNO$_3$ (5 mL) spiked with $^{(152+154)}$Eu(III) or ^{241}Am(III) tracer.

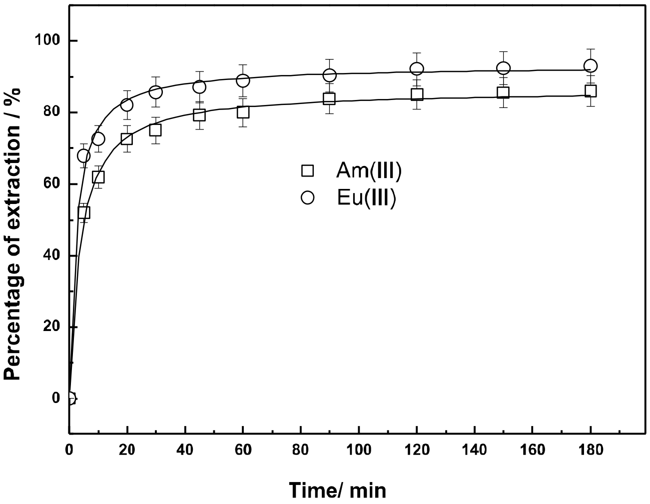


Figure 4.2. Variation in the percentage extraction of Eu(III) and Am(III) as a function of time, fitted by using pseudo-second order rate equation. Resin phase= 10% HDEHP + 30% TEHDGA – impregnated resin (0.05 g), Aqueous Phase= 1 M HNO$_3$ (5 mL) spiked with $^{(152+154)}$Eu(III) or ^{241}Am(III) tracer.

Rapid uptake of Am(III) and Eu(III) in the initial stages of equilibration followed by the establishment of equilibrium occurring in 100 min was observed. Therefore, for all batch studies, the equilibration experiments were carried out for 180 min to ensure the establishment of equilibrium. A couple of models have been considered for fitting the kinetics of extraction. They are the pseudo-first order model shown in equation 4.1 and the pseudo-second order model shown in equation 4.2. The rate of extraction of Am(III) and Eu(III) ion in the resin phase (mmol.g^{-1}) is directly proportional to the concentration of "free" sites, q_{free}, available for extraction.

$$\frac{dq_t}{dt} = k_1\, q_{free} \tag{4.1}$$

or

$$\frac{dq_t}{dt} = k_2\, q_{free}^2 \tag{4.2}$$

where q_t is the amount of metal ion extracted at time t (in mmol.g^{-1}), q_{free} is the "free sites"available for extraction (in mmol.g^{-1}), k_1 and k_2 are the pseudo-first order and pseudo second order rate constants, respectively. The q_{free} can be tacitly related to the amount of metal ions extracted at equilibrium by equation 4.3.

$$q_{free} = q_e - q_t \tag{4.3}$$

where, q_e is the amount of metal ion extracted at equilibrium (in mmol.g^{-1}). Substituting the equation 4.3 in equation 4.1, results in equation 4.4.

$$\frac{dq_t}{dt} = k_1\left(\mathrm{q_e} - \mathrm{q_t}\right) \tag{4.4}$$

Integrating the equation 4.4 between the limits = 0 to t q_t = 0 to q_t results in the Lagregren equation of the form shown in equation 4.5

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{4.5}$$

Similarly, q_{free} substituting in equation 4.2 and upon integration results in the pseudo second order equation of the form shown in equation 4.6.

$$q_t = \frac{q_e^2 \, \mathrm{k}_2 \, \mathrm{t}}{1 + \mathrm{q}_e \, \mathrm{k}_2 \, \mathrm{t}} \qquad (4.6)$$

The rate constants k_1 and k_2 can be determined by non linear regression of the experimental data using equation 4.5 and 4.6. The fitting of the kinetic data using equation 4.5 is shown in figure 4.1, and that using equation 4.6 is shown in figure 4.2. It can be seen that the kinetic data were described well by the pseudo second order rate equation 4.6 (Figure 4.2). The fitting constants and statistical parameters are tabulated in table 4.1.

Table 4.1. Fitting Constants and the statistical parameters obtained for the rate of extraction of Am(III) and Eu(III) in TEHDGA+HDEHP- impregnated resin

Metal ion	k_1/ min^{-1}.			k_2/ L.mol^{-1}.min^{-1}.		
	1 M HNO_3	χ^2	R^2	1 M HNO_3	χ^2	R^2
Am(III)	0.139	33.26	0.94	3.1×10^{-3}	2.32	0.996
Eu(III)	0.205	33.7	0.95	4.7×10^{-3}	4.82	0.993

Chi-Square goodness of fit test is a non-parametric test that is used to find out how the observed value of a given phenomena is significantly different from the expected value. In this test, the term goodness of fit is used to compare the observed sample distribution with the expected probability distribution. R^2 is a statistical measure of how close the data are to the fitted regression line. it is the percentage of the response variable variation that is explained by a linear model. R^2 is always between 0 and 100%. In general, the higher the R^2, the better the model fits the data.

It can be seen that the rate constant is more for Eu(III) as compared to Am(III) uptake. This is characteristic to the oxygen donor ligands such as diglycolamides [10] and HDEHP, which coordinates better with hard acid metal ions such as Eu(III) as compared to Am(III). Horwitz *et al.* [26] studied the kinetics of uptake of Eu(III) in 40 wt% TODGA impregnated resin and reported that the equilibrium was achieved within 10 min. Similarly, Van Hecke and Modolo [27] studied the rate of uptake of Am(III) and Eu(III) in 13 wt% TODGA impregnated resin. The equilibrium was achieved within 10 min of equilibration.

4.3. Extraction of Am(III) in TEHDGA impregnated resin

The extraction behavior of Am(III) in the combined resin (30% TEHDGA +10% HDEHP) was studied as a function of nitric acid concentrations. To understand the role of TEHDGA and HDEHP in the combined resin, the extraction of Am(III) was carried out in the resins containing either TEHDGA or HDEHP. The extraction of Am(III) in 30% TEHDGA-impregnated resin was studied over a range of nitric acid concentration (0.01 M to 3 M). The variation in the distribution ratio of Am(III) as a function of nitric acid concentration is shown in figure 4.3. It is observed that the distribution coefficient increased with increase in concentration of nitric acid as expected for a neutral extractant. The $D_{Am(III)}$ value of 3.6 and 2100 was obtained at 0.01 and 3 M nitric acid, respectively. A similar extraction trend was reported by Horwitz *et al.* [26] for the extraction of Am(III) from nitric acid medium in 40% (wt/wt) TODGA and TEHDGA impregnated Amberchrom CG-71 resins. Among these resins, TODGA-impregnated resins showed higher distribution coefficients as compared to TEHDGA impregnated resins. However, the differences in extraction were minimal at higher nitric acid concentration. The reason for the higher distribution ratio of trivalent metal ions achieved in TODGA was reported to be due to suitable conformational orientation of TODGA for efficient coordination with trivalent metal ions [33]. The extraction of Am(III) and Eu(III) in 30% CMPO impregnated in Tulsion ADS 400 polymers was reported in the previous chapter. Higher distribution coefficient of Am(III) observed in TEHDGA-impregnated resin as compared to CMPO-impregnated resins is due to the tridendate coordination of TEHDGA with Am(III) during extraction. In order to understand the number of molecules of TEHDGA are involved in the extraction of Am(III), the loading of TEHDGA in the resin phase was varied and the extraction of Am(III) was studied from 3 M nitric acid medium. Figure 4.4 displays the variation in the $D_{Am(III)}$ as a function of TEHDGA concentration. It can be seen that $D_{Am(III)}$ increases with increase in concentration of TEHDGA in resin phase. Linear regression of the extraction data results in a slope value of ~1.5. This indicates that one to two molecules of TEHDGA on an average are involved in the extraction of Am(III) from nitric acid medium. As TEHDGA is a neutral extractant, the extraction of Am(III) from nitric acid medium can be represented by the equilibrium expression shown in equation 4.7. The “bar” and “aq” in equation 4.7 indicates the molecule is in the resin phase and aqueous phase, respectively. The literature suggests that the number of TEHDGA molecules involved in the co-ordination with trivalent metal ions could vary from 1 to 4 [10], depending upon the polarity of the diluent and steric hindrance of the substituents, etc.,present in the diglycolamide molecule and medium.

$$M^{3+}_{aq} + 3NO^{-}_{3aq} + (1-2)\overline{TEHDGA} \Leftrightarrow \overline{M(NO_3)_3(TEHDGA)_{1-2}} \qquad (4.7)$$

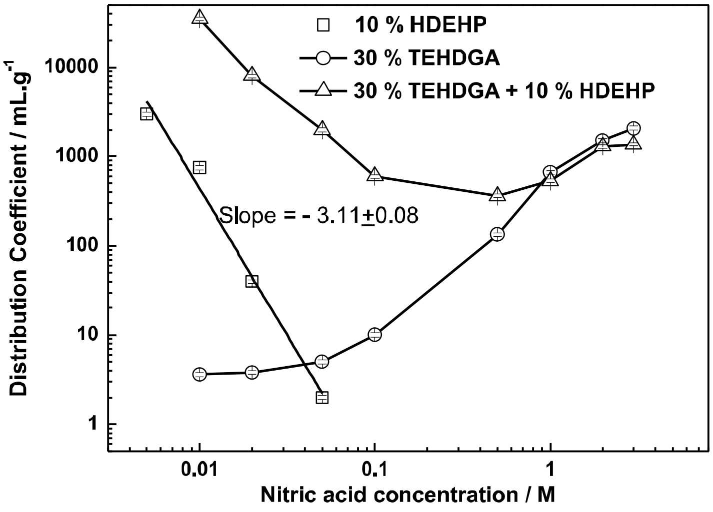


Figure 4.3. Variation in the distribution coefficient of Am(III) as a function of nitric acid concentration. Resin = 30%TEHDGA/ADS 400 or 10%HDEHP/ADS 400 or 30%TEHDGA+10%HDEHP/ADS 400. Aqueous phase = nitric acid from 0.01 M to 3 M.

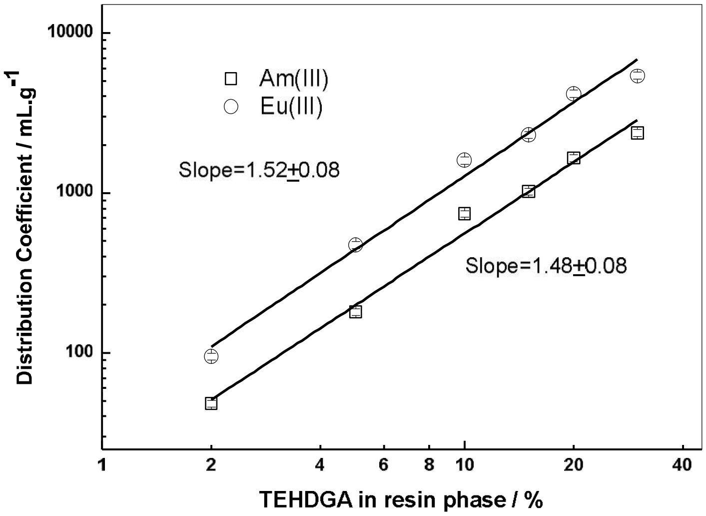


Figure 4.4. Dependence of distribution coefficient on the concentration of TEHDGA in resin phase for the extraction of Am(III) and Eu(III) at 3 M nitric acid concentration. Resin= TEHDGA/ADS 400.

4.4. Extraction of Am(III) in HDEHP impregnated resin

Similar to the extraction insights observed in TEHDGA impregnated resin, it is necessary to understand the extraction behavior of Am(III) in HDEHP-impregnated resin. The variation in the distribution coefficient of Am(III) as a function of nitric acid concentration in 10% HDEHP impregnated resin is shown in figure 4.3. As HDEHP is an acidic extractant, the distribution coefficient of Am(III) decreases with increase in the concentration of nitric acid, reached a minimum value of 2 at 0.1 M nitric acid concentration. Linear regression of the extraction data resulted in a slope of three indicating that three H^+ ions were released for the extraction of Am(III) during the extraction of trivalent metal ions as indicated in equation 4.8.

$$M^{3+}_{aq} + 3\overline{HDEHP} \Leftrightarrow \overline{M(DEHP)_3} + 3H^{+}_{aq} \qquad (4.8)$$

4.5. Extraction of Am(III) in 30%TEHDGA + 10%HDEHP (combined) impregnated resin

Figure 4.3 shows the variation in the distribution ratio of Am(III) in the combined resin (30% TEHDGA + 10% HDEHP impregnated resin) as a function of concentration of nitric acid. It can be seen that the distribution coefficient of Am(III) decreases with increase in the concentration of nitric acid, reaches a minimum value of distribution coefficient at 0.5 M nitric acid followed by increase in distribution coefficients. The trend observed in the combined system indicates that HDEHP seems to control the distribution coefficient of Am(III) at lower nitric acid concentration and TEHDGA governs at higher nitric acid concentration. At lower nitric acid concentration range (0.01 M to 0.5 M), the distribution coefficient of Am(III) obtained in 30% TEHDGA + 10% HDEHP resin is higher than those observed in both individual resins, indicating the synergic extraction of Am(III) in the combined resin. Synergic extraction indicates the involvement of both HDEHP and TEHDGA for the extraction of Am(III). This kind of synergism has been reported [15] in liquid–liquid extraction as well as solid–liquid extraction modes (Chapter 3) , that use combined extractants. In contrast to the extraction observed at lower acidities, the distribution coefficient of Am(III) in the combined resin is lower than those observed in 30% TEHDGA-impregnated resin at nitric acid concentrations above 0.5 M. This observation indicates the antagonistic extraction of Am(III) in the combined resin. A similar behavior has been reported in CMPO-HDEHP impregnated resins at high nitric acid concentrations. Tkac *et al.* [34] showed the formation of an adduct between neutral (CMPO) and acidic (HDEHP) extractants at higher acidity and that lowered the availability of free CMPO molecules for metal ion extraction. A similar adduct formation between TEHDGA and HDEHP is also possible in the present case and that could be responsible for the antagonism observed in the extraction of Am(III) at higher acidity.

4.6. Extraction of Eu(III) in individual and combined resins

The extraction behavior of Eu(III) in the individual and combined resins was studied as a function of nitric acid concentration (0.01 M to 3 M). The results are shown in figure 4.5. Similar to Am(III) extraction, the results shown in figure 4.5 indicates the release of three H^+ ions for the extraction of Eu(III) in 10% HDEHP-impregnated resin. Plot of log $D_{Eu(III)}$ against log [TEHDGA] showed (Figure 4.4) the involvement of on an average of 1–2 molecules of TEHDGA for the extraction of Eu(III) in 30% TEHDGA-impregnated resin at 3 M nitric acid. Therefore, the mechanism of Am(III) extraction shown in equations 4.7 and 4.8 is also valid for

Eu(III) extraction. Synergic extraction of Eu(III) in the combined resin is observed at nitric acid concentrations lower than 1 M and antagonistic extraction is observed at higher acidity. However, it is important to note that the distribution coefficient of Eu(III) observed in all these resins are higher than Am(III) at all acidities. This can be attributed to the characteristic property of oxygen donor ligands such as diglycolamides [10] and HDEHP, that coordinates better with hard acid metal ions such as Eu(III) as compared to Am(III).

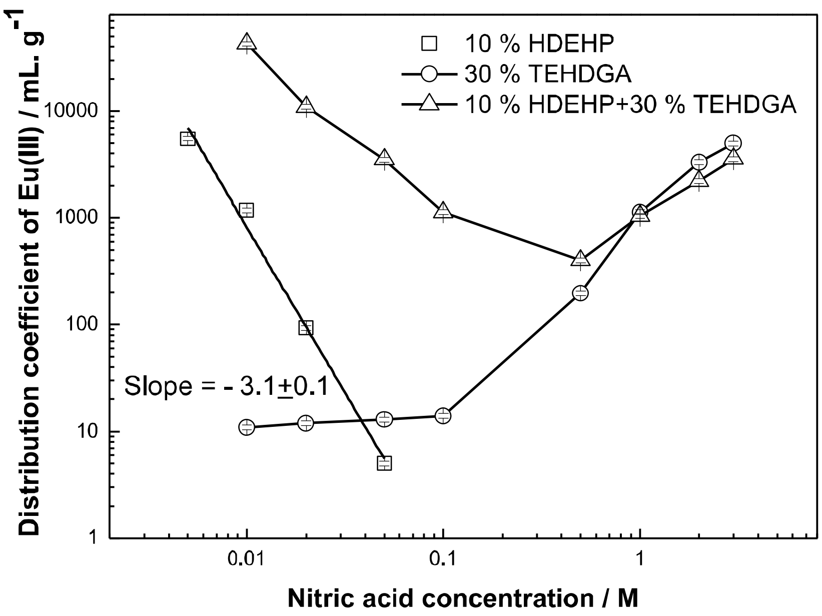


Figure 4.5. Variation in the distribution coefficient of Eu(III) as a function of nitric acid concentration. Resin = 30%TEHDGA/ADS 400 or 10%HDEHP/ADS 400 or 30%TEHDGA+10%HDEHP/ADS 400. Aqueous phase = nitric acid from 0.01 M to 3 M.

4.7. Extraction mechanism of Am(III) and Eu(III) in combined resin

To understand the insights of synergistic and antagonistic extraction of Am(III) and Eu(III) observed in the present study, the effect of TEHDGA and HDEHP concentration in the combined resin on the extraction of Am(III) and Eu(III) was studied. Figure 4.6 shows the extraction behavior of Eu(III) and Am(III) in the combined resin (TEHDGA + 10%HDEHP impregnated resin) at 0.01 M nitric acid. The loading of TEHDGA in the combined resin was varied from 2% to 20% (wt/wt). The distribution coefficient of Am(III) and Eu(III) in the combined resin increases with increase in the concentration of TEHDGA. Linear regression of the distribution coefficients results in a slope value of 0.5 for Eu(III) and 0.5 for Am(III). This indicates the participation of TEHDGA in the extraction of Am(III) and Eu(III) even at 0.01 M nitric acid concentration. Similarly, the variation of HDEHP loading in 30% TEHDGA + HDEHP impregnated resin was studied at 0.01 M nitric acid concentration. The results are shown in figure 4.7. As expected, the distribution coefficient of Am(III) and Eu(III) increases with increase in the loading of HDEHP (in wt.%). Linear regression of the extraction data results in a slope of 2.6 for both Am(III) and Eu(III). This value is lower than the slope of 3.0 observed when HDEHP alone is impregnated in the resin (Figures 4.3 and 4.5). Therefore, the dependence of distribution coefficient of Am(III) and Eu(III) on HDEHP is lowered to accommodate the participation of TEHDGA at 0.01 M nitric acid. These results confirm the involvement of both TEHDGA and HDEHP in the extraction of Am(III) and Eu(III) even at 0.01 M nitric acid and establishes the synergistic extraction of these metal ions in the combined extractant impregnated resin.

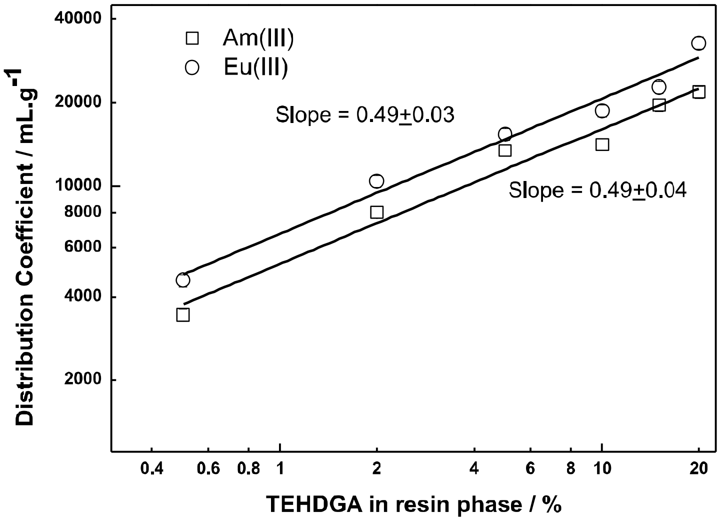


Figure 4.6. Dependence of distribution coefficient on the concentration of TEHDGA in resin phase for the extraction of Am(III) & Eu(III). Resin = TEHDGA + 10% HDEHP/ ADS 400. Aqueous phase = 0.01 M HNO_3.

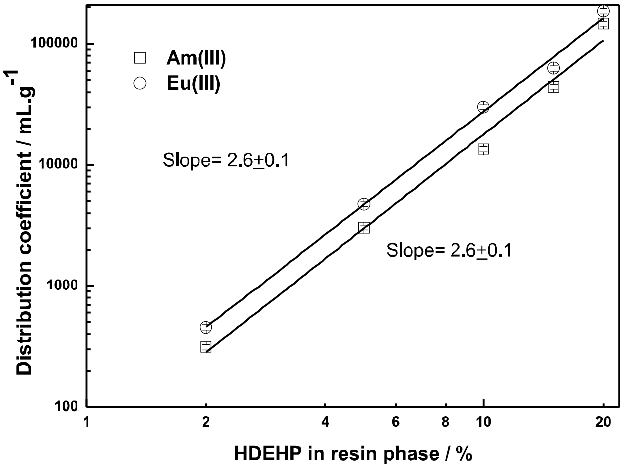


Figure 4.7. Dependence of distribution coefficient on the concentration of HDEHP in resin phase for the extraction of Am(III) & Eu(III). Resin = HDEHP + 30% TEHDGA/ ADS 400. Aqueous phase = 0.01 M HNO_3.

To understand the antagonism observed at higher nitric acid, the effect of TEHDGA loading on the extraction of Am(III) and Eu(III) in the TEHDGA + 10% HDEHP impregnated resin was studied at 3 M nitric acid concentration. The loading of TEHDGA in the resin was varied from 2 wt.% to 20 wt.% at a constant loading of 10 wt.% HDEHP in the resin. The results on the variation of the distribution coefficient of Am(III) and Eu(III) as a function of loading of TEHDGA is shown in figure 4.8. It can be seen that the distribution coefficient of Am(III) and Eu(III) increases with increase in the loading of TEHDGA. Linear regression of the extraction data results in a slope of ~1.5. This value compares well with the slope obtained in case TEHDGA alone impregnated resin (Figure 4.4). This shows that about 1–2 molecules of TEHDGA on an average are involved in the extraction of trivalent metal ion from 3 M nitric acid medium even in the combined resin, similar to the mechanism shown in equation 4.7. Similarly, the dependency of HDEHP loading on the extraction of Am(III) and Eu(III) in the combined extractant impregnated resin was studied and the results on the variation of distribution coefficient of Am(III) and Eu(III) as a function of HDEHP loading is shown in figure 4.9. The loading of HDEHP was varied from 5 wt.% to 20 wt.% in the resin at a fixed loading of 30 wt.% TEHDGA. It is interesting to note that the distribution coefficient of both Am(III) and Eu(III) decreases with increase in the loading of HDEHP in resin phase. This indicates that the presence of HDEHP antagonise the extraction of Am(III) and Eu(III) in the combined extractant impregnated resin.

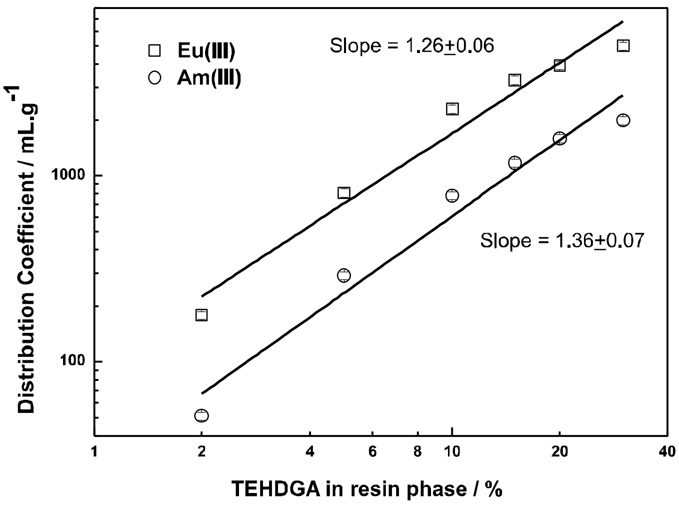


Figure 4.8. Dependence of distribution coefficient on the concentration of TEHDGA in resin phase for the extraction of Am(III) and Eu(III). Resin = TEHDGA + 10% HDEHP/ ADS 400. Aqueous phase = 3 M nitric acid.

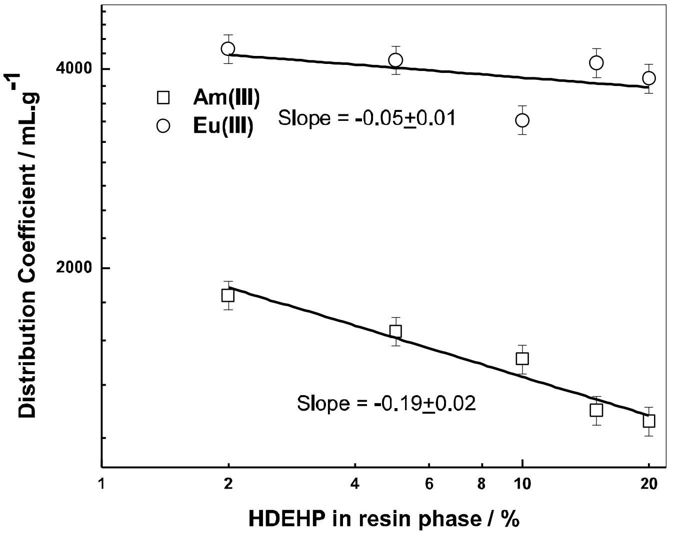


Figure 4.9. Dependence of distribution coefficient on the concentration of HDEHP in resin phase for the extraction of Am(III) & Eu(III). Resin = HDEHP + 30% TEHDGA/ ADS 400. Aqueous phase = 3 M HNO_3.

Based on the above studies, the mechanism of trivalent metal ion extraction in the combined extractant impregnated resin at lower acidities (< 0.5 M) can be given by equation 4.9. It should be noted that this equation is applicable only below 0.5 M nitric acid where synergistic extraction of Am(III) and Eu(III) is observed (Figure 4.3 and 4.5).

$$M^{3+}_{aq} + (3-x)NO^{-}_{3aq} + x\overline{HDEHP} + (1-y)\overline{TEHDGA} \Leftrightarrow \overline{M(NO_3)_{3-x}(DEHP)_x(TEHDGA)_{1-y}} + xH^{+}_{aq} \qquad (4.9)$$

Above synergistic region (above 0.5 M nitric acid), the extraction is governed by antagonism and the presence of HDEHP lowers the extraction of Am(III) and Eu(III). Under such condition TEHDGA alone is responsible for extraction and the mechanism shown in equation 4.7 is applicable during antagonism.

4.8. Studies with fast reactor simulated high-level liquid waste

The extraction of trivalent actinides (americium) from HLLW is always accompanied with the extraction of trivalent lanthanides, due to the chemical similarity of lanthanides and actinides [5, 10]. Also, it was reported that diglycolamides extract other fission products such as Pd(II), Ru(III), Zr(IV) and Sr(II) [10, 11]. Therefore, it is necessary to study the extraction behavior of fission products in 30% TEHDGA + 10% HDEHP impregnated resins. The composition of Fast Reactor Simulated High-Level Liquid Waste (FR-SHLLW) is shown in table 2.2. The studies were carried out with fast reactor simulated high level liquid waste (FR-SHLLW) containing 0.05 M of CyDTA, which was added to lower the extraction of palladium(II) and zirconium(IV), as reported elsewhere [35]. Table 4.2 shows the percentage of extraction of some of the fission products present in FR-SHLLW. It is noticed that, all the trivalent lanthanides (except La) are extracted more than 90% in a single contact. It is also observed that the extraction of americium was very high compared to the other trivalent metal ions. This may attributed to the trace level presence of americium in FR-SHLLW and thus high extraction. Moreover, other metal ions such as iron and molybdenum exhibit high extraction owing to the characteristics of HDEHP and diglycolamides. Therefore, the studies showed that the combined resins can be used for the extraction of trivalent metal ions from HLLW.

Table 4.2. Percentage of extraction of metal ions from FR-SHLLW. Resin = 30% TEHDGA + 10 % HDEHP impregnated resin. Aqueous phase = FR-SHLLW in 3 M HNO_3. Weight or resin = 1 g. Volume of aqueous phase = 5 mL

Metal ion	% of extraction	Metal ion	% of extraction
La(III)	84	Cr(VI)	2
Ce(III)	90	Cd(II)	3
Nd(III)	97	Ni(II)	4
Sm(III)	98	Pd(III)	6
Eu(III)	98	Zr(IV)	22
Gd(III)	98	Y(III)	94
Dy(III)	97	Sr(II)	28
Fe(III)	76	Ba(II)	1
Mo(VI)	81	Ru(III)	9
Pr(III)	94	Rh(III)	33
^{241}Am(III)	98		

4.9. Selective separation of Am(III)

As seen from the table 4.2, it is understood that the extraction of Am(III) from nitric acid medium is accompanied by the co-extraction of trivalent lanthanides. The separation of trivalent lanthanides from the minoractinides prior to transmutation is necessary in view of the negative role of lanthanides in reducing the efficiency of transmutation of actinides. The studies were made to separate these lanthanides from actinides by using aqueous soluble complexing agents, such as diethylenetriaminepentaacetic acid (DTPA) and citric acid (CA). It was reported that DTPA selectively hold americium(III) in aqueous phase to enable the separation of trivalent lanthanides and actinides [12]. The results on the extraction of Am(III) and Eu(III) from the aqueous solution containing DTPA and citric acid are shown in table 4.3. It can be seen that the distribution coefficient of Am(III) and Eu(III) decreases with increase of pH of aqueous phase, perhaps due to the retention of both Am(III) and Eu(III) in aqueous phase by DTPA. However, the separation factor (SF = D_{Eu}/D_{Am}) increases with increase of pH in all cases, due to the higher retention of actinides in aqueous phase. At pH 3.5 with the aqueous phase containing 0.005 M DTPA + 0.1 M CA + 1 M $NaNO_3$, a SF of 5 is obtained for the separation of Am(III) over Eu(III) using 30% TEHDGA + 20% HDEHP impregnated resin. Sodium nitrate was added to aqueous phase to maintain constant ionic strength as in the case of TALSPEAK process [12]. Even though the separation factor achieved in the batch extraction mode is less, the study shows the possibility of separating Am(III) from Eu(III) in nitric acid medium by adopting column chromatographic mode.

Table 4.3. Extraction of Am(III) and Eu(III) from the aqueous solution containing various concentration of DTPA and citric acid. SF = $D_{Eu(III)}$ / $D_{Am(III)}$ Resin Phase = HDEHP + 30% TEHDGA – impregnated resin (0.05 g), Aqueous phase = 0.005 M DTPA + 0.1 M CA + 1 M $NaNO_3$

pH	20% HDEHP + 30% TEHDGA extraction with 0.005 M DTPA + 0.1 M CA + 1 M $NaNO_3$			10% HDEHP + 30% TEHDGA extraction with 0.005 M DTPA + 0.1 M CA + 1 M $NaNO_3$		
	$D_{Am(III)}$	$D_{Eu(III)}$	S.F= $D_{Eu(III)}$ / $D_{Am(III)}$	$D_{Am(III)}$	$D_{Eu(III)}$	S.F= $D_{Eu(III)}$ / $D_{Am(III)}$
3	115	487	4.23	13	68	5.23
3.5	27	134	4.96	1	12	12

4.10. Conclusion

The solvent impregnated resins containing either TEHDGA or HDEHP or the combined solvent (TEHDGA + HDEHP) were prepared and studied for the extraction of Am(III) and Eu(III) from nitric acid medium. Rapid uptake of Am(III) and Eu(III) in the initial stages of equilibration followed by the establishment of equilibrium occured in 100 min was observed. The distribution coefficient and slope analysis of the distribution data indicated the participation of 1–2 molecules of TEHDGA and three molecules HDEHP for the extraction of trivalent metal ions in the individual resins. In a combined system, synergistic extraction of Am(III) and Eu(III) was observed at lower nitric acid concentration (< 0.5 M) and antagonism was observed at higher nitric acid concentration. Involvement of both TEHDGA and HDEHP was responsible for the synergic extraction of Am(III) and Eu(III).

During synergism, the participation of HDEHP was lowered to accommodate the involvement of TEHDGA, in the extraction of Am(III) and Eu(III) at low nitric acid concentration. However, at higher nitric acid concentration, addition of HDEHP reduced the distribution ratio of Am(III) and Eu(III) and the involvement of TEHDGA in the combined resin was similar to those observed for TEHDGA impregnated resin, confirming the antagonistic effect of combining these extractants. More than 90% trivalent lanthanides and Am(III) can be extracted in a single contact of the combined resin with FR-SHLLW and the SF of about 5 was achieved for the separation of Am(III) over Eu(III) in the batch extraction mode. Even though the separation factor achieved with the batch method is low, it is quite possible to achieve good separation of trivalent actinides from lanthanides by employing column method. However, our investigations also indicate that more studies are needed to develop efficient stripping reagents for separating Am(III) from other lanthanides.

4.11. References

1. J. N. Mathur, M. S. Murali, K. L. Nash, Actinide partitioning – a review, Solvent Extr. Ion Exch., 19 (2001) 357-390.

2. S. A. Ansari, P. N. Pathak, P. K. Mohapatra, V. K. Manchanda, Chemistry of diglycolamides: Promising extractants for actinide partitioning, Chem. Rev., 112 (2012) 1751-1772.

3. K. L. Nash, A review of the basic chemistry and recent developments in trivalent F-Elements separations, Solvent Extr. Ion Exch., 11 (1993) 729–768

4. E. Philip Horwitz, D. G. Kalina, L. Kaplan, G. W. Mason, H. Diamond, Selected alkyl(phenyl)-N,N-dialkylcarbomylmethylphophine oxides as extractants for Am(III) from nitric acid media, Sep. Sci. Technol., 17 (1982) 1261-1279.

5. J. N. Mathur, M. S. Murali, P. R. Natarajan, L. P. Badheka, A. Banerji, Extraction of actinides and fission products by octyl(phenyl)-N,N-diisobutylcarbamoylmethyl-phosphine oxide from nitric acid media, Talanta, 39 (1992) 493-498.

6. W. W. Schulz, E. Philip Horwitz, The Truex Process and the Management of Liquid Tru Uwaste, Sep. Sci. Technol., 23 (1988) 1191-1210.

7. M. P. Antony, R. Kumaresan, A. S. Suneesh, S. Rajeswari, B. Robertselvan, V. Sukumaran, R. Manivannan, K. V. Syamala, K. A. Venkatesan, T. G. Srinivasan, P. R. Vasudeva Rao, Development of a CMPO based extraction process for partitioning of minor actinides and demonstration with genuine fast reactor fuel solution (155 GWd/Te), Radiochim. Acta, 99 (2011) 207–215.

8. C. Cuillerdier, C. Musikas, P. Hoel, L. Nigond, X. Vitart, Malonamides as new extractants for nuclear waste solutions, Sep. Sci. Technol., 26 (1991) 1229.

9. Y. Sasaki, Y. Sugo, S. Suzuki, S. Tachimori, The novel extractants diglycolamides for extraction of lanthanides and actinides in HNO_3-n-dodecane system, Solvent Extr. Ion Exch., 19 (2001) 91-103.

10. S. A. Ansari, P. N. Pathak, P. K. Mohapatra, V. K. Manchanda, Chemistry of diglycolamides: Promising extractants for actinide partitioning, Chem. Rev., 112 (2012) 1751–1772.

11. J. Ravi, A. S. Suneesh, T. Prathibha, K. A. Venkatesan, M. P. Antony, T. G. Srinivasan, P. R. Vasudeva Rao, Extraction behavior of some actinide and fission products from nitric acid medium by a new unsymmetrical diglyolamide, Solvent Extr. Ion Exch., 29 (2011) 86–105.

12. M. Nilsson, K. L. Nash, A review of the development and op-erational characteristics of the TALSPEAK process, Solvent Extr. Ion Exch., 25 (2007) 665–701.

13. P. J. Panak, A. Geist, Complexation and extraction of trivalent actinides and lanthanides by triazinylpyridine N-donor ligands, Chem. Rev., 113 (2013) 1199–1236.

14. G. J. Lumetta, A. V. Gelis, F. Vandegrift, Solvent systems combining neutral and acidic extractants for separating trivalent lanthanides from the transuranic elements, Solvent Extr. Ion Exch., 28 (2010) 287-312.

15. P. K. Nayak, R. Kumaresan, K. A. Venkatesan, M. P. Antony, P. R. Vasudeva Rao, A new method for partitioning of trivalent actinides from high-level liquid waste, Sep. Sci. Technol., 48 (2013) 1409-1416.

16. G. J. Lumetta, J. C. Carter, A. V. Gelis, G. F. Vandegrift, Combining Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine Oxide and Bis-(2-

ethylhexyl)phosphoric acid extractants for recovering transuranic elements from irradiated nuclear fuel, In: Nuclear Energy and the Environment, C. M. Wai and B. J. Mincher, eds., ACS Symposium Series 1046, American Chemical Society, Washington, DC, 107-118.

17. G. J. Lumetta, A. V. Gelis, J. C. Braley, J. C. Carter, J. W. Pittman, M. G. Warner, G. F. Vandegrift, The TRUSPEAK concept: combining CMPO and HDEHP for separating trivalent lanthanides from the transuranic elements, Solvent Extr. Ion Exch., 31 (2013) 223-236.

18. B. Gannaz, R. Chiarizia, R. K. Antonio, C. Hill, G. Cote, Extraction of lanthanides(III) and Am(III) by mixtures of malonamide and dialkylphosphoric acid, Solvent Extr. Ion Exch., 25 (2007) 313-337.

19. P. S. Dhami, R. R. Chitnis, V. Gopalakrishnan, P. K. Wattal, A. Ramanujam, A. K. Bauri, Studies on the partitioning of actinides from high level waste using a mixture of HDEHP and CMPO as extractant, Sep. Sci. Technol., 42 (2007) 439-452.

20. G. Modolo, R. Odoj, Synergistic selective extraction of actinides(III) over lanthanides from nitric acid using new aromatic diorganyldithiophosphinic acids and neutral organophosphorus compounds, Solvent Extr. Ion Exch., 17 (1999) 33-53.

21. Z. Kolarik, Complexation and separation of lanthanides(III) and actinides(III) by heterocyclic N-donors in solutions, Chem. Rev., 108 (2008) 4208–4252.

22. V. Hubscher-Bruder, J. Haddaoui, S. Bouhroum, F. Arnaud-Neu, Recognition of some lanthanides, actinides, and transition- and heavy-metal cations byN-donor ligands: thermodynamic and kinetic aspects, Inorg. Chem., 49 (2010) 1363–1371

23. R. Rodríguez, J. Avivar, L. O. Leal, V. Cerdà, L. Ferrer, Strategies for automating solid-phase extraction and liquid-liquid extraction in radiochemical analysis, TrAC Trends in Analytical Chemistry, 76 (2016) 145-152.

24. É. A. Souza-Silva, N. Reyes-Garcés, G. A. Gómez-Ríos, E. Boyacı, B. Bojko, J. Pawliszyn, A critical review of the state of the art of solid-phase microextraction of complex matrices III. Bioanalytical and clinical applications, TrAC Trends in Analytical Chemistry, 71 (2015) 249-264.

25. E. Philip Horwitz, R. Chiarizia, M. L. Dietz, H. Diamond, D. M. Nelson, Separation and preconcentration of actinides from acidic media by extraction chromatography, Anal. Chem. Acta., 281 (1993) 361-372.

26. E. Philip Horwitz, D. R. McAlister, A. H. Bond, R. E. Barrans, Novel extraction of chromatographic resins based on tetraalkyldiglycolamides: characterization and potential applications, Solvent Extra. Ion Exch., 23 (2005) 319-344.

27. K. Van Hecke, G. Modolo, Separation of actinides from low level liquid wastes (LLLW) by extraction chromatography using novel DMDOHEMA and TODGA impregnated resins, J. Radioanal. Nucl. Chem., 261 (2004) 269 – 275.

28. S. A. Ansari, P. N. Pathak, P. K. Mohapatra, V. K. Manchanda, Chemistry of diglycolamides: Promising extractants for actinide partitioning, Chem. Rev., 112 (2012) 1751-1772

29. J. Ravi, K. A. Venkatesan, M. P. Antony, T. G. Srinivasan, P. R. Vasudeva Rao, Tuning the diglycolamides for modifier-free minor actinide partitioning, J. Radioanal. Nucl. Chem., 295 (2013) 1283-1292

30. J. Ravi, A. S. Suneesh, T. Prathibha, K. A. Venkatesan, M. P. Antony, T. G. Srinivasan, P. R. Vasudeva Rao, Extraction behaviour of some actinides and fission products from nitric acid medium by a new unsymmetrical diglycolamide, Solvent Extr Ion Exch., 29 (2011) 86-105.

31. Y. Sasaki, Y. Sugo, S. Suzuki, S. Tachimori, The novel extractants, the diglycolamides, for the extraction of lanthanides and actinides in HNO_3-n-dodecane system, Solvent Extr. Ion Exch., 19 (2001) 91-103.

32. H. Narita, T. Yaita, K. Tamura, S. Tachimori, Solvent extraction of trivalent lanthanoid ions with N,N'-dimethyl-N,N'-diphenyl-3-oxapentanediamide, Radiochim. Acta, 81 (1998) 223-226.

33. A. S. Suneesh, K. A. Venkatesan, M. P. Antony, P. R. VasudevaRao, Molecular dynamic simulations in diglycolamides–$Eu(NO_3)_3$ system, SDRP J. Comput. Chem. Mol. Model., 1 (2016).

34. P. Tkac, G. F. Vandegrift, G. J. Lumetta, A. V. Gelis, Study of the interaction between HDEHP and CMPO and its effect on the extraction of selected lanthanides, Ind. Eng. Chem. Res., 51 (2012) 10433-10444.

35. P. K. Nayak, R. Kumaresan, Shivkumar Chaurasia, K. A. Venkatesan, G. G. S. Subramanian, T. Prathibha, K. V. Syamala, B. Robert Selvan, S. Rajeswari, M. P. Antony, P. R. Vasudeva Rao, Studies on the feasibility of using completely incinerable reagents for the single-cycle separation of americium(III) from simulated high-level liquid waste, Radiochim. Acta, 103 (2015) 265–275.

CHAPTER 5

Chapter 5: Radiolytic degradation studies of SIRs containing neutral extractants such as CMPO and TEHDGA in conjunction with an acidic extractant HDEHP

5.1. Introduction

In Chapter 3 and Chapter 4, the results on the solid phase extraction of Am(III) and Eu(III) from nitric acid medium by using the Solvent impregnated resin (SIR) containing (CMPO and HDEHP) as well as (TEHDGA and HDEHP) were discussed [1, 2]. Synergistic extraction was observed at lower nitric acid concentration and antagonism at higher nitric acid concentration in both the systems. When the Solvent Impregnated Resin (SIR) is proposed for the separation of actinides from HLLW, it is quite likely that the solvent present in the resin is exposed to the high amount of α, β, and γ-radiation and can undergo radiolytic degradation. The energy associated with various radiations either partially or fully is deposited on the solvent molecules present in SIRs. This results in adverse effects of the performance of the resin depending on the type of radiation, and duration of exposure [3-7]. The effects include the rupture of chemical bonds present in the solvent molecules. The stability of the solvent towards radiation is one of the concerns when the solvent is proposed for the treatment of radioactive wastes [7, 8]. Therefore study of radiation stability is another important requirement that needs to be evaluated when the SIRs are proposed for actinide partitioning. The radiolytic products formed in the resin could combine with each other or combine with the resin matrix (both degraded and undegraded) leading to the formation of several degradation products in the resin phase. The presence and formation of these degradation products alter the physical, chemical and extraction properties of the solvent to a significant extent [9-16]. The degradation products present in the resin phase may interfere in the complex formation of extractants with the metal ions. Therefore, the extraction and stripping behavior of Am(III) and Eu(III) from nitric acid medium may vary under the exposure. The degradation of SIR not only reduces the extraction efficiency, but also alters the separation factors to be achieved. Thus, the reusability of these resins strongly depends on its radiolytic stability and the nature of degradation products. The ligand decomposition yield should be sufficiently low, and the nature of the decomposition products sufficiently benign, that significant process efficiency is not lost with time and absorbed radiation dose. In this context, it is very important to understand the radiation stability of a SIR proposed for the extraction under extraction and stripping conditions.

In view of this, it is necessary to study the radiolytic stability of the SIR phase containing CMPO+HDEHP and TEHDGA+HDEHP. Therefore, the present chapter deals with evaluation of radiolytic stability of the solvent impregnated resins containing both neutral and acidic extractants, such as CMPO+HDEHP and TEHDGA+HDEHP/ADS 400. This was studied by determining the distribution coefficient and loading behavior of Eu(III) or Am(III) from nitric acid medium in the gamma irradiated SIRs at various absorbed dose levels. Since the extraction of trivalents (An(III) + Ln(III)) from HLLW was carried out from 3-4 M and recovery of trivalents from the loaded resin phase was carried out from 0.01 M nitric acid medium, the concentration of nitric acid in the present study was fixed at 3 M during extraction, and 0.01 M during stripping. The neutral extractant used in the present study was either CMPO or TEHDGA and the acidic extractant used was HDEHP. The composition of neutral and acidic extractant in the SIR was optimized to be 30wt% and 10 wt% respectively, based on our previous study.

5.2. Extraction behavior of Am(III) and Eu(III) at 3 M nitric acid in CMPO+HDEHP and CMPO systems.

The variation in the distribution coefficient of Am(III) from 3 M nitric acid studied as a function of absorbed dose is shown in figure 5.1(a). The absorbed dose was varied from 1 kGy to 550 kGy and the results were compared with un-irradiated condition (0 kGy). The resin phase contained 30% CMPO + 10% HDEHP or 30% CMPO. Since, the extraction behavior of trivalent metal ion from 3 M nitric acid medium is predominantly governed by the neutral extractant, the distribution coefficient of Am(III) and Eu(III) in the binary SIR was compared only with the neutral extractant impregnated resin. It can be seen that the distribution coefficient (K_d) of Am(III) decreases with increase of absorbed dose. The K_d value of Am(III) decreases from 760 mL.g^{-1} to 480 mL.g^{-1} in case of 30% CMPO SIR and, from 450 mL.g^{-1} to 350 mL.g^{-1} in case of 30% CMPO + 10% HDEHP SIR, with the increase of absorbed dose from 0 kGy to 550 kGy. It should be noted that the distribution coefficient of Am(III) in CMPO SIR is higher than that observed for CMPO + HDEHP SIR at 3 M nitric acid. This could be due to the antagonistic effect of combining CMPO with HDEHP for the extraction of Am(III) from 3 M nitric acid medium. Figure 5.1(b) shows the variation in the percentage extraction of Am(III) as a function of absorbed dose. Since the percentage extraction is related directly to the distribution coefficient, the percentage extraction of Am(III) also decreases with increase in the absorbed dose. A similar behavior is also observed in the case of

Eu(III) extraction in 30% CMPO and 30%CMPO+10%HDEHP SIR phase as shown in figures 5.2(c) & 5.2 (d).

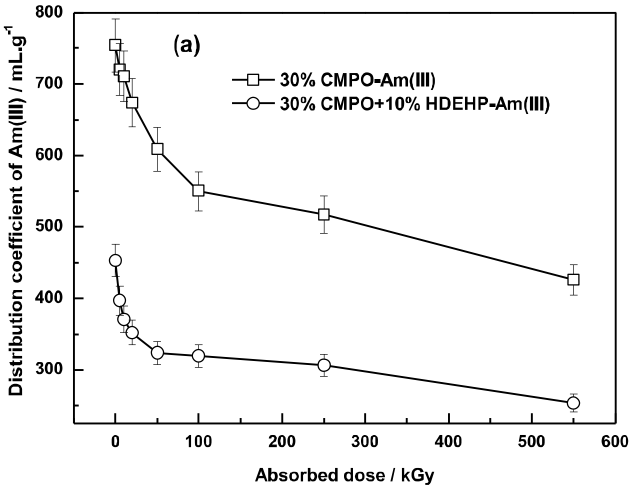


Figure 5.1. (a) Variation of distribution coefficient of Am(III) as a function of absorbed dose. Resins=30% CMPO/ADS 400 or 30% CMPO+10% HDEHP/ADS 400, Aqueous phase =3 M HNO_3, v/m=100.

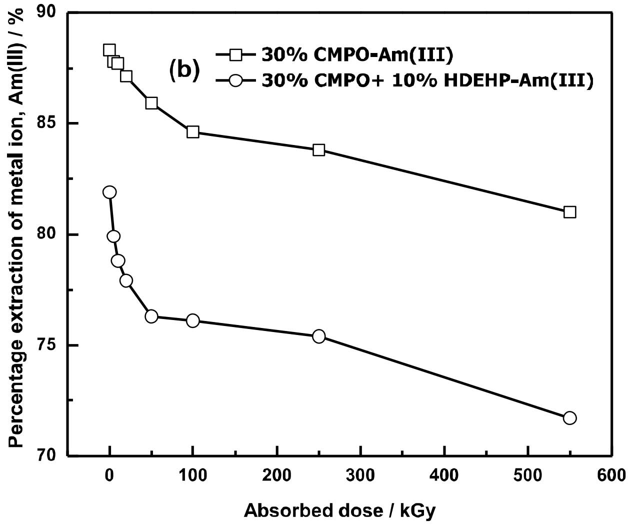


Figure 5.1. (b) Variation of percentage extraction of Am(III) as a function of absorbed dose. Resins=30% CMPO/ADS 400 or 30% CMPO+10% HDEHP/ADS 400, Aqueous phase =3 M HNO_3, v/m=100.

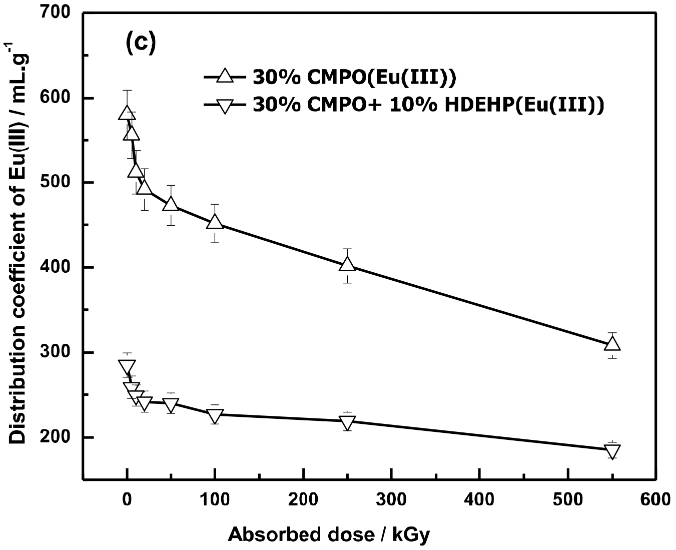


Figure 5.1. (c) Variation of distribution coefficient of Eu(III) as a function of absorbed dose. Resins=30% CMPO/ADS 400 or 30% CMPO+10% HDEHP/ADS 400, Aqueous phase =3 M HNO_3, v/m=100.

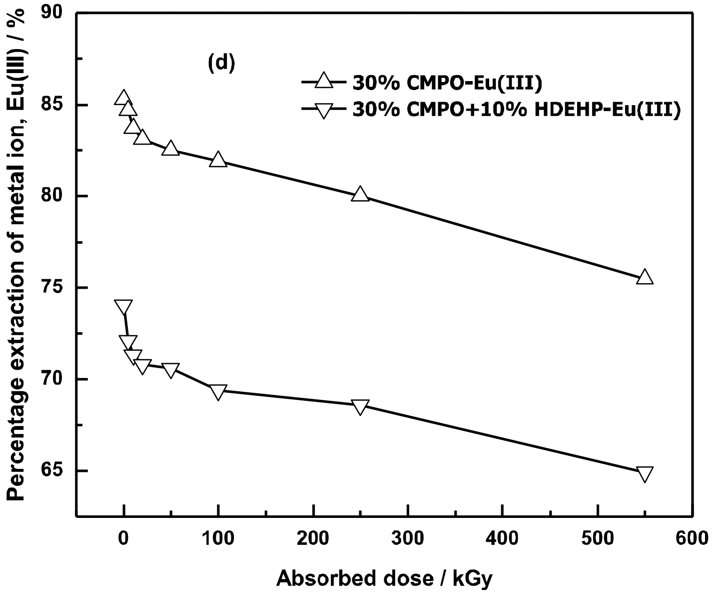


Figure 5.1 (d) Variation of percentage extraction of Eu(III) as a function of absorbed dose. Resins=30% CMPO/ADS 400 or 30% CMPO+10% HDEHP/ADS 400, Aqueous phase =3 M HNO_3, v/m=100.

5.3. Extraction behavior of Am(III) and Eu(III) at 3 M nitric acid in TEHDGA+HDEHP and TEHDGA systems.

The extraction behavior of Am(III) and Eu(III) in 30% TEHDGA or 30% TEHDGA+ 10% HDEHP SIR at 3 M nitric acid is shown in figures 5.2 (a) and 5.2 (c). The variation in the percentage extraction of Am(III) and Eu(III) as a function of absorbed dose is shown in figures 5.2(b) and 5.2(d). The distribution coefficient of Am(III) decreases with increase of absorbed dose in this case also. Since TEHDGA exhibits higher affinity towards trivalent metal ions as compared to CMPO, the distribution coefficient and percentage extraction of Am(III) in SIR phase containing TEHDGA is more as compared to CMPO SIR. A similar behavior is also observed in case of Eu(III) extraction in TEHDGA and TEHDGA+HDEHP SIR phases. The distribution coefficient of Am(III) and Eu(III) decreases from 2250 mL.g^{-1} and 6000 mL.g^{-1} to 1400 mL.g^{-1} and 2700 mL.g^{-1}, respectively, with the increase of absorbed dose from 0 kGy to 550 kGy in case of 30% TEHDGA SIR. Since the addition of HDEHP to TEHDGA SIR phase lowers [17] the distribution coefficient of Am(III) and Eu(III) due to antagonistic effect, the K_d value of these metal ions in the TEHDGA+HDEHP SIR phase is lower than that observed in TEHDGA SIR as shown in figures 5.2 (a) and 5.2 (c). Moreover, the decrease in the distribution coefficient of Am(III) and Eu(III) is very sharp in the initial period of irradiation up to 100 kGy (approx) absorbed dose, thereafter the variation in the distribution coefficient as a function of absorbed dose is only marginal. The distribution coefficients observed for Eu(III) in TEHDGA and TEHDGA+HDEHP are very close to each other when the absorbed dose is 500 kGy.

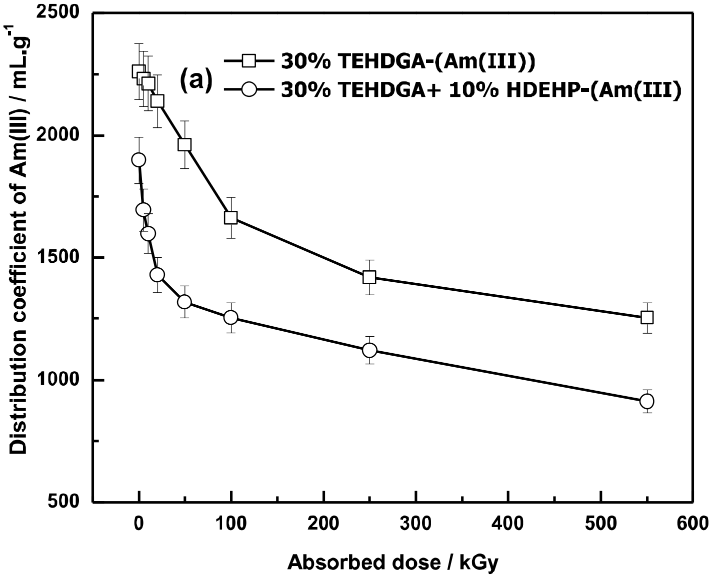


Figure 5.2. (a) Variation of distribution coefficient of Am(III) as a function of absorbed dose. Resins = 30% TEHDGA/ADS 400 or 30% TEHDGA+10% HDEHP/ADS 400, Aqueous phase= 3 M HNO_3, v/m=100.

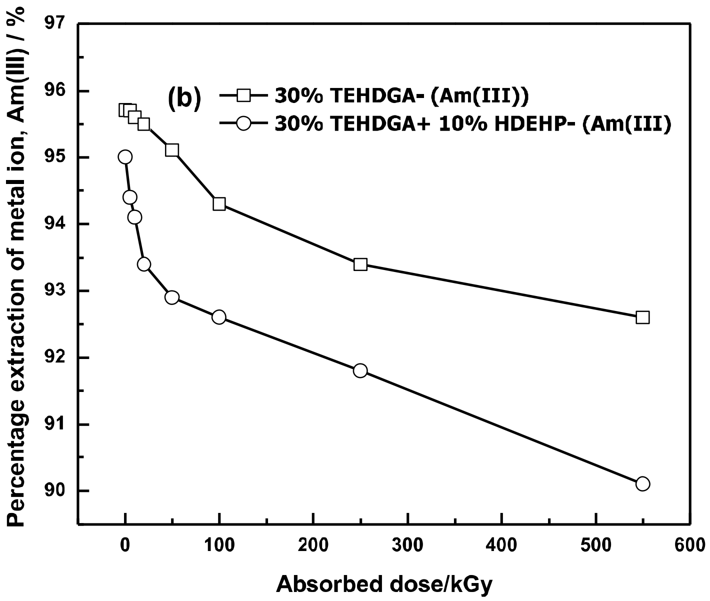


Figure 5.2. (b) Variation of percentage extraction of Am(III) as a function of absorbed dose. Resins = 30% TEHDGA/ADS 400 or 30% TEHDGA+10% HDEHP/ADS 400, Aqueous phase= 3 M HNO_3, v/m=100.

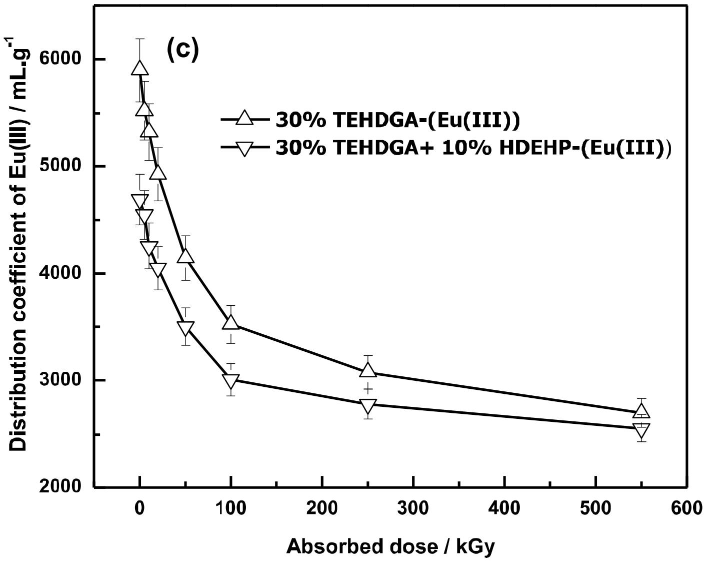


Figure 5.2. (c) Variation of distribution coefficient of Eu(III) as a function of absorbed dose. Resins = 30% TEHDGA/ADS 400 or 30% TEHDGA+10% HDEHP/ADS 400, Aqueous phase = 3 M HNO_3, v/m=100.

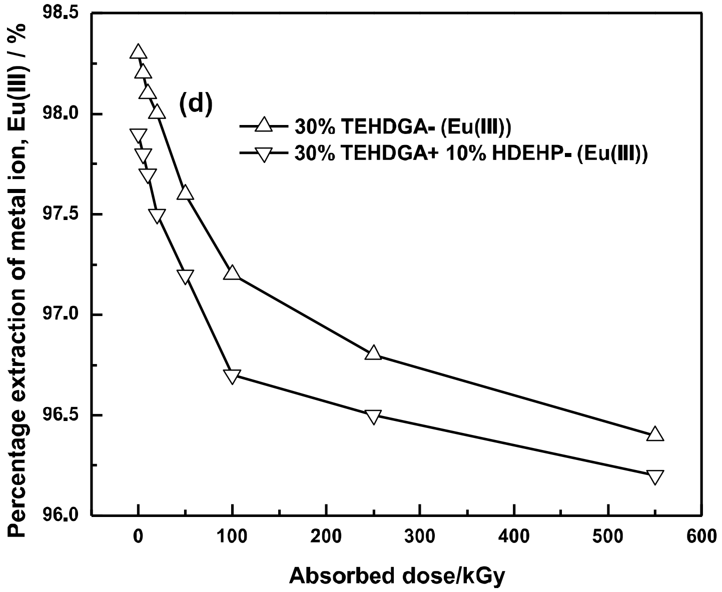


Figure 5.2. (d) Variation of percentage extraction of Eu(III) as a function of absorbed dose. Resins = 30% TEHDGA/ADS 400 or 30% TEHDGA+10% HDEHP/ADS 400, Aqueous phase= 3 M HNO_3, v/m=100.

5.4. Extraction behavior of Am(III) and Eu(III) at 0.01 M nitric acid in CMPO+ HDEHP and HDEHP systems.

The extraction behavior of trivalent metal ion at lower nitric acid (0.01 M) in the binary SIR is essentially governed by the acidic extractant. Therefore, the distribution coefficient of Am(III) and Eu(III) in the binary SIR was compared only with HDEHP impregnated resin. Figure 5.3 (a) shows the variation in the distribution coefficient of Am(III) in 30% CMPO + 10% HDEHP SIR at 0.01 M nitric acid determined as a function of absorbed dose. The data are compared with those obtained in 10% HDEHP SIR. It can be seen that the distribution coefficient of Am(III) decreases with increase in the absorbed dose in both cases. Since the presence of CMPO in HDEHP SIR enhances [1] the extraction of Am(III) due to synergism, the distribution coefficient of Am(III) in CMPO+HDEHP is more as compared to HDEHP SIR. A similar behavior is also observed for the extraction of Eu(III) in CMPO+HDEHP and HDEHP SIR, as shown in figure 5.3(c). However, the distribution coefficient of Eu(III) is always higher than those observed for Am(III) under similar conditions, at all absorbed dose levels. In addition, the distribution coefficient observed for Eu(III) in un-irradiated SIR is about 2-3 times higher than those observed for Am(III). The percentage extraction of Am(III) and Eu(III) in these SIR as a function of absorbed dose is shown in figures 5.3 (b) and 5.3 (d).

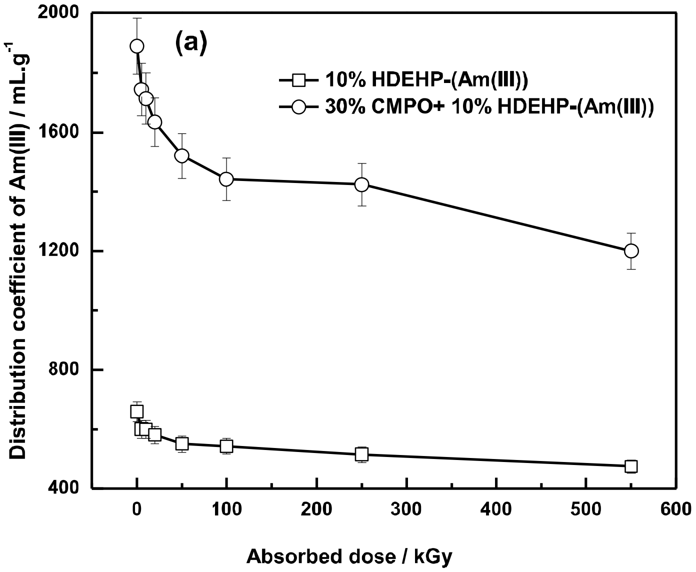


Figure 5.3. (a) Variation of distribution coefficient of Am(III) as a function of absorbed dose. Resins = 10% HDEHP/ADS 400 or 30% CMPO+10% HDEHP/ADS 400, Aqueous phase =0.01 M HNO_3, v/m=100.

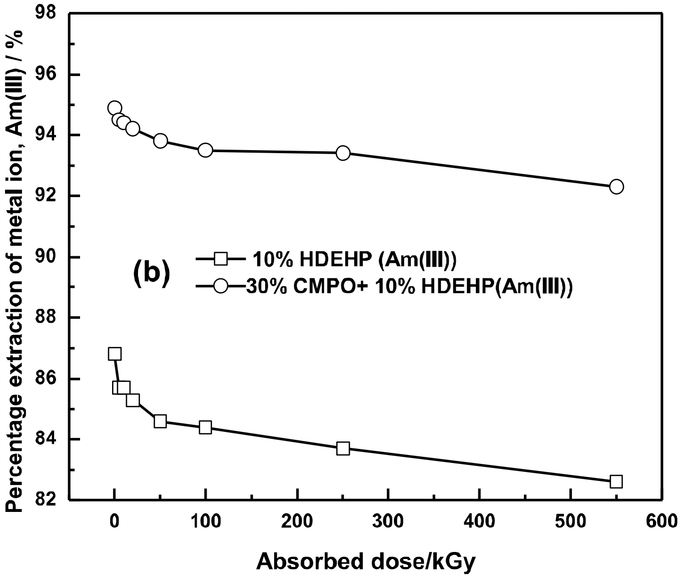


Figure 5.3.(b) Variation of percentage extraction of Am(III) as a function of absorbed dose. Resins = 10% HDEHP/ADS 400 or 30% CMPO+ 10%HDEHP/ADS 400, Aqueous phase =0.01 M HNO_3, v/m=100.

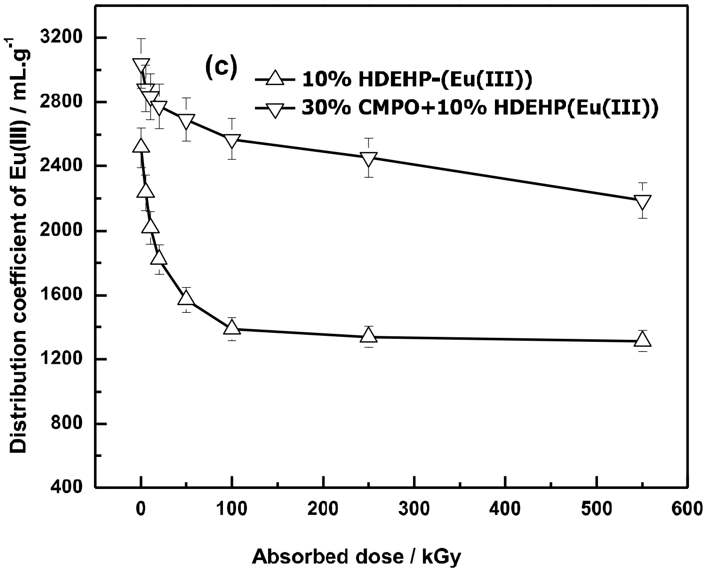


Figure 5.3. (c) Variation of distribution coefficient of Eu(III) as a function of absorbed dose. Resins = 10% HDEHP/ADS 400 or 30% CMPO+10%HDEHP/ ADS 400, Aqueous phase =0.01 M HNO$_3$, v/m=100.

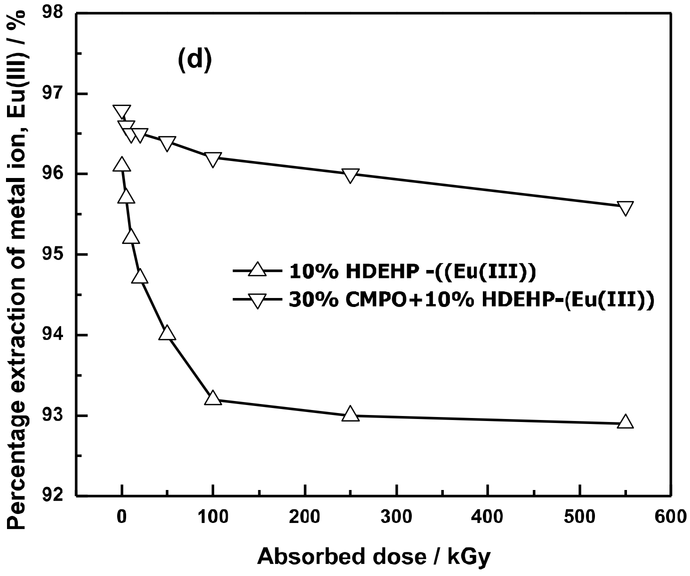


Figure 5.3. (d) Variation of percentage extraction of Eu(III) as a function of absorbed dose. Resins = 10% HDEHP/ADS 400 or 30% CMPO+ 10%HDEHP/ ADS 400, Aqueous phase =0.01 M HNO$_3$, v/m=100.

5.5. Extraction behavior of Am(III) and Eu(III) at 0.01 M nitric acid in TEHDGA+HDEHP and HDEHP systems.

The variation in the distribution coefficient of Am(III) and Eu(III) as a function of absorbed dose in 10% HDEHP and 30% TEHDGA+10% HDEHP SIR at 0.01 M nitric acid is shown in figures 5.4 (a) and 5.4 (c). The variation in the percentage extraction of Am(III) and Eu(III) as a function of absorbed dose is shown in figures 5.4 (b) and 5.4 (d). It can be seen that distribution coefficient of Am(III) and Eu(III) decreases with increase of absorbed dose as expected. Since TEHDGA is a tridentate ligand and strongly binding ligand as compared to the bidendate CMPO, the distribution coefficients of Am(III) and Eu(III) observed in the presence of TEHDGA at 0.01M nitric acid are much higher than those observed in case of CMPO+HDEHP SIR at all absorbed dose levels. In view of this, the distribution coefficient of Am(III) and Eu(III) observed in TEHDGA+HDEHP SIR is much higher than 10000 $mL.g^{-1}$ even at the absorbed dose of 550 kGy; where as in CMPO+HDEHP SIR it is nearly 2000 $mL.g^{-1}$.

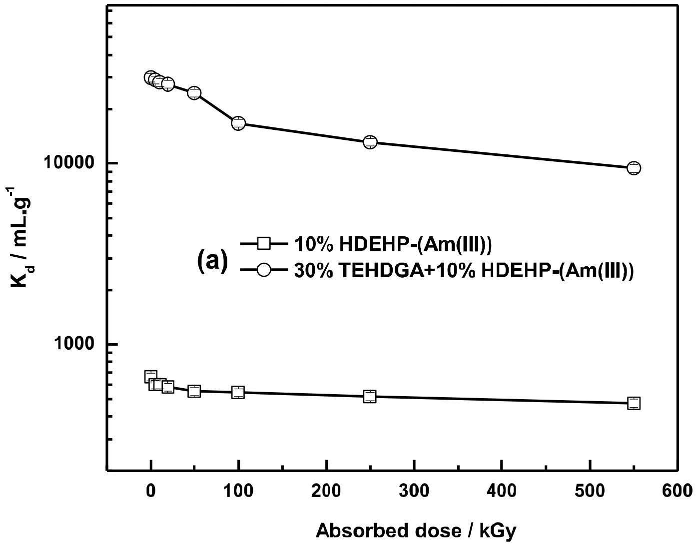


Figure 5.4. (a) Variation of distribution coefficient of Am(III) as a function of absorbed dose. Resin=10% HDEHP/ADS 400 or 30% TEHDGA+10%HDEHP/ ADS 400, Aqueous phase =0.01 M HNO_3, v/m=100.

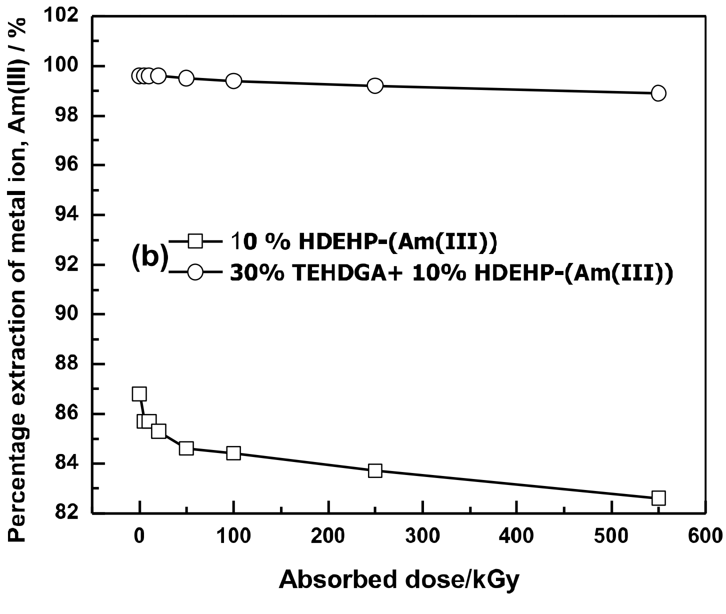


Figure 5.4. (b) Variation of percentage extraction of Am(III) as a function of absorbed dose. Resin=10% HDEHP/ADS 400 or 30% TEHDGA+10%HDEHP/ ADS 400, Aqueous phase =0.01 M HNO_3, v/m=100.

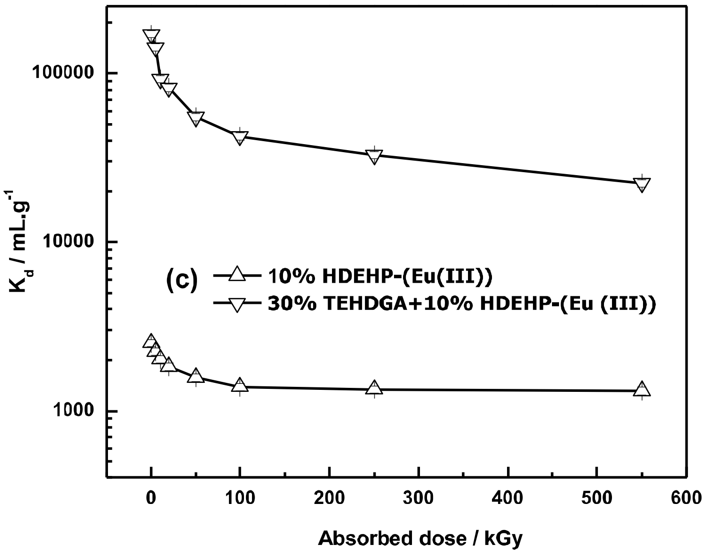


Figure 5.4. (c) Variation of distribution coefficient of Eu(III) as a function of absorbed dose. Resin=10% HDEHP/ADS 400 or 30% TEHDGA+10%HDEHP/ ADS 400, Aqueous phase =0.01 M HNO_3, v/m=100.

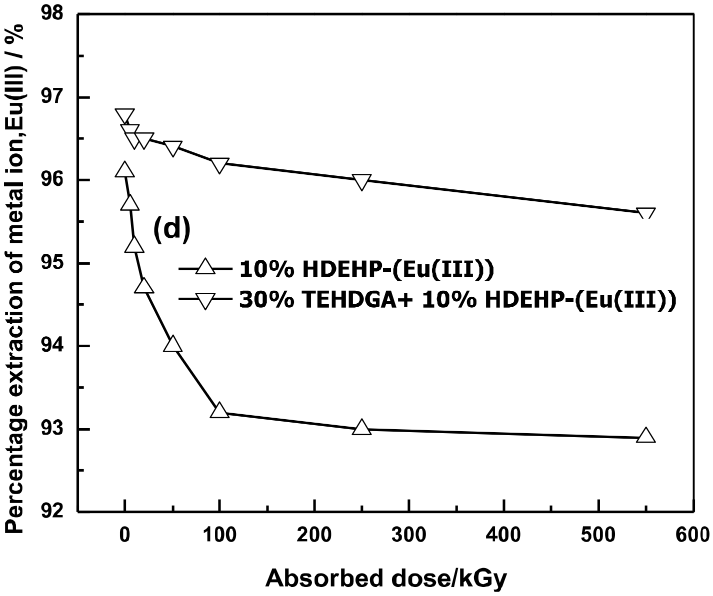


Figure 5.4. (d) Variation of percentage extraction of Eu(III) as a function of absorbed dose. Resin=10% HDEHP/ADS 400 or 30% TEHDGA+10%HDEHP/ ADS 400, Aqueous phase =0.01 M HNO_3, v/m=100.

5.6. Separation factor of Eu(III) over Am(III)

Table 5.1 shows the separation factor of Eu(III) over Am(III) achieved in all SIRs as a function of absorbed dose at 3 M and 0.01 M nitric acid. It can be seen that the variation in the SF of Eu(III) over Am(III) as a function of absorbed dose is quite insignificant at 3 M nitric acid. In CMPO SIR the SF remains at a constant value of 0.75 at all absorbed dose levels even though the distribution coefficients decrease with increase of absorbed dose. Addition of HDEHP to CMPO SIR decreases the SF to some extent at 0 kGy and the SF increases marginally with increase of absorbed dose. In case of TEHDGA SIR, the SF decreases marginally with increase of absorbed dose. Addition of HDEHP to TEHDGA SIR decreases the SF to some extent at 0 kGy and the SF increases marginally with increase of absorbed dose. Nevertheless, the variation in the separation factors at 3 M nitric acid are not quite significant as the extraction of Am(III) and Eu(III) at 3 M nitric acid are controlled essentially by the neutral extractant.

The SF of Eu(III) over Am(III) achieved at 0.01M nitric acid is also shown in table 5.1. Since the distribution coefficient of trivalent metal ion is predominantly controlled by HDEHP at 0.01 M nitric acid, the SF of Eu(III) over Am(III) obtained in HDEHP SIR at 0.01 M nitric acid is also shown in table 5.1. It can be seen that the SF decreases marginally from 3.8 to 2.7 with increase of absorbed dose in HDEHP SIR. Even though the presence of CMPO increased the distribution coefficient of Am(III) and Eu(III), as shown in figure 5.3 and 5.4, the SF decreased from 3.8 to 1.6 for the un-irradiated CMPO+HDEHP SIR. The SF then increases marginally from 1.6 to 1.8. In contrast to this, the presence of TEHDGA increases the SF of Eu(III) over Am(III) for the un-irradiated TEHDGA+HDEHP SIR and then the SF decreases with increase in the absorbed dose.

Table 5.1. Variation in the separation factor of Eu(III) over Am(III) at 3 M and 0.01 M nitric acid. Resins = 30% CMPO + 10% HDEHP, 30% TEHDGA + 10% HDEHP, 30% CMPO, 30% TEHDGA, 10% HDEHP (un-irradiated and irradiated up to 550 kGy)

Dose	SF at 3 M nitric acid in				SF at 0.01 M nitric acid in		
(kGy)	CMPO	CMPO + HDEHP	TEHDGA	TEHDGA + HDEHP	HDEHP	CMPO + HDEHP	TEHDGA + HDEHP
0	0.77	0.63	2.61	2.47	3.82	1.61	5.71
5	0.77	0.65	2.47	2.68	3.72	1.65	4.90
10	0.72	0.67	2.40	2.66	3.36	1.65	3.27
20	0.73	0.69	2.30	2.83	3.13	1.70	2.90
50	0.78	0.74	2.11	2.65	2.84	1.77	2.24
100	0.82	0.71	2.12	2.40	2.55	1.78	2.53
250	0.78	0.71	2.17	2.50	2.60	1.72	2.50
550	0.72	0.73	2.15	2.80	2.76	1.82	2.37

5.7. Conclusion

Solvent impregnated resins containing the neutral and acidic extractants namely CMPO, HDEHP, TEHDGA, CMPO+HDEHP and TEHDGA+HDEHP have been prepared and the radiolytic stability was evaluated at various absorbed dose levels. The SIRs were irradiated up to the absorbed dose level of 550 kGy. The results were compared with gamma irradiated CMPO or TEHDGA or HDEHP SIRs as well as with the un-irradiated SIRs. The extraction of Am(III) in SIR was studied at 3 M nitric acid and 0.01 M nitric acid. At 3 M nitric acid, the distribution coefficient of these metal ions in the neutral extractant impregnated was higher than that observed in the neutral + acidic extractant impregnated resin due to antagonistic effect.

On the other hand, at 0.01 M nitric acid, the presence of neutral extracant along with HDEHP in the resin, enhanced the extraction Am(III) and Eu(III) due to synergism. Since TEHDGA exhibits higher affinity towards trivalent metal ions as compared to CMPO, the distribution coefficient and percentage extraction of Am(III) and Eu(III) were more whenever TEHDGA is present in the resin phase as compared to CMPO SIR. The separation factor of Eu(III) over Am(III) was achieved in all SIRs as a function of absorbed dose at 3 M and 0.01 M nitric acid. The variation in the SF of Eu(III) over Am(III) as a function of absorbed dose is quite insignificant at 3 M nitric acid. The SF decreases marginally with increase of absorbed dose in HDEHP SIR at 0.01M nitric acid. It is concluded that radiation dose up to 550 kGy is not affecting the separation factor of Am(III) over Eu(III) significantly. Hence, these SIRs can be used in the plant for the separation of minor actinides from high level liquid waste.

5.8. References

1. K. Saipriya, R. Kumaresan, P. K. Nayak, K. A. Venkatesan, T. Kumar, M. P. Antony, Extraction behaviour of Am (III) and Eu (III) from nitric acid medium in CMPO-HDEHP impregnated resins, Radiochimica Acta, 104 (2016) 67-75.

2. G. Saipriya, R. Kumaresan, P. K. Nayak, K. A. Venkatesan, T. Kumar, M. P. Antony, Extraction behaviour of Am (III) and Eu (III) from nitric acid medium in TEHDGA-HDEHP impregnated resins, Radiochimica Acta, 104 (2016) 781-790.

3. B. J. Mincher, G. Modolo, S. P. Mezyk, Review: The Effects of Radiation Chemistry on Solvent Extraction 4: Separation of the Trivalent Actinides and Considerations for Radiation-Resistant Solvent Systems, Solvent Extr. Ion Exch., 28 (2010) 415-436.

4. B. J. Mincher, G. Modolo, S. P. Mezyk, Review Article: The Effects of Radiation Chemistry on Solvent Extraction 3: A Review of Actinide and Lanthanide Extraction, Solvent Extr. Ion Exch., 27 (2009) 579-606.

5. Y. Sugo, Y. Sasaki, S. Tachimori, Studies on hydrolysis and radiolysis of N,N,N′,N′-tetraoctyl-3-oxapentane-1,5-diamide, Radiochim. Acta, 90 (2002) 161-165.

6. Y. Sugo, Y. Izumi, Y. Yoshida, S. Nishijima, Y. Sasaki, T. Kimura, T. Sekine, H. Kudo, Influence of diluent on radiolysis of amides in organic solution, Rad. Phys. Chem., 76 (2007) 794-800.

7. Y. Sugo, M. Taguchi, Y. Sasaki, K. Hirota, T. Kimura, Radiolysis study of actinide complexing agent by irradiation with helium beam, Rad. Phys. Chem., 78 (2009) 1140-1144.

8. R. Chiarizia, E. P. Horwitz, Radiolytic stability of some recently developed ion exchange and extraction chromatographic resins containing diphosphonic acid groups, Solvent Extr. Ion Exch., 18 (2000) 109-132.

9. K. L. Nash, R. C. Gatrone, G. A. Clark, P. G. Rickert, E. Philip Horwitz, CMPO degradation, Hydrolytic and Radiolytic Degradation of OΦD (iB) CMPO: Continuing Studies, Sep. Sci. Technol., 23 (1988) 1355-1372.

10. R. B. Gujar, S. A. Ansari, A. Bhattacharyya, A. S. Kanekar, P. N. Pathak, P. K. Mohapatra, V. K. Manchanda, Radiolytic stability of N,N,N',N'-tetraoctyl diglycolamide (TODGA) in the presence of phase modifiers dissolved in n-dodecane, Solvent Extr. Ion Exch., 30 (2012) 278-290.

11. R. B. Gujar, S. A. Ansari, A. Bhattacharyya, P. K. Mohapatra, A. S. Kanekar, P. N. Pathak, V. K. Manchanda, Studies on the radiolytic stability of N,N,N',N'-tetra-2-ethylhexyl diglycolamide in n-dodecane solution containing different phase modifiers, J. Radioanal. Nucl. Chem., 288 (2011) 621-627.

12. J. N. Sharma, R. Ruhela, K. K. Singh, M. Kumar, C. Janardhanan, P. V. Achutan, S. Manohar, P. K. Wattal, A. K. Suril, Studies on hydrolysis and radiolysis of tetra(2-ethylhexyl)diglycolamide (TEHDGA)/isodecyl alcohol/n-dodecane solvent system, Radiochim. Acta, 98 (2010) 485–491.

13. P. Deepika, K. N. Sabharwal, T. G. Srinivasan, P. R. Vasudeva Rao, Studies on the use of N,N,N',N'-tetra(2-ethylhexyl) diglycolamide (TEHDGA) for actinide partitioning II: investigation on radiolytic stability, Solvent Extr. Ion Exch., 29 (2011) 230–246.

14. A. K. Pikaev, S. A. Kabakchi, G. F. Egorov, Some radiation chemical aspects of nuclear engineering, Radiat. Phys. Chem., 31 (1988) 789–803.

15. S. C. Tripathi, P. Bindu, A. Ramanujam, Proceedings of Indian Soc. of Analytical Scientists (ISAS) XIth Symposium (PETPHARMACHEM-95), Baroda, INDIA, 8 (1995) 141–143.

16. J. C. Neace, Diluent degradation products in the Purex solvent, Sep. Sci. Technol., 18 (1983) 1581.

17. P. K. Nayak, R. Kumaresan, K. A. Venkatesan, M. P. Antony, P. R. Vasudeva Rao, A new method for partitioning of trivalent actinides from high-level liquid waste, Sep. Sci. Technol., 48 (2013) 1409-1416.

CHAPTER 6

Chapter 6: Studies on the Adsorption behavior of Eu(III) on Irradiated and Un-irradiated Solvent Impregnated Resins Containing Neutral and Acidic Extractants

This present chapter explains about the adsorption behavior of Eu(III) from nitric acid medium on irradiated and un-irradiated Solvent Impregnated Resins (SIR) containing CMPO+HDEHP and TEHDGA+HDEHP. The adsorption behavior of Eu(III) in SIRs was evaluated by fitting the isothermal adsorption data into various models such as Langmuir [1, 2], Freundlich [3], Temkin [4] and Dubinin-Radushkevich [5]. Each adsorption model provides an insight into the nature of adsorption and the interaction happening between the adsorbent and adsorbate. In addition, the useful parameters such as apparent experimental capacity of the adsorbent and energy of adsorption can also be determined from adsorption models.

6.1. Introduction

An adsorption isotherm is a curve that relates the equilibrium concentration of a solute in the adsorbent phase, q_e, with that concentration in the liquid phase, C_e, at equilibrium and constant temperature. The adsorption isotherm can be described by an equation that relates the amount of solute adsorbed onto the solid phase with the equilibrium concentration of the solute in solution, at a given temperature. It should be noted that the adsorption isotherms were initially developed for describing the adsorption behavior of gases on solid surfaces and most often they were also utilized for describing the adsorption behavior of metal ions from aqueous solution on solid surfaces. There are several models for predicting the equilibrium distribution. However, the following four models are most commonly observed.

6.1.1. Langmuir adsorption isotherm

Among the various adsorption models, the Langmuir model is the simplest form of adsorption isotherm employed for describing the adsorption data. It is based on the assumption that the adsorbent surface is homogeneous [6, 7] in terms of energy of adsorption and there is no migration of adsorbate across the surface. It also assumes that the maximum adsorption corresponds to monolayer [8, 9] adsorption of the adsorbate, usually applicable for gaseous adsorption on solid surfaces. The non-linear expression for describing the Langmuir adsorption isotherm is shown in equation 6.1.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (6.1)$$

where q_e (in mg.g^{-1}) is the equilibrium concentration of the adsorbate on the adsorbent, q_m is the maximum concentration of the adsorbate on the solid phase at equilibrium, K_L is the Langmuir adsorption constant that determines the affinity of the adsorbent towards the adsorbate, and C_e (mg.mL^{-1}) is the equilibrium concentration of the adsorbate. At high concentration of C_e the value of q_m tends to approach the value q_e, i.e the apparent adsorption capacity equal to the equilibrium concentration of the adsorbate on the adsorbent, according to equation 6.1.

6.1.2. Freundlich adsorption isotherm

It was initially proposed as an empirical model for describing the adsorption of gaseous molecules on solid surfaces, applicable in several cases. Later, Sips et al. [10]

theoretically derived the Freundlich model and provided physical significance to the adsorption isotherm. This model assumes that the surface of the adsorbent was heterogeneous [11-14] and therefore the energy of adsorption was not uniform. The non-linear form of Freundlich adsorption model is represented by the relation shown in equation 6.2.

$$q_e = K_f C_e^{1/n} \tag{6.2}$$

where K_f (mL.g^{-1}) is the Freundlich adsorption constant, '*n*' represents the degree of heterogeneity of the surface. When $1/n$ is equal to 1, the surface is said to be homogeneous (similar to Langmuir) and the value lower than unity represents heterogeneous nature of surface.

6.1.3. Temkin isotherm

The Temkin isotherm considers only the chemical interactions happening between the adsorbate and adsorbent [15, 16]. The model assumes that the energy of adsorption of the adsorbate on the surface decreases linearly with coverage rather than logarithmically [17]. The non-linear expression for the Temkin model is shown in equation 6.3.

$$q_e = \left(\frac{RT}{b}\right)\ln\alpha + \left(\frac{RT}{b}\right)\ln C_e \tag{6.3}$$

where b is the variation in adsorption energy and α is the binding constant corresponding to the maximum binding energy. R is the gas constant and T is the temperature in Kelvin.

6.1.4. Dubinin-Radushkevich (D-R) isotherm

The physical and chemical nature of interactions happening between the adsorbent and adsorbate can be determined from the D-R adsorption model [18-20]. The non-linear form of D-R model is represented in the following equations.

$$q_e = q_m \exp\left(-K_{DR}\left[RT\ln\left(1+\frac{1}{C_e}\right)\right]^2\right) \quad (6.4$$

$$q_e = q_m \exp\left(-K_{DR}\varepsilon^2\right) \quad (6.5)$$

where K_{DR} is the D-R constant, ε is known as the Polanyi potential, R is the gas constant and T is the temperature in Kelvin. The D-R constant, K_{DR} is related to the mean free energy of adsorption E (in kJ.mole^{-1}) by equation 6.6.

$$E = \frac{1}{\sqrt{2K_{DR}}} \quad (6.6)$$

Depending upon the value of E, the nature of adsorption can be classified into physical or chemical adsorption [21-23]. When the value of E is lower than 8 kJ.mol^{-1}, the interaction happening between the adsorbent and adsorbate is considered as physical interaction and if it is more than 8 kJ.mol^{-1}, the interaction is chemical in nature. However, it should be noted that this is applicable for gases adsorption on solid surfaces.

6.2. Adsorption isotherm of Eu(III)

Eu(III) adsorption capacity of solvent impregnated resins containing neutral extractants such as CMPO, TEHDGA and acidic extractant HDEHP was measured by equilibrating 0.05 g of the adsorbent with 5 mL of nitric acid solution containing various quantities of europium nitrate spiked with $^{(152+154)}$Eu(III) tracer. Aliquots were collected from the aqueous phase before and after extraction. The amount of Eu(III) adsorbed was measured from the initial and final radioactivity values. The adsorption isotherm of Eu(III) on all SIRs (irradiated and un-irradiated) were determined, and the variation in the loading behavior of Eu(III) as a function of Eu(III) concentration in aqueous phase is shown in figures 6.1 to 6.8. Since the concentration of nitric acid in HLLW is in the range of 3-4 M, the loading of Eu(III) was studied only at 3 M nitric acid medium.

The initial concentration of Eu(III) in aqueous phase was varied from 10 mg.L^{-1} to 500 mg.L^{-1}. It can be seen from figures 6.1 to 6.8 that the loading of Eu(III) in the SIR phase increases rapidly with increase in the concentration of Eu(III) in aqueous phase in the beginning of the isotherm and thereafter the variation is gradual leading to saturation. The adsorption data were fitted with various model equations, discussed above and the non-linear fitting of the data are also shown in figures 6.1 to 6.8. The fitting constants determined from the non-linear curve fitting of various adsorption isotherms for un-irradiated and irradiated SIRs are displayed in table 6.1 and 6.2, respectively.

It can be seen from the tables, that the adsorption data were described well by the Langmuir model with R^2 value >0.96 in all cases. The apparent experimental capacity of Eu(III) adsorption on the un-irradiated CMPO SIR is about 12 mg.g^{-1} and its magnitude increased to 17.4 mg.g^{-1} in the presence of HDEHP i.e. in CMPO+HDEHP SIR. A similar behavior is also observed for TEHDGA SIR and TEHDGA+HDEHP SIR. It is important to note that the value of K_L, that determines the affinity of Eu(III) towards the adsorbent, is more when TEHDGA is present in the adsorbent as compared to CMPO SIR. In addition, the presence of HDEHP in TEHDGA SIR lowered the value of K_L to a significant extent. Comparing the apparent experimental capacity value determined for irradiated and un-irradiated SIRs, it can be seen that the capacity (q_m) was not affected to any significant extent with the increase of absorbed dose in case of CMPO or TEHDGA SIRs. However, in case of CMPO+HDEHP or TEHDGA+HDEHP SIR, the q_m values decreased upon irradiation (550 kGy).

The Freundlich fitting constants obtained from non-linear curve fitting of the experimental data are displayed in table 6.1 and 6.2. It can be seen that fitting of the data is not as good as Langmuir model fitting. The R^2 value for Freundlich fitting ranges from 0.78 to 0.93. In the un-irradiated SIR, the K_f values increased upon adding the acidic extractant to the neutral extractant present in the resin. However, there is no definite sequence in case of irradiated SIR. The values of 1/n ranges from 0.13 to 0.26 for both irradiated and un-irradiated SIR indicating the surface is heterogeneous. The tables 6.1 and 6.2 also show the parameters derived from the fitting of the Temkin adsorption model to the experimental data. The adsorption energy, b (in kJ.mol^{-1}) obtained for both un-irradiated and irradiated adsorbent are nearly comparable.

Among the various models described above, the experimental data were best fitted using the D-R adsorption model. Based on the value of correlation coefficients (R^2 value) and low Chi-square values, the Eu(III) adsorption data in irradiated and un-irradiated adsorbents follows the order, D-R model > Langmuir > Temkin > Freundlich. The fitting constants obtained for the experimental data using D-R isotherm are displayed in table 6.1 and 6.2. It can be seen that the adsorption capacity (q_m) obtained from D-R isotherm is comparable to the value of q_m, obtained from Langmuir model. Moreover, the study shows that the adsorption capacity of the adsorbent was not affected to a significant extent even after irradiation upto 550 kGy absorbed dose as discussed above.

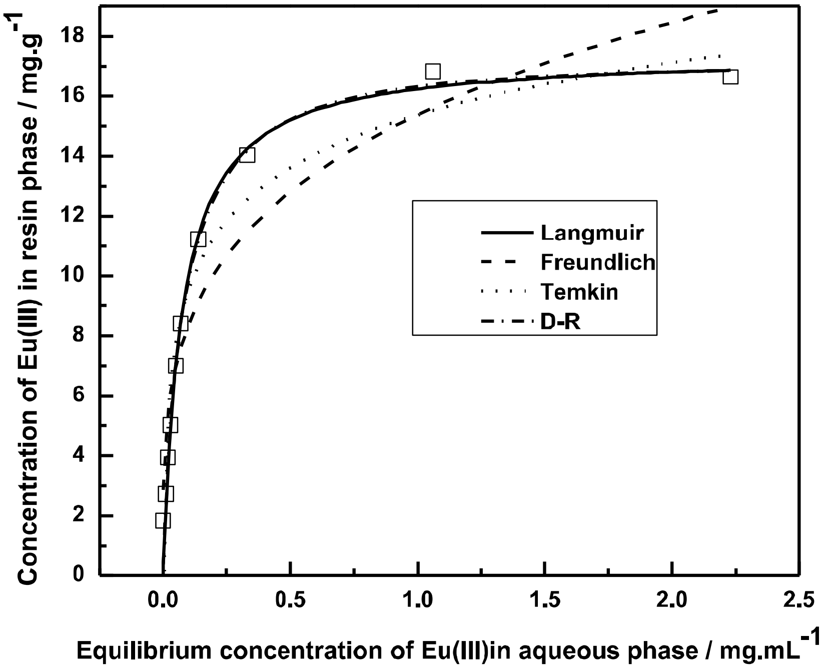


Figure 6.1. The non-linear fitting of various adsorption isotherm models on un-irradiated 30% CMPO+10% HDEHP/ADS 400 resin. Aqueous phase = 3 M nitric acid.

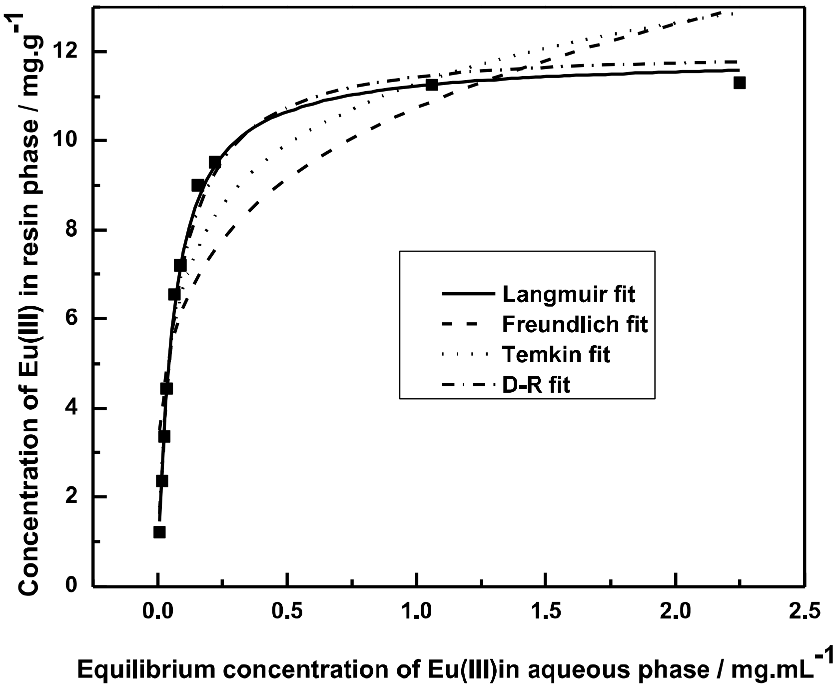


Figure 6.2. The non-linear fitting of various adsorption isotherm models on 550 kGy irradiated 30% CMPO+10% HDEHP/ADS 400 resin. Aqueous phase = 3 M nitric acid.

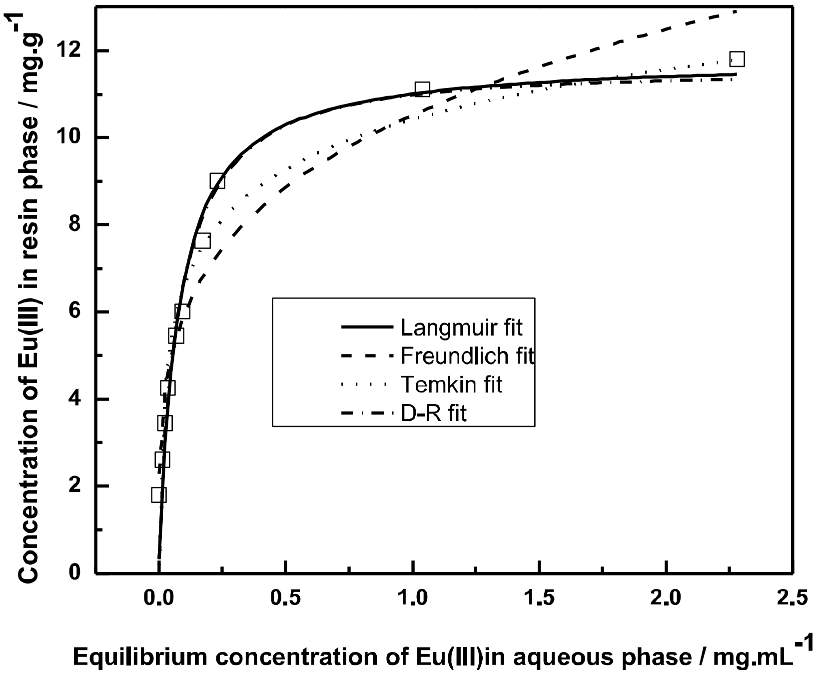


Figure 6.3. The non-linear fitting of various adsorption isotherm models on un-irradiated 30% CMPO /ADS 400 resin. Aqueous phase = 3 M nitric acid.

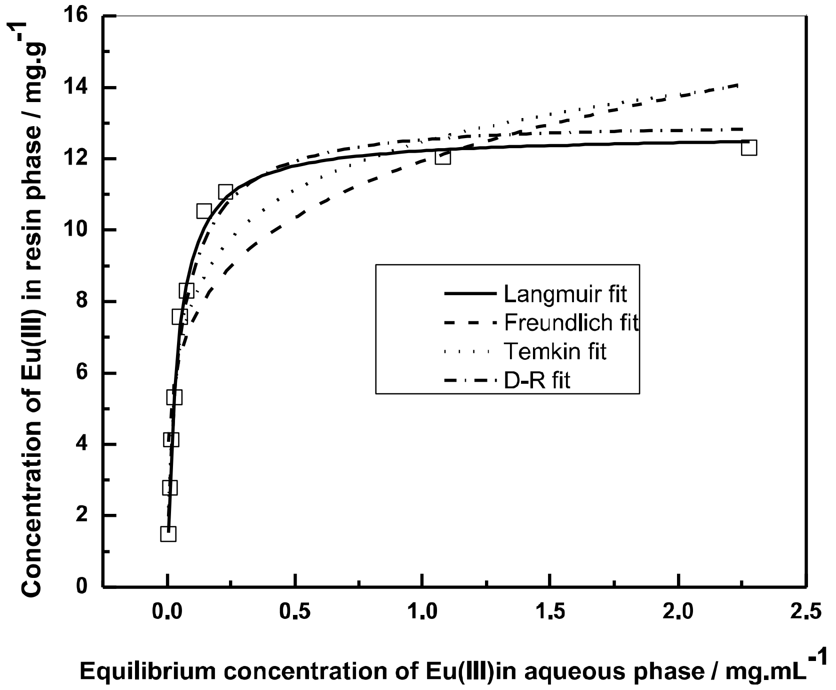


Figure 6.4. The non-linear fitting of various adsorption isotherm models on 550 kGy irradiated 30% CMPO /ADS 400 resin. Aqueous phase = 3 M nitric acid.

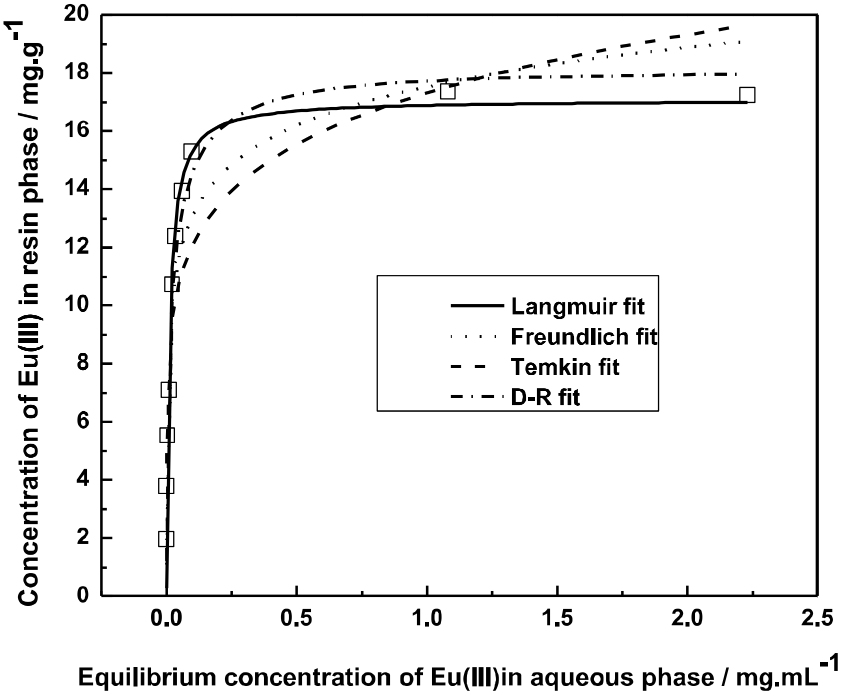


Figure 6.5. The non-linear fitting of various adsorption isotherm models on un-irradiated 30% TEHDGA+10% HDEHP/ADS 400 resin. Aqueous phase = 3 M nitric acid.

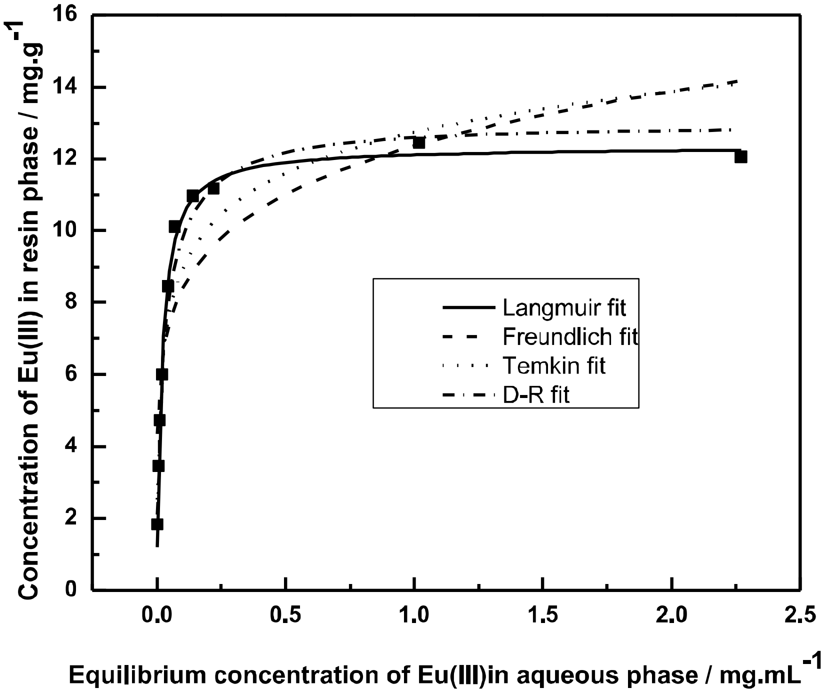


Figure 6.6. The non-linear fitting of various adsorption isotherm models on 550 kGy irradiated 30% TEHDGA +10% HDEHP/ADS 400 resin. Aqueous phase = 3 M nitric acid.

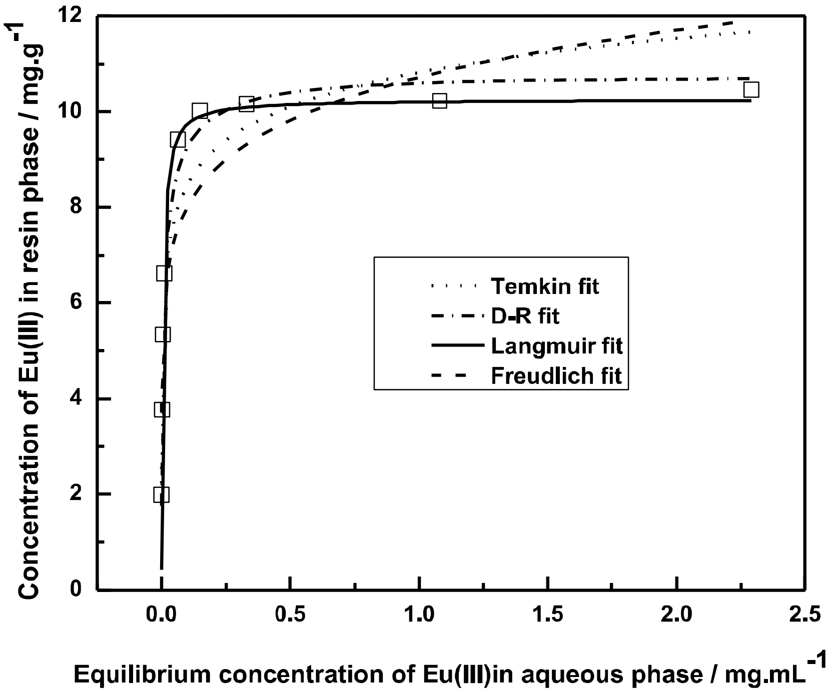


Figure 6.7. The non-linear fitting of various adsorption isotherm model on un-irradiated 30% TEHDGA/ADS 400 resin. Aqueous phase = 3 M nitric acid.

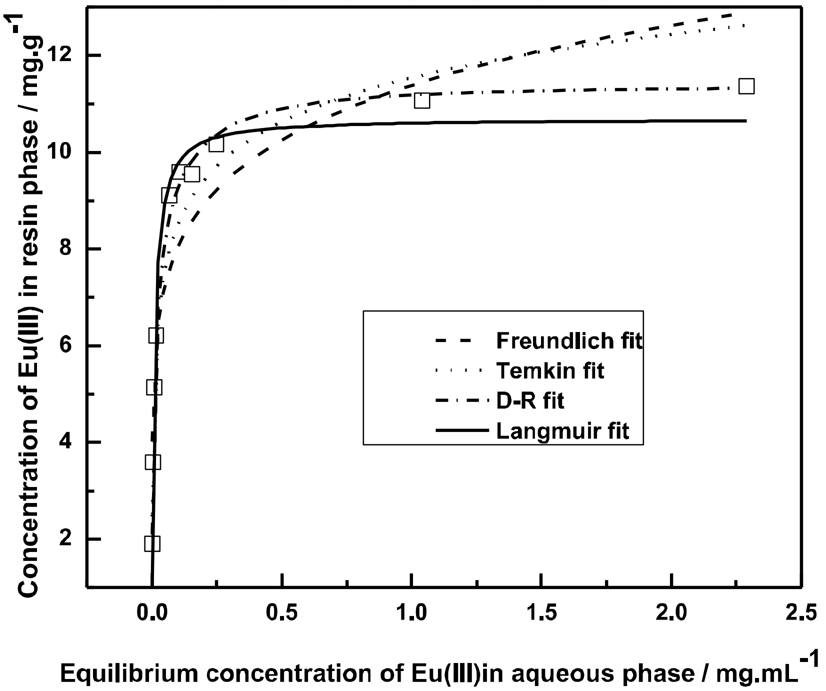


Figure 6.8. The non-linear fitting of various adsorption isotherm models on 550 kGy irradiated 30% TEHDGA/ADS 400 resin. Aqueous phase = 3 M nitric acid.

Table 6.1. Fitting constants and statistical parameters obtained from various adsorption isotherms for un-irradiated SIR systems

Un-irradiated				
Langmuir adsorption Isotherm				
	q_m(mg.g^{-1})	K_L(mL.mg^{-1})	R^2	χ^2
30%CMPO	11.83	13.36	0.96	0.47
30%CMPO+10%HDEHP	17.43	13.50	0.99	0.32
30%TEHDGA	10.26	187.05	0.96	0.49
30%TEHDGA+10%HDEHP	17	86.01	0.98	0.67
Freundlich adsorption Isotherm				
	K_f(mL.g^{-1})	1/n	R^2	χ^2
30%CMPO	10.51	0.25	0.93	0.91
30%CMPO+10%HDEHP	15.37	0.26	0.9	3.47
30%TEHDGA	10.72	0.13	0.83	1.96
30%TEHDGA+10%HDEHP	17.31	0.16	0.82	6.27
Temkin adsorption Isotherm				
	b(kJ.mol^{-1})	α (mL.g^{-1})	R^2	χ^2
30%CMPO	1.5	534	0.94	0.81
30%CMPO+10%HDEHP	0.97	423	0.93	2.48
30%TEHDGA	2.4	38194	0.92	0.89
30%TEHDGA+10%HDEHP	1.3	8523	0.92	2.83
D-R adsorption Isotherm				
	Q_m(mg.g^{-1})	E(kJ.mol^{-1})	R^2	χ^2
30%CMPO	11.47	5.78	0.97	0.40
30%CMPO+10%HDEHP	17	5.68	0.99	0.32
30%TEHDGA	10.73	10.92	0.988	0.14
30%TEHDGA+10%HDEHP	18.04	9.05	0.98	0.51

Table 6.2. Fitting constants and statistical parameters obtained from various adsorption isotherms for irradiated SIR systems (550 kGy)

Irradiated				
Langmuir adsorption Isotherm				
	q_m(mg.g^{-1})	K_L(mL.mg^{-1})	R^2	χ^2
30%CMPO	12.67	26.69	0.99	0.07
30%CMPO+10%HDEHP	11.9	17.43	0.99	0.066
30%TEHDGA	10.69	107.53	0.98	0.29
30%TEHDGA+10%HDEHP	12.33	54.17	0.99	0.15
Freundlich adsorption Isotherm				
	K_f(mL.g^{-1})	1/n	R^2	χ^2
30%CMPO	11.92	0.2	0.79	3.68
30%CMPO+10%HDEHP	10.74	0.23	0.81	2.87
30%TEHDGA	11.37	0.15	0.84	1.93
30%TEHDGA+10%HDEHP	12.35	0.16	0.78	3.56
Temkin adsorption Isotherm				
	b(kJ.mol^{-1})	α (mL/g)	R^2	χ^2
30%CMPO	1.3	615	0.91	1.55
30%CMPO+10%HDEHP	1.2	307	0.93	1.06
30%TEHDGA	1.8	6633	0.94	0.68
30%TEHDGA+10%HDEHP	1.5	2318	0.90	1.60
D-R adsorption Isotherm				
	Q_m(mg.g^{-1})	E(kJ.mol^{-1})	R^2	χ^2
30%CMPO	12.93	6.75	0.98	0.32
30%CMPO+10%HDEHP	11.91	6.66	0.988	0.18
30%TEHDGA	11.37	9.30	0.99	0.07
30%TEHDGA+10%HDEHP	12.87	8.13	0.98	0.29

6.3. Conclusion

The SIRs containing the neutral extractants such as CMPO, TEHDGA and acidic extractant namely HDEHP and their combined solvent systems CMPO+HDEHP and TEHDGA+HDEHP have been prepared and Eu(III) adsorption behavior was studied at 3 M nitric acid. In similar way, Eu(III) adsorption behavior was also studied for the irradiated systems. The loading behavior of Eu(III) as a function of Eu(III) concentration in aqueous phase in various SIRs was fitted using Langmuir, Freundlich, Temkin and D-R models. The loading of Eu(III) in SIR phase increased rapidly with increase in the concentration of Eu(III) in the beginning of the isotherm. Later, the variation was gradually leading to saturation. The apparent experimental capacity of Eu(III) adsorption was high in CMPO+HDEHP SIR compared to CMPO SIR. A similar behavior was also observed for TEHDGA SIR and TEHDGA+HDEHP SIR.

Langmuir adsorption constant (K_L) was determined for various SIR's to compare the affinity towards Eu(III). The Freundlich fitting constants indicated that both irradiated and un-irradiated SIR is having heterogeneous surfaces. The adsorption energy b (in $kJ.mol^{-1}$) obtained for both un-irradiated and irradiated adsorbents were obtained using Temkin model. The apparent experimental capacities of these SIR's were obtained also from D-R model. Based on the statistics of fitting, the Eu(III) adsorption data was best fitted in the following order, D-R model > Langmuir > Temkin > Freundlich. The adsorption capacity obtained from D-R isotherm was comparable with the capacity obtained from Langmuir model and the results also revealed that the adsorption capacity was not affected to any significant extent in these SIRs, even at the absorbed dose level of 550 kGy. Therefore, these SIRs can be used for the single cycle separation of Eu(III) from high-level liquid waste.

6.4. References

1. I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc., 40 (1918) 1361-1403.

2. I. Langmuir, The constitution and fundamental properties of solids and liquids. Part I, Solids, J. Am. Chem. Soc., 38 (1916) 2221-2295.

3. H. M. F. Freundlich, Over the adsorption in solution, J. Phys. Chem., 57 (1906) 1100-1107.

4. M. I. Temkin, V. Pyzhev, Kinetics of ammonia synthesis on promoted iron catalysts, Acta physiochim. URSS, 12 (1940) 217-222.

5. M. M. Dubinin, The potential theory of adsorption of gases and vapors for adsorbents with energetically nonuniform surfaces, Chem. Rev., 60 (1960) 235-241.

6. H.M. Li, J.S. Liu, L.L. Zhu, X.Z. Gao, S.L. Wei, L. Guo, Recovery of indium (III) from a hydrochloric acid medium with two types of solvent impregnated resins containing sec-octylphenoxy acetic acid, Solvent Extr. Res. Dev. Jpn., 21 (2014) 147-161.

7. A. Hosseini-Bandegharaei, M. Karimzadeh, M. Sarwghadi, A. Heydarbeigi, S. H. Hosseini, M. Nedaie, H. Shoghi, Use of a selective extractant-impregnated resin for removal of Pb (II) ion from waters and wastewaters: Kinetics, equilibrium and thermodynamic study, Chem. Eng. Res. Des., 92 (2014) 581–591.

8. N. Van Nguyen, J. C. Lee, M. K. Jha, K. Yoo, J. Jeong, Copper recovery from low concentration waste solution using Dowex G-26 resin, Hydrometallurgy, 97 (2009) 237–242.

9. J. Eastoe, J. S. Dalton, Dynamic surface tension and adsorption mechanisms of surfactants at the air water interface, Adv. Colloid Interf. Sci., 85 (2000) 103-144.

10. R. Sips, On the structure of a catalyst surface, J. Chem. Phys., 16 (1948) 490 – 495.

11. S. Kocaoba, Comparison of Amberlite IR 120 and dolomite's performances for removal of heavy metals, J. Hazard. Mater., 147 (2007) 488–496.

12. N. D Hutson, R. T Yang, A Dynamic Approach to Brownian Coagulation of Electrostatically Stabilized Colloid Particles, Adsorption J. Colloid. Interf. Sci., (2000) 189.

13. N. Van Nguyen, J. C. Lee, J. K. Jeong, B. D. Pandey, Enhancing the adsorption of chromium (VI) from the acidic chloride media using solvent impregnated resin (SIR), Chem. Eng. J., 219 (2013) 174–182.

14. G. B. McKay, H. S. Blair, J. R. Garden, Adsorption of dyes on chitin. I. Equilibrium studies, J. Appl. Polym. Sci., 27 (1982) 3043-3057.

15. I. Zawierucha, J. Kozlowska, C. Kozlowski, A. Trochimczuk, Sorption of Pb (II), Cd (II) and Zn (II) performed with the use of carboxyphenylresorcinarene-impregnated Amberlite XAD-4 resin, Desalin. Water Treat., 52 (2014) 314–323.

16. S. Memon, A. Ali Bhatti, Arsenate and Dichromate Removal Efficiency of a New Calix [4] arene Impregnated Resin, Polycyclic Aromat. Compd., 34 (2014) 280–308.

17. C. Aharoni, M. Ungarish, Kinetics of activated chemisorption. Part 2. Theoretical models, J. Chem. Soc. Faraday Trans., 73 (1977) 456–464.

18. A. O. Dada, A. P. Olalekan, A. M. Olatunya, O. Dada, Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn^{2+} onto phosphoric acid modified rice husk, IOSR J. Appl. Chem., 3 (2012) 38-45.

19. M. M. Dubinin, E. D. Zaverina, L. V. Radushkevich, Sorption and structure of active carbons. I. Adsorption of organic vapors, Zh. Fiz. Khim., 21 (1947) 1351–1362.

20. A. Gunay, E. Arslankaya, I. Tosun, Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics, J. Hazard. Mater., 146 (2007) 362–371.

21. A. Dabrowski, Adsorption-from theory to practice, Adv. Colloid Interface Sci., 93 (2001) 135–224.

22. H. Zheng, Y.Wang, Y. Zheng, H. Zhang, S. Liang, M. Long, Equilibrium, kinetic and thermodynamic studies on the sorption of 4-hydroxyphenol on Cr-bentonite, Chem. Eng. J., 143 (2008) 117–123.
23. K. Saltalı, A. Sarı, M. Aydın, Removal of ammonium ion from aqueous solution by natural Turkish (Yıldızeli) zeolite for environmental quality, J. Hazard. Mater., 141 (2007) 258–263.

CHAPTER 7

Chapter 7: Summary and Conclusions

This chapter summarizes the results of the work described in the thesis. The present study was undertaken to study the use of solvent impregnated resins containing neutral extractant such as CMPO, TEHDGA and acidic extractant HDEHP, and their combination CMPO+HDEHP, TEHDGA+HDEHP for the extraction of Am(III) and Eu(III) from nitric acid medium. Extraction studies were carried out with simulated fast reactor high level liquid waste (FR-SHLLW) using TEHDGA+HDEHP solvent impregnated resin. The radiolytic stability of the solvent impregnated resins towards gamma radiation was also studied. The loading behavior of Eu(III) as a function of Eu(III) concentration in aqueous phase in various SIRs was explained. The data were fitted using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models. The summary of the results is described below.

7.1. Extraction behavior of Am(III) & Eu(III) in CMPO-HDEHP impregnated resins

Solvent impregnated resins containing octyl(phenyl)-*N*,*N*-diisobutylcarbamoyl methylphosphine oxide (CMPO) or bis-(2-ethylhexyl)phosphoric acid (HDEHP) and CMPO+HDEHP were prepared and studied for the extraction of Am(III) and Eu(III) from nitric acid medium. These extractants were impregnated over a solid polymeric support, Tulsion ADS 400. The extraction of Am(III) and Eu(III) was studied as a function of various parameters such as concentration of nitric acid in aqueous phase and the concentration of CMPO and HDEHP in the resin phase. The distribution coefficient of Am(III) and Eu(III) in the impregnated resin increased with increase in the concentration of nitric acid for CMPO-impregnated resin, whereas a reverse trend was observed in HDEHP impregnated resin. In case of combined resin containing both the extractants, synergism was observed at low nitric acid concentration and antagonism at high nitric acid concentration. The antagonism observed at high nitric acid concentration could be due to the formation of HDEHP-CMPO adduct that seems to lower the concentration of free CMPO available for complexation of trivalent metal ion. The mechanism of extraction was probed by slope analysis method at 0.01 and 2M nitric acid concentrations. The separation factor of Eu(III) over Am(III) was obtained as 3-4, when citrate-buffered DTPA was present in aqueous phase at pH 3.

7.2. Extraction behavior of Am(III) and Eu(III) in TEHDGA-HDEHP impregnated resins

The extraction behavior of Am(III) and Eu(III) from nitric acid medium was studied in the solvent impregnated resins containing neutral extractant (obey CHON principle) tetra-bis(2-ethylhexyl)diglycolamide (TEHDGA) or bis-(2-ethylhexyl)phosphoric acid (HDEHP) or mixture of TEHDGA+HDEHP. The kinetics of Am(III) and Eu(III) extraction in the impregnated resin was studied at 1 M nitric acid. It was observed that rapid uptake of Am(III) and Eu(III) in the initial stages of equilibration followed by the establishment of equilibrium occurred in 100 min. The effect of various parameters, such as the concentration of nitric acid in aqueous phase and concentration of TEHDGA and HDEHP in resin phase, on the distribution coefficient of Am(III) and Eu(III) was studied. The distribution coefficient and slope analysis of the distribution data indicated the participation of on an average of 1–2 molecules of TEHDGA and three molecules HDEHP for the extraction of trivalent metal ions in the individual resins. The distribution coefficient of Am(III) and Eu(III) in HDEHP-impregnated resin decreased and that in TEHDGA-impregnated resin increased, with increase in the concentration of nitric acid. In a combined (TEHDGA+ HDEHP) system, synergic extraction of Am(III) and Eu(III) was observed at lower nitric acid concentration and antagonism was observed at higher nitric acid concentration. The synergistic behavior was attributed by the involvement of both TEHDGA and HDEHP in the extraction of Am(III) and Eu(III). During synergism, the participation of HDEHP was lowered to accommodate the involvement of TEHDGA, in the extraction of Am(III) and Eu(III) at low nitric acid concentration. However, at higher nitric acid concentration, addition of HDEHP reduced the the involvement of TEHDGA for the complexation of metal ions.

The extraction of various metal ions present in FR-SHLLW using the solvent impregnated resin containing TEHDGA+ HDEHP was studied. The elemental composition of fast reactor simulated high level liquid waste (FR-SHLLW) before & after equilibration was analyzed by ICP-OES. To avoid the extraction of Pd(II) and Zr(IV), 0.05 M of CyDTA was added. At pH 3.5 with the aqueous phase containing 0.005 M DTPA + 0.1 M CA + 1 M $NaNO_3$, a SF of 5 was obtained for the separation of Am(III) over Eu(III) using 30% TEHDGA + 20% HDEHP impregnated resin.

7.3. Radiolytic degradation studies of SIRs containing neutral extractants such as CMPO and TEHDGA in conjunction with an acidic extractant HDEHP

Since the solvent impregnated resins (SIR) such as CMPO+HDEHP and TEHDGA+HDEHP were studied for the extraction of Am(III) and Eu(III) from nitric acid, and proposed for the single cycle separation of Am(III) from HLLW, it was necessary to understand the radiolytic stability of the combined solvent system with respect to gamma radiation. In view of this, the SIR was irradiated to various dose levels by γ-radiation and the distribution ratio of Am(III) and Eu(III) was measured as a function of absorbed dose. The absorbed dose was varied from 1 kGy to 550 kGy and the results were compared with un-irradiated condition (0 kGy). The distribution coefficient of Am(III) decreased with increase of absorbed dose. The extraction of Am(III) and Eu(III) in SIR was studied at 3 M nitric acid and 0.01 M nitric acid. At 3 M nitric acid, the distribution coefficient of these metal ions in the neutral extractant impregnated resin was higher than that observed in the neutral+acidic extractant impregnated resin due to antagonistic effect. On the other hand, at 0.01 M nitric acid, the presence of neutral extractant along with HDEHP in the resin, enhanced the extraction of Am(III) and Eu(III) due to synergism. Since TEHDGA exhibited higher affinity towards trivalent metal ions as compared to CMPO, the distribution coefficient of Am(III) and Eu(III) was more whenever TEHDGA was present in the resin phase as compared to CMPO SIR. The distribution coefficient of Eu(III) was always higher than those observed for Am(III) under similar conditions, at all absorbed dose levels. In addition, the distribution coefficient observed for Eu(III) in un-irradiated SIR was about 2-3 times higher than those observed for Am(III). The variation in the SF of Eu(III) over Am(III) as a function of absorbed dose was quite insignificant at 3 M nitric acid. The extraction of Am(III) and Eu(III) at 3M nitric acid was essentially controlled by the neutral extractant (TEHDGA). The presence of TEHDGA increased the SF of Eu(III) over Am(III) for the un-irradiated TEHDGA+HDEHP SIR and then the SF decreased with increase in the absorbed dose. The separation factor of Eu(III) over Am(III) for CMPO+HDEHP resin increased with increase in the absorbed dose.

7.4. Studies on the adsorption behavior of Eu(III) on irradiated & un-irradiated SIRs containing neutral (CMPO, TEHDGA) and acidic extractant (HDEHP)

The trivalent actinide selective neutral extractants, carbamoylmethylphosphine oxide (CMPO) and bis-(2-ethylhexyl)diglycolamide (TEHDGA) in conjunction with an acidic extractant bis-2-ethylhexylphosphoric acid (HDEHP) was impregnated in Tulsion ADS 400, and the resultant solvent impregnated resin (SIR) was studied for the extraction of Eu(III) from dilute nitric acid medium. The extraction behavior of Am(III) and the loading behavior of Eu(III) in the SIR was studied as a function of absorbed dose up to 550 kGy, at different nitric acid concentrations in aqueous phase. The extraction isotherm of Eu(III) in various SIRs have been fitted using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) adsorption models. Each adsorption model provides an insight into the nature of adsorption and the interaction happening between the adsorbent and adsorbate. Langmuir model was based on the assumption that the adsorbent surface is homogeneous in terms of energy of adsorption and there was no migration of adsorbate across the surface. The maximum amount of adsorption was limited to monolayer coverage of the surface sites. Freundlich model explained the adsorption of the metal ion over the heterogeneous surface. Here the energy of adsorption was not uniform. The physical or chemical nature of interactions happening between the adsorbent and adsorbate can be determined from the D-R adsorption model. Temkin model was based on the assumption that adsorbate-adsorbate repulsions the heat of adsorption of all the molecules in the layer decreased linearly with the coverage of molecules.

The adsorption studies were carried out at 3M nitric acid, as the concentration of nitric acid in HLLW was in the range of 3-4 M. The loading of Eu(III) in the SIR phase increased rapidly with increase in the concentration of Eu(III) in aqueous phase in the beginning of the isotherm and thereafter the variation was gradual leading to saturation. The adsorption data were fitted with various model equations, such as Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) adsorption models.

The adsorption data were described well by the Langmuir model with R^2 value >0.96 in all cases. The apparent experimental capacity of Eu(III) on irradiated and unirradiated resins of all types (CMPO, TEHDGA, CMPO+HDEHP and TEHDGA+HDEHP) were obtained. The Langmuir adsorption constant (K_L) was measured to find out the affinity of Eu(III) towards the adsorbent. It was observed that K_L was more when TEHDGA is present in the adsorbent as compared to CMPO SIR. The apparent experimental capacity values were determined and compared for irradiated and un-irradiated SIRs, it was observed that the capacity (q_m) was not affected to any significant extent with the increase of absorbed dose in case of CMPO or TEHDGA SIRs. However, in case of CMPO+HDEHP or TEHDGA+HDEHP SIR, the q_m values decreased upon irradiation (550 kGy). The R^2 value for Freundlich fitting ranges from 0.78 to 0.93. The values of 1/n ranges from 0.13 to 0.26 for both irradiated and un-irradiated SIR indicating the surface is heterogeneous. The adsorption energy b (in $kJ.mol^{-1}$) obtained for both un-irradiated and irradiated adsorbent were nearly comparable based on Temkin model. Based on the value of correlation coefficients (R^2 value) and low Chi-square value, the Eu(III) adsorption data in irradiated and un-irradiated adsorbents, the D-R adsorption model was found to fit the experimental data over other models. The adsorption capacity (q_m) obtained from D-R isotherm was comparable to the value of q_m, obtained from Langmuir model. The study shows that the adsorption capacity of the adsorbent was not affected to a significant extent even after irradiation upto 550 kGy.

CHAPTER 8

Chapter 8: Scope of Future Studies

The combined solvent impregnated resins (SIR) such as CMPO+HDEHP, TEHDGA+HDEHP have been prepared and studied for the extraction of Am(III) and Eu(III) from nitric acid medium. Synergistic extraction of Am(III) and Eu(III) was observed at lower nitric acid concentration (< 0.5 M) and antagonism was observed at higher nitric acid concentration. The extraction profile of Am(III), lanthanides and some fission products were studied in the combined system (TEHDHA+HDEHP) from FR-SHLLW. Selective separation of Am(III) was studied with aqueous soluble complexing agents such as diethylenetriaminepentaacetic acid (DTPA) and citric acid (CA). The radiolytic stability of a SIRs such as CMPO, TEHDGA, HDEHP, CMPO + HDEHP and TEHDGA + HDEHP were evaluated at various absorbed γ-dose levels.

The adsorption isotherm of Eu(III) on all SIRs (irradiated and un-irradiated) were determined and the variation in the loading behavior of Eu(III) as a function of Eu(III) concentration in aqueous phase was studied. Adsorption isotherm was determined by equilibrating the SIR's with different initial concentrations of europium in the range of 10–500 $mg.L^{-1}$ at 3 M nitric acid concentration. Adsorption isotherm describes the relationship between the amount of adsorbate adsorbed on the adsorbent and the concentration of dissolved adsorbate in the aqueous at equilibrium and constant temperature.

The analysis of the adsorption isotherm data was studied by fitting them to different isotherm models such as Langmuir, Freundlich, Temkin and Dubini–Radushkevich isotherms. The useful parameters such as apparent experimental capacity of the adsorbent and energy of adsorption were determined from adsorption models. In continuation to the work presented in this thesis, further studies can be carried out to improve the extraction performance and to achieve the better separation of Am(III) over Eu(III). The following studies were suggested.

1. In the present study, solvent impregnated resins were used for the extraction of Am(III) and Eu(III). However, due to the poor chemical stability of these impregnated resins, the ligands can be chemically anchored. The utility of the resin phase will be more in chemically anchored solid phase extractants (SPEs) (or also known as anchored resins). Similarly, chemically inert inorganic solid supports such as silica grafted with various organic compounds can be replaced to overcome the problems associated with radiolytic degradation and disposal of spent organic resins.

2. In the present study, CMPO and TEHDGA acted as neutral extractant and HDEHP acted as acidic extractant. The extraction studies with FR-SHLLW indicated that it was necessary to develop ligands that can minimize or eliminate the extraction of unwanted metal ions. These unwanted metal ions always interfere during stripping and subsequent lanthanide-actinide separation. Instead of these extractants, other neutral extractants such as DMDOHEMA, and DMDOTDMA and some acidic extractant such as PC88A and CYANEX 272 can be combined and studied extensively for better separation factor for lanthanides over actinides.

3. Real HLLW contains trivalent minor actinides, lanthanides and fission products along with small concentrations of U(VI) and Pu(IV). This shows

that the detailed extraction studies were required with respect to all metal ions present in the actual fast reactor HLLW. In this context, more studies need to be carried out for establishing a solid phase extraction based mutual separation of lanthanides and actinides.

4. In batch studies selective separation of Am(III) was tried with aqueous soluble complexing agents, such as diethylenetriaminepentaacetic acid (DTPA) and citric acid (CA). The separation factor achieved using these reagents was not adequate. For the better improvement of the mutual separation of Am(III) from Eu(III) column method can be employed. However, our investigations also indicate that more studies are needed to develop efficient stripping reagents for separating Am(III) from other lanthanides.

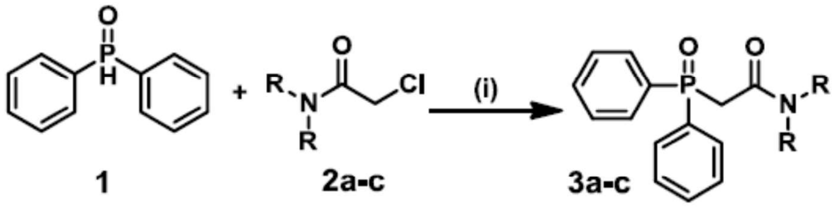
5. The CMPO+HDEHP and TEHDGA+HDEHP solvent impregnated resins (SIR) showed adequate radiation stability upto 550kGy gamma dose. However, the present work was restricted only to the influence of γ-dose. During the irradiation, the SIRs can form a wide variety of degradation products. No attempt was made to understand the degradation pattern, and nature of degradation products. The characterization of degradation product can be studied. The role of degradation products on extraction and stripping of metal ions can be studied. The radiation stability under alpha-exposure and the hydrolytic stability can also be studied.

6. The adsorption isotherm was determined only w.r.t. Eu(III) ion. The adsorption isotherm of other metal ions can be studied. The effects of

various system parameters such as acidity of solution, adsorbent dosage, initial europium concentration time and temperature can be examined. All adsorption studies can also be studied in column chromatographic mode.

Appendix-1

Synthesis of diphenyl-N, N-dialkyl carbamoylmethylphosphine Oxide (CMPO)



Into a 500 mL, two-necked, round-bottomed flask equipped with a reflux condenser and a septum, was placed a solution of diphenyl phosphineoxide (1 equivalent), corresponding chloroacetamide (1.1 equivalents) and 0.5 g of aliquot 336 in 75 mL of dichloromethane. The reaction mixture was cooled to 0 °C and added 50% of aqueous sodium hydroxide (3 equivalents). The solution was stripped at reflux until completion of reaction as monitored by TLC. Organic layer is separated and washed with water followed by saturated sodium chloride solution. The organic layer was dried over anhydrous sodium sulphate and concentrated under reduced pressure. The resulted solid was purified by washing several times with petroleum ether.

Glossary

ACSEPT	Actinide reCycling by SEParation and Transmutation
ADS	Accelerator Driven System
AHWR	Advanced Heavy Water Reactors
An(III)	Trivalent Actinides
BRIT	Board of Radiation and Isotope Technology
BTBP	Bis Triazine Bis Pyridine
BTP	Bis Triazine Pyridine
BWR	Boiling water reactor
CA	Citric Acid
CMPO	n-Octyl(phenyl)-N,N-diisobutylCarbamoylMethyl Phosphine Oxide
CyDTA	Trans-1,2-Cyclohexanediamine-N,N,N',N'-tetraacetic acid
CyMe4-BTBP	2,6-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo [1,2,4]triazy-3-yl)-[2,2']bipyridine
D^3DODGA	N,N-di-dodecyl-N',N'-di-octyl-3-oxapentane-1,5-diamide or Di-DoDecyl-Di-Octyl-DiGlycolAmide
DCC	Dicyclohexylcarbodiimide
DGAs	Diglycolamides
DIAMEX	DIAMide EXtraction
DIDPA	Di-IsoDecyl-Phosphoric Acid
D_M	Distribution ratio of Metal ion, M
DMDBTDMA	N,N’-DiMethyl-N,N’-DiButylTetraDecyl MalonAmide
DMDOHEMA	N,N’-DiMethyl-N,N’-DiOctyl-2-HexylEthoxy MalonAmide

DTPA	Diethylenetriamine pentaacetic acid
ECIL	Electronic Corporation of India Limited
EDTA	Bis(ethylenediaminetetraacetic acid)
FBRs	Fast Breeder Reactors
FBTR	Fast Breeder Test Reactor
FPs	Fission Products
FR	Fast Reactor
FTIR	Fourier Transformation Infra Red spectrospcopy
GWe	Giga Watt electric
HAW	High Active Waste
HDEHDGA	N,N-di-2-ethylhexyl diglycolamic acid
HDEHP	Di(2-ethylhexyl) Phosphoric Acid
HDHP	Di-n-hexyl Phosphoric acid
HLLW	High Level Liquid Waste
HPGe	High Pure Germanium
HSAB	Hard and Soft Acids and Bases
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
KAMINI	KAlpakkam MINI
K_d	Distribution coefficient of metal ions
keV	Kilo electron volts
kGy	Kilo Gray
kWh	Kilo Watt hour
LIX 63	5,8-diethyl-7-hydroxy-6-dodecanone oxime

LIX 64	2-Hydroxy-5-dodecylbenzophenone oxime
Ln(III)	Trivalent Lanthanides
LWR	Light water reactor
MA	Minor actinide
MeV	Million electron Volt
MWd	Mega Watt days
NaI(Tl)	Sodium Iodide (Thalium)
n-DD	*n*-Dodecane
NMR	Nuclear magnetic resonance spectrum
OFS	Organo Functionalized Silica
ORNL	Oak Ridge National Laboratory
P&T	Partitioning and Transmutation
PALADIN	Partition of Actinides and Lanthanides with Acidic extractant, Diamide, and INcinerable complexants
PHWR	Pressurized Heavy Water Reactors
PMT	photo multiplier tube
PUREX	Plutonium Uranium Recovery by Extraction process
SANEX	Selective ActiNide Extraction
SF	Separation factor
SHLLW	Simulated High Level Liquid Waste
SIRs	Solvent impregnated resins
SMART	Single cycle method for Minor Actinide partitioning using completely incinerable ReagenTs
SNF	Spent Nuclear Fuel

SPE	Solid phase extractants
TALSPEAK	Trivalent Actinide Lanthanide Separation with Phosphorus-Reagent Extraction from Aqueous Komplexes
TBP	Tri-*n*-Butyl Phosphate
Te	Tonne
TEHDGA	N,N ,N’,N’-ethylhexyl 3-oxapentane-1,5-diamide or N,N,N’,N’-tetra-2-ethylhexyl diglycolamide
TLC	Thin-Layer Chromatography
TODGA	N,N,N',N'-tetra-octyl-3-oxapentane-1,5-diamide or N,N,N’,N’-tetra-octyl diglycolamide
TRUEX	TRans Uranium element EXtraction
TRUSPEAK	TRansUranic elements Separation by Phosphours based Extractants from Aqueous Komplexes
TTA	Thenoyltrifluoro acetone
UDGAs	Unsymmetrical Diglycolamides
XAD2 / XAD4	hydrophobic cross-linked polystyrene copolymer
XAD-7	Acrylic ester

SOLID PHASE EXTRACTION BEHAVIOR OF Am(III) AND Eu(III) IN SOLVENT IMPREGNATED RESINS CONTAINING CMPO, TEHDGA AND HDEHP AND THEIR DEGRADATION STUDIES

By

G. SAIPRIYA

Enrolment No: CHEM01201104006

Bhabha Atomic Research Centre, Mumbai

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