SYNTHESIS AND CHARACTERIZATION OF SUBSTITUTED HYDROXAMIC ACID AND ITS PERFORMANCE IN THE SEPARATION AND PURIFICATION OF Pu AND U

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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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Publications

Journals

1. **S.Sukumar**, Pradeep Kumar Sharma, P. Govindan and R.V. Subba Rao, "Purification of uranium product from Pu contamination using acetohydroxamic acid (AHA) based process", J. Radioanal. Nucl. Chem. (2013) 295: 191-196.

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DEDICATIONS

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(S. Sukumar)

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SYNOPSIS

1. Introduction

The Indian nuclear power program envisaged three stages for effective utilization of limited resources for the production of nuclear energy [1]. The first stage is based on the concept of pressurized heavy water reactors (PHWRs) which use natural uranium as the fuel. In the second stage, the reprocessed plutonium and depleted uranium from PHWRs are used in fast breeder reactors (FBRs) for effective utilization of the limited resources of uranium. In the FBR, Th/ThO_2 is used as blanket material, which produces ^{233}U. The isotope ^{233}U thus obtained is reprocessed and used as fuel along with Pu/Th in the third stage. The success of the Indian nuclear power program depends on the efficiency in reprocessing the spent fuel discharged from the nuclear reactors. Matured technology for the reprocessing of spent fuels discharged from the thermal reactors

(PHWR) is available in India, whereas, reprocessing technologies are being developed for the fuels discharged from fast reactors.

In order to realize the three stages of Indian nuclear power program, reprocessing of the spent fuel is essential for separating uranium and plutonium from the fission products, with the view to effective using of limited uranium resources. For both thermal and fast reactor spent fuel reprocessing, India has chosen the aqueous based PUREX process [2]. This process involves the following steps.

- Fuel transport from the reactor and storage
- Head end process, which involves chemical or mechanical decladding, dissolution of fuel material using nitric acid, feed clarification and adjustment of chemical conditions of the solution suitable for solvent extraction.
- Co-decontamination process involves solvent extraction of uranium and of plutonium from the bulk of the solution containing fission products using Tri Butyl Phosphate (TBP) in hydrocarbon diluent as the solvent.
- Scrubbing involves contacting the organic stream with nitric acid to back extract the fission products to the aqueous phase.
- Separation of uranium and plutonium by complexation or reduction process, known as partitioning.
- Reconversion of partitioned uranium and plutonium products to their respective oxides
- Washing of the used solvents for recycling.

In the case of fast reactor spent fuel reprocessing, the fission product inventory, plutonium content and burn-up vary when compared to thermal reactor spent fuel reprocessing. Higher fission product content due to high burnup, higher plutonium content (20-30%) and advanced fuels like carbide or nitride are unique features of fast reactor spent fuels. Therefore, reprocessing of fast reactor spent fuel needs certain modifications in the flow-sheet as compared to thermal reactor fuel.

2. Partitioning of uranium and plutonium

Separation of uranium and plutonium after fission product decontamination is called partitioning. Partitioning of uranium and plutonium can be achieved by selective complexation or reduction of one of the metal ions, preferably plutonium. The preference to plutonium is due to its high ionic potential, easy reduction in the case of Pu(IV) ion and to avoid further radiation induced solvent damage. Two types of feed exist for uranium - plutonium. One contains higher uranium with plutonium content up to 1% (especially reprocessing of thermal reactor spent fuels). The other contains higher plutonium (up to 20 – 30 %), as in the case of fast reactor spent fuel reprocessing. Hence, the method selected for partitioning of fast reactor spent fuel reprocessing should be efficient to handle higher plutonium content.

Partitioning of uranium and plutonium by selective complexation

Uranium and plutonium along with traces of fission products are present in the loaded organic obtained after co-decontamination step of PUREX process. In the loaded organic, uranium exists as $UO_2(NO_3)_2.2TBP$ and Pu as $Pu(NO_3)_4.2TBP$ along with the extracted nitric acid. A complexant which selectively complexes with plutonium leaving uranium in the organic phase is required for partitioning. The complexing ligands preferentially complex metal ions with larger ionic potential. Pu^{4+} ion has higher ionic potential than UO_2^{2+} ion and therefore, forms stronger complexes with various ligands[2].

The selectivity of the complexing agent for U/Pu separation can be compared based on the distribution ratio. It has been reported that if the distribution ratio differs by more than '50', then the selectivity of separation is good [2]. Sulphate ion in H_2SO_4 is a strong complexing ligand, and it was tested for complexing plutonium in the presence of nitric acid [3,4]. In 1 M HNO_3 + 1 M H_2SO_4, the distribution ratios differed by a factor of 90. In the fast breeder reactor fuel reprocessing plant at Dounreay, UK, a combination of 1 M HNO_3 + 1 M H_2SO_4 with small additions of ferrous sulphamate was successfully used as the partitioning reagent for uranium and plutonium [5]. Corrosive nature of SO_4^{2-} ion did not find application in large scale due to requirements of proper non-corrosive materials of construction. Other than SO_4^{2-} ion, formate [6] and acetate [7,8] were also tested for plutonium complexation. But they did not find any industrial application because of their partial extractability into 30% TBP-hydrocarbon diluent system [2].

Partitioning of uranium and plutonium by reduction process

TBP in n-dodecane system exhibits difference in the extractability of different valence states of metal ions. The order of TBP extractability of different valency states of actinide ions is as follows [2].

$$M(VI) \sim M(IV) >> M(III) \sim M(V)$$

If a reagent reduces Pu(IV) to Pu(III) without affecting the U(VI) valency, high separation factor of plutonium from uranium can be achieved. The reagent to be employed as reducing agent should have the following characteristics:

(a) Salt free reagent (containing C, H, O and N)

(b) Should undergo decomposition at moderate chemical conditions

(c) Compatible with all types of contactors which have low or high residence time, ie, fast kinetics.

(d) Reasonable stability under process conditions

(e) No effect on phase separation

Some of the reducing agents investigated for the separation of plutonium from uranium are hydrazine [9,10], hydroxylamine [11,12], ferrous ion [13-15], uranous ion [16], ascorbic acid [17] and hydrogen [18,19]. Hydrazine did not find any industrial application due to its slow kinetics of reduction. Hydroxylamine nitrate (HAN) is an efficient reducing agent only in low acid medium. Further, HAN cannot strip plutonium completely from the organic phase due to the interference of solvent degradation products [20]. In the case of reduction with ferrous ion, high Fe^{2+}/Fe^{3+} ratio should be maintained in order to achieve good separation of uranium and plutonium. Nevertheless, usage of ferrous ion results in high salt waste output which is undesirable in the reprocessing of fast reactor fuels. Even though, hydrazine stabilized uranous ion is an efficient reducing agent and has been employed extensively in thermal reactor spent fuel reprocessing, it is expected that high metal ion loading will result in the case of fast reactor spent fuel reprocessing, due to the high plutonium content involved in the fast reactor spent fuel reprocessing. Hence, salt free reagents have been explored for the reduction of plutonium.

Salt free reagents for the partitioning of uranium and plutonium

Iso-butyraldehyde is one of the salt free reagents for the reduction of Np(VI) and Pu(IV) and it does not affect U(VI) [21]. However, slow kinetics and moderate extraction of iso-butyraldehye into the organic phase restricts the use of iso-butyraldehyde.

Acetoldoxime (CH_3CHNOH) in nitric acid has also been examined for the reduction of plutonium and neptunium ions [22]. As these two reagents have moderate extractability into the organic phase, they are not considered for plant applications.

Acetohydroxamic acid ($CH_3CONHOH$) is one of the salt free reagents, used in the development of UREX process [23]. Acetohydroxamic acid (AHA) is a molecule possessing combined character of complexation and reduction. Its dual role is effective for plutonium reduction in higher acidic medium. As AHA shows faster kinetics in the reduction of plutonium, it can be used for partitioning in contactors like centrifugal extractors. It decomposes into gases in 6 M nitric acid medium. The small organic backbone of AHA allows only limited solubility in TBP /hydrocarbon solvent system. This solubility is found to enhance the reduction reaction. Aquaphilic nature of AHA aids in the removal of traces of AHA-plutonium complex in the organic phase. Since AHA can scavenge nitrous acid, additional reagents (e.g. hydrazine) as stabilizers are not warranted. However, AHA degrades into acetic acid and hydroxylamine under acidic conditions. Since, most of the operations in spent fuel reprocessing involve acidic conditions, the reduction reaction using AHA should be carefully controlled. Instantaneous mixing of AHA and nitric acid, prior to partitioning reaction can avoid the degradation of AHA [23].

Scope of the present study

The issues relevant to the handling of large quantities of plutonium in fast reactor spent fuel reprocessing needs to be addressed. Since reducing agents involving metal ions are expected to give rise to problems in the waste treatment, they are not desirable for the separation of uranium and plutonium. In the present thesis work, the salt free reagent, AHA has been examined for the purpose of serving as the reducing agent for partitioning of uranium and plutonium. A simple method was developed for the preparation of AHA and the compound prepared was characterized by spectroscopic techniques. Prior to employing AHA as a reducing agent in fast reactor spent fuel reprocessing, its reaction with metal ions particularly with uranium, plutonium and fission products needs to be evaluated. In a previous study, Govindan et al. [24] investigated the behaviour of AHA in the partitioning of a simulated feed solution of uranium and plutonium. In present work, AHA in nitric acid medium has been used in the partitioning of uranium and plutonium from the actual loaded organic. This loaded organic was generated from the Compact facility for the reprocessing of mixed, Pu-rich carbide fuel discharged from Fast Breeder Test Reactor (FBTR) at Kalpakkam. The concentration of AHA and HNO_3 required has been optimized in the purification of uranium product efficiently from plutonium contaminated solutions. The flowsheet for this purification process is different from that for UREX process [23, 44]. In UREX process, plutonium goes along with the fission products instead of recovering as PuO_2 powder, as in the present method proposed for partitioning. The analytical method to determine the concentration of AHA in aqueous solutions by spectrophotometry has also been standardised.

Organization of the thesis

The present thesis comprises the following seven Chapters:

CHAPTER 1	Introduction
CHAPTER 2	Materials and methods
CHAPTER 3	Synthesis and characterization of acetohydroxamic acid (AHA)
CHAPTER 4	Reduction and complexation of AHA with metal ions – Possible mechanism
CHAPTER 5	A comparative study on the performance of uranous nitrate and AHA as partitioning agents and the distribution behaviour of Ru and Cs during partitioning of plutonium from uranium
CHAPTER 6	Purification of uranium product from plutonium contamination using AHA based process
CHAPTER 7	Summary

A brief overview of the each Chapter is given below.

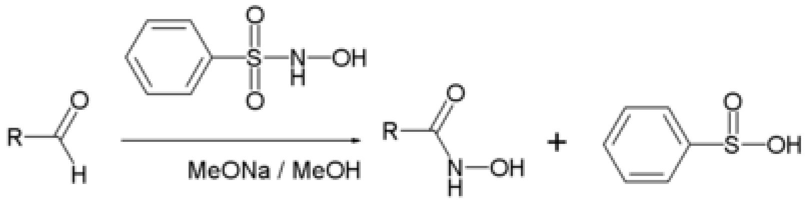
In Chapter 1, the need for nuclear energy as one of the clean energy resources is discussed. The necessity for reprocessing the spent fuels to recover useful nuclear materials and closing the fuel cycle are elaborated. The flowsheet for aqueous reprocessing by PUREX process is introduced. In aqueous reprocessing, one of the major steps namely partitioning of uranium and plutonium is described in detail with the mention of various chemical reducing agents reported in the literature to adjust the valency of Pu, their advantages and limitations. The need for alternative salt free reagents with emphasis on the issues related to the reprocessing of high burnup and short cooled, fast reactor fuel reprocessing is addressed. This Chapter concludes with the complete chemistry of AHA, its applications in the various process steps in the flowsheet for the aqueous reprocessing of spent fuels of FBRs and the merits and demerits of AHA compared to other partitioning reagents.

Chapter 2 describes the various methods employed to investigate the partitioning behaviour of plutonium and uranium as well as the synthesis of AHA. Job's variation method has been used to study the metal to ligand ratio for Fe^{3+}: AHA and Pu^{4+}: AHA complexes. To estimate the concentration of AHA in the feed solutions and during the experiments a spectrophotometric method was adopted and has been standardized. Hydroxamic acids are used as spectrophotometric and gravimetric reagents due to their reduction/complexation behaviour with metals (25,26). Hydroxamic acids with O, O donor ligands have a strong affinity for the metal ions like Fe^{3+}, Pu^{4+} and Np^{4+}. As AHA is one of the lower homologues of hydroxamic acids, it forms a deep red coloured complex with Fe^{3+}, which is exploited for its determination by spectrophotometric method. The λ_{max} and molal extinction coefficients were found out to be 498 nm and 865 L mol^{-1} cm^{-1} respectively. Stability of the AHA-Fe^{3+} complex as a function of pH and time has been evaluated. Based on these studies, the analytical procedure for the estimation of AHA was standardised. The procedure for the estimation of uranium and plutonium in ppm and in gram level concentrations in the partitioning experiments has also been discussed in this Chapter. Davies and Gray method and PAR (Pyridyl azo resorcinol) method were employed for the measurement of uranium in g/L and ppm concentrations respectively. Redox titrimetry method after perchloric acid evaporation and radiometry after HTTA extraction were discussed for estimating plutonium in g/L and ppm level respectively. Characterisation of AHA using XRD, FTIR and FTNMR methods and Coulometric Karl Fisher titration method for moisture determination in organic solvents have also been discussed.

Synthesis of AHA by a modified procedure is presented in Chapter 3 of the thesis. The basic procedure for the preparation of hydroxamic acids involves reaction of esters with hydroxylamine hydrochloride in the presence of an alkali. Free hydroxamic acid is liberated by the addition of calculated quantity of a mineral acid to the cold reaction mixture (Eq. 1) [27]. Several modifications of this mentioned procedure have been made [28-32]. In all these methods, the purity of the product could not be ascertained owing to the presence of salt impurities. In addition, complete extraction of AHA (prepared by the above methods) into organic solvents is difficult due to the presence of side-products such as salts. The Angeli-Rimini reaction [33-35] between aldehydes and *N*-hydroxybenzenesulfonamide in the presence of a base such as methoxide leads to hydroxamic acids (Eq. 2). Although hydroxamic acids are intermediates in the reaction of primary nitroalkanes with sulfuric acid (Eq. 3), they can only be isolated under very strictly controlled conditions [36,37].

$$CH_3CO_2Et \quad + \quad H_2NOH{\cdot}HCl \xrightarrow[2.H_3O^+]{1.KOH} CH_3CONHOH$$

(1)



(2)

$$CH_3CH_2NO_2 \xrightarrow{H_2SO_4} [CH_3CONHOH] \xrightarrow[H+]{H_2O} CH_3CO_2H \; + \; H_2NOH$$

(3)

Furthermore, the last two methods (Eqs. 2 and 3) generate products that contain corrosive species such as sulfate and sulfite ions which result in corrosion related problems in the bulk preparation of AHA in stainless steel vessels.

In the present work, the preparation of AHA from the reaction of hydroxylamine hydrate (50%) with acetic anhydride (Eq. 4) is reported. This procedure does not use any alkali, thus making the extraction of AHA into ethyl acetate solvent much easier.

$$(CH_3CO)_2O + H_2NOH \longrightarrow CH_3CONHOH + CH_3CO_2H \quad (4)$$

Instead of acetic anhydride in the reaction 4, use of carboxylic acid chlorides and acetamide as acylation reagents have been reported [38]. Further acylation cannot be avoided if acetyl chloride is used as the acylation reagent [39]. Experiments have shown that the yield was less than 1% in the case of acetamide as acylation reagent at room temperature (30° C).

The reaction product from the acylation of hydroxylamine hydroxide using acetic anhydride does not involve any salt content. Most of the AHA in the reaction medium was extracted into the solvent, ethyl acetate within two contacts of solvent extraction. The ethyl acetate extract was concentrated and AHA was crystallised out from the extract upon refrigeration. The AHA crystals were further purified by recrystallisation from acetone. The spectral data obtained from IR, NMR and UV-Visible spectrophotometric methods for the synthesized compound were compared with those of the commercially available compound (M/s. Sigma Aldrich). Feasibility studies performed with Fe^{3+}-AHA complex confirmed that the synthesized AHA could be employed for the separation of U and Pu.

In Chapter 4 the reduction/complexation behaviour of acetohydroxamic acid with metal ions and the possible mechanism have been discussed. This study is divided into four parts.

1. UV-Visible spectral study of the complex of acetohydroxamic acid with metal ions such as Fe^{3+}, Fe^{2+}, Pu^{4+}, Pu^{3+}, PuO_2^{2+}, Ce^{4+} and Ce^{3+}
2. Solubility of plutonium oxalate (both Pu(III) oxalate and Pu(IV) oxalate) in AHA
3. Oxalate precipitation study of AHA partitioned solutions and
4. Solvent extraction of Th^{4+} ions with and without AHA in sodium nitrate medium.

The UV-Visible spectrophotometric studies revealed that AHA forms complexes with Fe^{3+} whose absorption lies in the visible range of electronic spectrum. AHA does not form any complex with Fe^{2+} ion, which was confirmed by the absence of absorption peaks in the electronic spectrum. Among Pu^{4+} and Pu^{3+}, Pu^{4+} ion only forms intense red coloured chelate, whose signature appears in the visible range of electronic spectrum. In the case of PuO_2^{2+} also, there was no change in the spectra after the addition of AHA. Likewise, among Ce^{4+} and Ce^{3+} ions, AHA shows absorption signatures only with Ce^{4+} and not with Ce^{3+}.

The solubility of Pu in Pu(IV) oxalate was found to increase in the presence of AHA. Nevertheless, AHA did not have any effect on the solubility of Pu with Pu(III) oxalate. Oxalate precipitation of AHA partitioned plutonium solutions resulted in plutonium oxalate similar to Pu(III) oxalate. Pu loss in the oxalate filtrate was observed to be lower than that in Pu(III) oxalate precipitation. Distribution studies of Th^{4+} ion in 30% TBP indicated that AHA has no tendency to form a complex with Th^{4+} ion. The results of these studies imply that AHA reduces those metal ions which have a reducible lower valency and forms a chelate immediately after the reduction process. This suggests that the product of the reduction reaction, produced initially readily reacts with AHA to form a five membered chelate ring, with absorption in the visible range of electronic spectrum. The possible mechanism for the reaction of metal ion, M^{n+} (Fe^{3+}, Pu^{4+}, Ce^{4+}) with AHA is also reported.

Chapter 5 comprises a comparative study on the performance of uranous nitrate and acetohydroxamic acid (AHA) as partitioning agents for the separation of plutonium and uranium from the actual "loaded organic" resulted from the reprocessing plant. Aqueous feeds containing 7 g/l uranous nitrate with 0.5 M hydrazine nitrate in 1 M nitric acid and 0.3 M AHA in 1.5 M nitric acid were used as partitioning agents. Volume ratio of organic to aqueous was maintained as one. Two aqueous contacts for uranous and five contacts for AHA were required for quantitative stripping of plutonium from the loaded organics. Gamma spectrum was recorded for the lean organic and strip product to evaluate the behaviour of Ru and Cs distribution during partitioning. As a partitioning agent, uranous was found to be more effective in stripping plutonium, but it was always accompanied by significant amount of uranium in the strip product. Use of AHA on the other hand, required more stages for effective partitioning, but provided plutonium with minimum uranium content in the strip product. Uranous significantly stripped ruthenium in second contact but cesium was intact in the lean organic. AHA was observed to strip cesium from the loaded organic, which could be due to the salt formation of AHA with Cs($CH_3CONHO^+Cs^-$). These results are also reported in this Chapter.

The purification of uranium product from plutonium contamination using acetohydroxamic acid based process is described in Chapter 6. Spent fuels of different burn ups (25, 50, 100, 155 GWd/t) discharged from the fast breeder test reactor (FBTR) have been reprocessed employing Modified PUREX process [40] at Kalpakkam. This process involves co-decontamination cycle, partitioning and reconversion of U and Pu to their respective oxides. In the partitioning cycle, uranium and plutonium are separated from each other by selective oxalate precipitation. The uranium oxide obtained from the reprocessing campaign contains significant amount of plutonium (up to 1 wt%) which is higher than the uranium product specification for table top handling. Therefore, it is essential to purify uranium product from plutonium. Methods for the purification of uranium product include the use of U^{4+} or inorganic ion exchangers like stannic phosphate [41]. Usage of U^{4+} increases the uranium load to the plant. In the inorganic ion exchange method, early break through was observed with uranium feed containing higher plutonium. Hence, an alternate method of purification of Pu contaminated uranium product with a reagent which does not add salt load to the plant is essential. It has been reported that the stability constant of Pu-AHA ($\log\beta = 14.2$) complex is 10^6 times higher than that for UO_2^{2+}-AHA ($\log\beta = 8.22$) complex [24,42]. Uranium and plutonium extraction from nitric acid in the presence of AHA into 30% TBP has been studied and reported earlier [24]. The results of this study indicated that uranium and plutonium can be separated. A detailed study on the extraction of uranium from nitric acid by 30% TBP in the presence of AHA was reported by Tkac et al. [43]. In this study, the effect of nitric acid or $HNO_3/LiNO_3$ on the extraction percentage of uranium was evaluated and the complex formation tendencies were reported. Data on the purification of the uranium product from plutonium through solvent extraction by employing 30% TBP in presence of AHA are not known reliably. In view of the inherent advantages of the salt-free AHA reagent (AHA), it was proposed to carry out systematic studies to suppress the extraction of plutonium into 30% TBP using AHA, while extracting uranium from nitric acid medium for purifying uranium product and the results of the parametric study are discussed.

The concentrations of AHA and nitric acid for extraction and scrubbing medium have been optimized. The results obtained are in agreement with the results reported elsewhere [23, 42]. McCabe-Thiele diagrams computed for uranium extraction with and without AHA revealed that the effect of AHA on uranium extraction was insignificant. In the purification of uranium product from plutonium contamination two types of feed with different "U/Pu" ratio were used (i.e. U/Pu = 25 and 125). Two options namely (1) plutonium complexation in aqueous phase followed by extraction and scrubbing and (2) Extraction followed by scrubbing were chosen. In the first option uranium was extracted in presence of AHA and subsequent scrubbing of organic phase was carried out with the optimized scrubbing reagent (0.3 M AHA in 1.5 M or 3.0 M HNO_3). In the second option, uranium was extracted without AHA followed by scrubbing with AHA in nitric acid. Plutonium contamination in uranium product after purification was about 91 ppm when lower uranium containing feed (U/Pu = 25) was studied with both options. Plutonium contamination after purification was 2 ppm when higher uranium containing feed (U/Pu = 125) was used. Higher amount of loading of uranium into organic phase avoids the extraction of plutonium. Hence, plutonium contamination was less when high uranium containing feed was used. Plutonium in uranium product achieved by this method was 1.6 ppm (wt/wt). This can be improved further to the table top specification of 0.4 ppm (wt/wt) using continuous mode multi stage contactors.

Chapter 7 summarises all the experimental results. Scope of future work is also discussed.

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Publications

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2. S. Sukumar, R.V. Subba Rao and R. Natarajan, "Improved preparation of AHA", Organic Preparations Procedures Internatl. (2014) 46: 85-87.

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Date: 19 08. 2013 **Signature of Student:**

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LIST OF ACRONYMS

AHA	Acetohydroxamic acid
CCD	Chlorinated cobalt dicarbolide
CORAL	Compact Reprocessing of Advanced fuels in Lead shielded cells
CyDTA	1,2-diamino cyclohexane tetra acetic acid
DBP	Dibutyl Phosphate
FHA	Formohydroxamic acid
FBR	Fast breeder reactor
FBTR	Fast breeder test reactor
FTIR	Fourier Transform Infra Red spectrum
HAN	Hydroxylamine nitrate
HPGe	High Purity Germanium detector
HTTA	Theonyl Trifluoro Acetone
IGCAR	Indira Gandhi Centre for Atomic Research
INPP	Indian Nuclear Power Program
NMR	Nuclear Magnetic Resonance spectrum
NPEX	Neptunium Plutonium Extraction
NPH	Normal Paraffin Hydrocarbon
PAR	4-(2-Pyridylazo) resorcinol
PEG	Polyethylene Glycol
PHWR	Pressurized Heavy Water Reactor

ppm	parts per million
PUREX	Plutonium Uranium Reduction Extraction
TALSPEAK	Trivalent Actinide Lanthanide Separations by Phosphorous reagents from Aqueous Komplexes
TBP	Tri Butyl Phosphate
TRUEX	Transuranium Extraction
UREX	Uranium Extraction
UREX+	Uranium Extraction (combination of various extraction processes)

CHAPTER 1

INTRODUCTION

1. NUCLEAR ENERGY

Electricity is one of the key parameters to scale the economic growth of any country. In India, per capita electricity consumption is 597 kWh/capita/year as against the world average of 2730/capita/year [1]. Hence, to improve the standard of living in the country, India needs to generate electricity around 40 % of the present global electricity output. To achieve this goal, the resources at hand should be used efficiently. India uses various energy resources such as thermal, hydroelectric and other renewable energy sources. Even though fossil fuel (used in thermal power plants) is the major contributor in the production of electrical energy, it releases significant quantities of green house gases to the atmosphere thereby causing globlal warming. At this juncture, alternate energy resources, free from green house emission are required. Nuclear energy is considered to be a viable alternative energy without emitting any green house gases.

Fermi's experiment on the fission of heavy atoms led to the discovery of a new energy resource. The isotope of uranium, ^{235}U on bombardment with a neutron yields around 200 MeV of energy. This nuclear fission reaction is represented by the following equation:

$$^{235}U + \ ^{1}n \longrightarrow \ ^{89}Kr + \ ^{144}Ba + 3\ ^{1}n + 193\ \text{MeV} \quad (1)$$

This nuclear energy released during fission is converted into electricity through heat engines in nuclear reactors. According to the reaction (1), nuclear fission also yields 2.5

neutrons per fission, on an average. In the nuclear reactor, controlled and steady rate of nuclear fission takes place using these evolved neutrons. If the reaction is not carefully controlled, the fission reaction is called as supercritical. Supercritical reaction actually occurs in nuclear explosions. After a certain amount of burning up of the fuel (technically called as burn-up of the fuel), it cannot be used further in the reactor due to various reasons. The main reason is the formation of neutron poisons which are sufficient to decrease the performance of the nuclear reactor. With regard to the management of spent fuels discharged from nuclear reactors, two options exist. The first option is storing the spent nuclear fuel as such, called as 'once through fuel cycle' or open nuclear fuel cycle. The other option is to reprocess the spent fuel to separate the unused U and Pu fuel elements and subsequent nuclear waste management, called as 'closed nuclear fuel cycle'.

India has chosen the second option, i.e. closed nuclear fuel cycle in its nuclear power program, because of the dwindling uranium resources in India and to avoid the long time monitoring of nuclear waste in the case of open nuclear fuel cycle. The Indian nuclear fuel resources have been estimated to be about 60,000 tons of natural uranium and about 3,60,000 tons of thorium [2]. In terms of fossil fuel, this estimate is approximately equivalent to about 1.2 billion tons of coal equivalent through pressurized heavy water reactor (PHWR), 800 billion tons of coal equivalent through fast breeder reactor (FBR) and other reactor systems using thorium. India has its own nuclear power program, known as Indian Nuclear Power Program (INPP) [3]. The INPP comprises three stages. First stage involves the utilization of natural uranium resources in pressurized heavy water reactors (PHWR). Natural uranium consists of 0.7 % ^{235}U, which is a fissile isotope and the remaining 99.27 % consists of ^{238}U, which is a fertile isotope. On neutron bombardment, the fissile isotope undergoes fission and fertile isotopes transform into fissile isotopes. In the reactor, fertile isotope, ^{238}U is converted to fissile (useful) isotope, ^{239}Pu. ^{239}Pu and unused uranium in the spent fuel requires to be reprocessed for closing the nuclear fuel cycle, which involves the separation of uranium and plutonium with very high purity from the spent fuel by some chemical process. In the second stage of INPP, the separated plutonium along with uranium is used as a fuel in FBRs. In fast breeder reactors, fast neutrons of energy, about 1 MeV are used for fission instead of thermal neutrons (energy $\approx$ 0.025 eV). In FBRs, in addition to nuclear fission, breeding of fissile isotopes from fertile isotopes like ^{238}U and ^{232}Th to ^{239}Pu and ^{233}U respectively, also take place. These ^{239}Pu and ^{233}U isotopes produced by breeding in FBRs would be utilized as fuel along with thorium in the third stage thermal breeder reactors.

2. SPENT FUEL REPROCESSING

In order to realize the three stages of Indian nuclear power programme [3], reprocessing of reactor-burnt fuel is essential for the purpose of effective utilization of limited uranium resources. India has adopted the aqueous based PUREX process for the separation of U and Pu from the waste fission products, for thermal as well as fast reactor spent fuel reprocessing. PUREX process involves the following steps:

(a) Fuel transport from the reactor and storage

(b) Head end process, which involves chemical or mechanical decladding, dissolution of fuel material using nitric acid, feed clarification and adjustment of chemical conditions of the solution suitable for solvent extraction

(c) Co-decontamination process involving solvent extraction of uranium (U(VI)) and plutonium (Pu(IV)) from the bulk of the solution containing fission products

(d) Scrubbing involves contacting the organic stream with nitric acid to back extract the fission products to the aqueous phase

(e) Separation of U and Pu by complexation or reduction process, known as partitioning

(f) Reconversion of partitioned U and Pu products to their respective oxides and

(g) Washing of the used solvents for recycling.

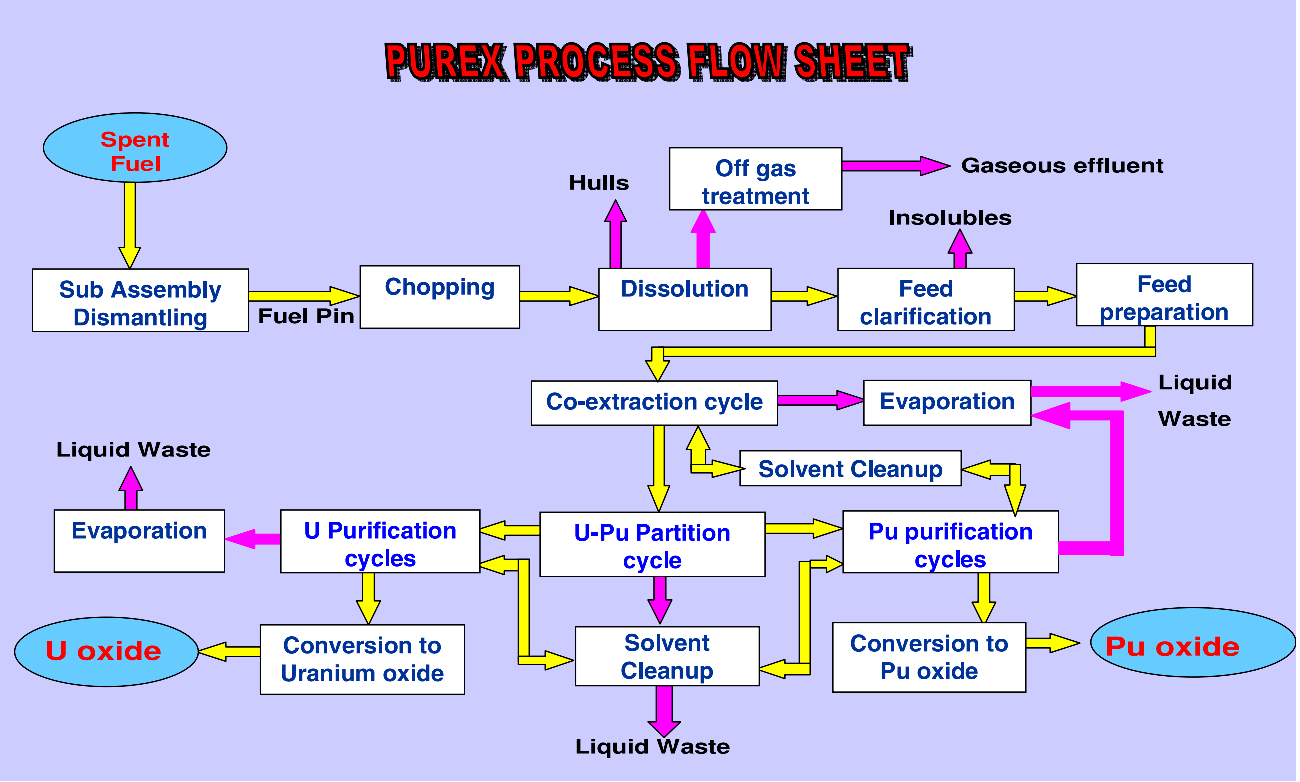


Fig. 1.1. PUREX process - general flowsheet

The flowsheet being followed in the PUREX process is shown in Fig. 1.1. In the case of fast reactor spent fuel reprocessing, the fission product inventory, plutonium content and burn-up vary from that of thermal reactor spent fuel reprocessing. High fission product content due to high burn-ups, high plutonium content (20-30 %) and advanced Pu-mixed fuels of oxide, carbide or nitride are the unique features of fast reactor spent fuels. Therefore, modifications are required in the flowsheet for reprocessing the spent fuels of fast breeder reactors to make the process compatible with the spent fuel properties.

2.a. Partitioning of Uranium and Plutonium

Separation of uranium and plutonium after the decontamination of fission products is called partitioning. Partitioning of uranium and plutonium can be achieved by selective complexation or reduction of the one of the metal ions, preferably plutonium. The preference to plutonium is due to its high ionic potential, easy reduction in the case of Pu(IV) ion and for avoiding further solvent damage due to high radiation. Two types of feeds exist for uranium, plutonium partitioning. One feed contains higher uranium content with plutonium content up to 1 %, especially in thermal reactor spent fuel reprocessing. The second feed contains higher plutonium content up to 20 – 30 % (in fast reactor spent fuel reprocessing). Any method selected for the partitioning of fast reactor spent fuel reprocessing should be efficient to handle high plutonium content.

2.a.i. Partitioning by selective complexation

Uranium and plutonium along with traces of fission products would be present in the loaded organic obtained after co-decontamination step of PUREX process. In loaded organic, uranium exists as $UO_2(NO_3)_2 \cdot 2TBP$ complex and Pu as $Pu(NO_3)_4 \cdot 2TBP$ with some nitric acid. Any complexant which selectively complexes with plutonium, leaving behind uranium in the organic phase is desirable for partitioning. The ligand should preferentially complex the metal ion with larger ionic potential. Pu^{4+} ion has higher ionic potential than UO_2^{2+} ion and therefore, forms stronger complexes with various ligands [4]. Table 1.1 gives the effective cationic charges of different actinide ions.

.Table 1.1 Effective cationic charges of actinides

Actinide ion	Effective cationic charges
An^{4+}	4.0
AnO_2^{2+}	3.3
An^{3+}	3.0
AnO_2^{+}	2.2

The selectivity of the complexing agent for U/Pu separation can be compared from the values of distribution ratio. It has been reported that if the distribution ratio differs by more than 50, then the selectivity of separation is better [4]. Sulphate ion in H_2SO_4 is a strong complexing ligand and it was tested for plutonium complexing in the presence of nitric acid [5, 6]. In 1 M HNO_3 + 1 M H_2SO_4 the distribution ratios differ by a factor of 90. Nitric acid (1 M) acts as a salting out reagent to keep uranium in the organic phase itself; otherwise, uranium also will strip along with plutonium. In the fast breeder reactor fuel reprocessing plant at Dounreay, UK, the combination of 1 M HNO_3 + 1 M H_2SO_4 with small additions of ferrous sulfamate was successfully used as uranium, plutonium partitioning reagent [7]. Sulphate ion did not find application in large scale due to its corrosive nature and the need for proper materials of construction. Other than SO_4^{2-} ion, formate [8] and acetate [9, 10] were also tested for plutonium complexation.

But they did not find any industrial application because of their partial extractability into 30 % TBP-hydrocarbon diluent system [4].

2.a.ii. Partitioning of uranium and plutonium by reduction process

The extractability behaviour of TBP in n-dodecane (diluent) system differs for different valency states. The order of TBP extractability for the different valency states of actinide ions is given below [4].

$$M(VI) \sim M(IV) >> M(III) \sim M(V) \qquad (2)$$

If a reagent reduces Pu(IV) to Pu(III) without affecting the valency of U(VI), very high separation factor of plutonium from uranium can be achieved. The reagent to be employed as reducing agent should have the following characteristics:

(a) Salt-free reagent (containing C, H, O and N only)

(b) Decompose at moderate chemical conditions

(c) Compatible with most of the contactors, which have low or high residence times, ie, fast kinetics is needed.

(d) Reasonable stability under process conditions

(e) No effect on phase separation

Reducing agents which have been investigated for the separation of plutonium from uranium are hydrazine [11, 12], hydroxylamine [13, 14], ferrous ion [15-17], uranous ion [18-30], ascorbic acid [31] and hydrogen [32, 33].

(a) Hydrazine as a reducing agent

Fontenary aux-roses pilot plant [11] employed hydrazine for the reduction of Pu(IV) in the reprocessing of low burn-up fuels. The main disadvantage of hydrazine as a reducing agent is its slow rate of reducing action. The half-cell reactions for the reduction by hydrazine are as follows:

$NH_2NH_2 \leftrightarrows NHNH_2 + H^+ + e^-$ (3)

$NHNH_2 \longrightarrow NNH_2 + H^+ + e^-$ (4)

$NNH_2 \longrightarrow N_2 + 2H^+ + 2e^-$ (5)

In acidic medium, the reactions (3) to (5) are shifted to the left side, which causes the reduction kinetics by hydrazine to be slow.

(b) Hydrazine stabilized hydroxylamine nitrate (HAN) as a reducing agent

Hydroxylamine nitrate (HAN) is considered as an advantageous reducing agent because its oxidation products do not introduce any salt content and it can be employed at acidities lower than 1 M. With higher acidities, decline in the performance of HAN on Pu reduction could be explained by reaction (6).

$2NH_2OH \longrightarrow N_2O + H_2O + 4\,H^+ + 4e^-$ (6)

The rate of this reaction is inversely proportional to the fourth power of hydrogen ion concentration (i.e. rate α $1/[H^+]^4$). Hydrazine is included as a stabiliser in order to avoid the autocatalytic reaction of Pu(III) ion with nitric acid [34, 35]. The products N_2O_4, HNO_2 and NO produced from the reactions (7) – (10) react with hydrazine; otherwise, they oxidize Pu^{3+} ion to Pu^{4+} ion which is undesirable.

$2Pu(NO_3)_3 + 4HNO_3 \longrightarrow 2Pu(NO_3)_4 + N_2O_4 + 2H_2O$ (7)

$2Pu(NO_3)_3 + N_2O_4 + 2HNO_3 \longrightarrow 2Pu(NO_3)_4 + 2HNO_2$ (8)

$2Pu(NO_3)_3 + 3HNO_3 \longrightarrow 2\,Pu(NO_3)_4 + HNO_2 + H_2O$ (9)

$Pu(NO_3)_3 + HNO_2 + HNO_3 \longrightarrow Pu(NO_3)_4 + NO + H_2O$ (10)

$HNO_2 + HNO_3 \leftrightarrows N_2O_4 + H_2O$ (11)

$2NO + HNO_3 + H_2O \leftrightarrows 3HNO_2$ (12)

Application of HAN for Pu(IV) reduction also requires high residence time in the settler part of the mixer-settler to obtain high separation factors (10^4-10^8) [36]. High residence time is required because of the low solubility of HAN in organic phase. Further, HAN cannot strip plutonium completely from the organic phase, owing to the interference of solvent degradation products. Hydroxylamine nitrate in combination with ferric ion is also receiving attention for the reduction of Pu(IV). Ferrous ions produced instantaneously can strip the Pu bound by solvent degradation products.

(c) Ferrous sulphamate as a reducing agent

Ferrous sulphamate has been used extensively as the reducing agent for plutonium in the earlier PUREX flowsheets [15]. Ferrous ions rapidly reduce Pu(IV) to Pu(III) by a simple one electron transfer as per the equation

$Fe^{2+} + Pu^{4+} \longrightarrow Pu^{3+} + Fe^{3+}$ (13)

The sulphamate ion scavenges nitrous acid present in the process solutions, thereby protecting ferrous ions from autocatalytic oxidation by HNO_2.

$NH_2SO_3H + HNO_2 \longrightarrow N_2 + H_2SO_4 + H_2O$ (14)

$Fe^{2+} + HNO_2 + H^+ \longrightarrow Fe^{3+} + H_2O + NO$ (15)

In 1 M HNO_3 medium, the normal redox potentials of the two half reactions in reaction (13) are

$Pu^{3+} \longrightarrow Pu^{4+} + e^-$ $E^o = -0.92$ V vs SHE (16)

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$ $E^o = 1.128$ V vs SHE (17)

The Nernst equation for the reduction of Pu^{4+} ion by Fe^{2+} is given below.

$$E = E^{o} - \frac{RT}{F} \ln \frac{a_{Pu}^{3+} \cdot a_{Fe}^{3+}}{a_{Pu}^{4+} \cdot a_{Fe}^{2+}} \tag{18}$$

Equation (18) indicates that a high $[Fe^{2+}]/[Fe^{3+}]$ ratio must be maintained to ensure complete reduction of Pu(IV), because of the marginal difference between the reduction potentials of Pu^{4+}/Pu^{3+} and Fe^{3+}/Fe^{2+} couples [20]. With 0.02 to 0.04 M ferrous sulphamate present in the aqueous phase as reductant, D_{Pu} values of 10^4 could be achieved [36]. The major drawbacks of using ferrous sulphamate as the reducing agent in the partitioning of uranium and plutonium are

(i) It introduces non-volatile impurities as well as undesirable anions in the process streams like corrosive sulphate ions which cannot be recycled in addition to its forming a strong complex with plutonium

(ii) It is necessary to maintain high ferrous to ferric ratio (20 to 40 fold) to ensure complete reduction of Pu(IV) and hence, waste treatment cost is intolerably high for the fuel with large plutonium concentrations

(iii) Ferrous sulphamate cannot be used for FBR fuels with high plutonium content because of high loading of the metal ion (ferrous).

(d) Uranous nitrate as a reducing agent

Unduly cost of waste treatment in the case of ferrous sulphamate as a reducing agent diverted the attention to consider other reducing agents like hydrazine stabilized uranous nitrate. In the 1960’s, U(IV) was introduced as a reducing agent for plutonium/uranium partitioning, replacing the ferrous sulphamate reducing agent, previously used.

Exhaustive data are available in literature about the preparation, behaviour and application of uranous nitrate for the stripping of plutonium [20, 21]. Plant scale experience using mixer-settler unit [22-24] and pulse columns [25] have also been reported.

The major reaction for the partitioning reaction by U^{4+} is

$$Pu^{4+} + U^{4+} + 2H_2O \longrightarrow Pu^{3+} + UO_2^{2+} + 4H^+ \qquad (19)$$

The U^{4+} ion is a more powerful reducing agent than Fe^{2+}. The redox potential involved is

$$U^{4+} + 2H_2O \longrightarrow UO_2^{2+} + 4H^+ + 2e^- \quad [E^o = -0.33 \text{ V vs SHE}] \qquad (20)$$

Owing to the large potential difference between $[U^{4+}]/[UO_2^{2+}]$ and $[Pu^{3+}]/[Pu^{4+}]$ couples, only a slight excess of U(IV) over the stoichiometric amount should reduce Pu(IV) quantitatively to Pu(III). With respect to waste handling, U(IV) does not introduce any corrosive anions like SO_4^{2-}. Therefore, uranium(IV) is a superior reducing agent compared to ferrous sulphamate.

In the reprocessing of fast reactor spent fuels, the presence of plutonium in loaded organic is 20 fold higher than that of thermal reactor's spent fuel reprocessing. In the spent fuels of FBRs, around 20-30 % plutonium is present as against 1 % in thermal reactor spent fuel. Hence, uranium load to the plant will be very high, if uranous is chosen as the reducing agent.

(e) Other reagents for Pu(IV) reduction

Ascorbic acid [31] and catalytic hydrogen [32, 33] have been tested in laboratory scale for Pu(IV) reduction. The oxidation products of ascorbic acid generate some solid substances which are undesirable for the stripping operations in any type of the contacting equipment. In the case of catalytic hydrogen, it was demonstrated that with 4 % H_2 in argon as the reductant, 99 % of plutonium(IV) could be reduced when 30 % TBP in kerosene (containing plutonium(IV) and uranium(VI)) was passed counter currently to an equal volume of 0.5 M nitric acid through columns packed with 0.5 % platinum on alumina pellets. However, as per the kinetics is concerned, ferrous sulphamate and uranous nitrate were found to exhibit fast kinetics in the reduction of Pu(IV).

2.a.iii. Salt-free reagents for partitioning of uranium and plutonium

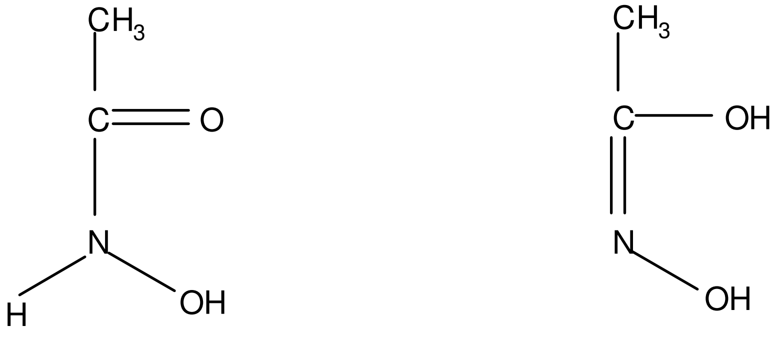
High cost of waste treatment in the application of ferrous ion as a reducing agent and the high concentration of uranous ions required in the partitioning process of fast reactor spent fuel reprocessing led to the search for salt-free reagents, which can selectively reduce or complex Pu(IV) ions. Iso-butyraldehyde is one of the salt-free reagents considered for Np(VI) and Pu(IV) reduction, without affecting U(VI) [37]. However, slow kinetics and moderate extraction of iso-butyraldehye into organic phase restricted the use of iso-butyraldehyde. Acetoldoxime (CH_3CHNOH) in nitric acid was also tested for the reduction of plutonium and neptunium ions [38]. But, these two reagents did not find any industrial application.

Acetohydroxamic acid ($CH_3CONHOH$) is one of the salt-free reagents, which has been used extensively in the UREX process due to its superior properties as a partitioning agent. The chemistry of acetohydroxamic acid (AHA) relevant to the reprocessing process is discussed in the following Section:

2.b. Chemistry of Acetohydroxamic Acid

Acetohydroxamic acid is a lower homologue of hydroxamic acid after formohydroxamic acid. Even though formo hydroxamic acid is a much simpler hydroxamic acid, acetohydroxaic acid has higher stability in acid medium than formohydroxamic acid [39]. Therefore, AHA finds application in the uranium extraction

Process (UREX). The small organic backbone facilitates its mixing with organic solvents. Acetohydroxamic acid exists in two tautomeric forms; keto form and enol form (Fig. 1.2).



Keto form Enol form

Fig.1.2. Tautomeric forms of acetohydroxamic acid

Keto form is the predominant form in acid medium [40]. Since AHA has a carbonyl group and a hydroxyl group attached to the nitrogen atom, it reacts with metal ions in two ways. One is in complexant mode and other one is in reductant mode.

2.b.i. Complexing ability of AHA in nitric acid medium

Complexing behaviour of AHA towards various metal ions has been reported by Chatterjee [41]. AHA is a weak donor with pK value of 7.397 [42]. It has been reported that AHA shows strong affinity for hard metal ions such as Fe^{3+}, Np^{4+} and Pu^{4+}. The stability constant of the complexes formed by AHA with various actinide ions increases in the following order [43]:

$$\beta_{U(VI)} < \beta_{H+} < \beta_{U(IV)} < \beta_{Np(IV)} < \beta_{Pu(IV)} \tag{21}$$

AHA forms a five membered chelate ring with the common structure [41] given in Fig. 1.3. The ring structure often absorbs in the visible range of electromagnetic radiation with a broad absorbance peak in UV-Visible spectrum [39].

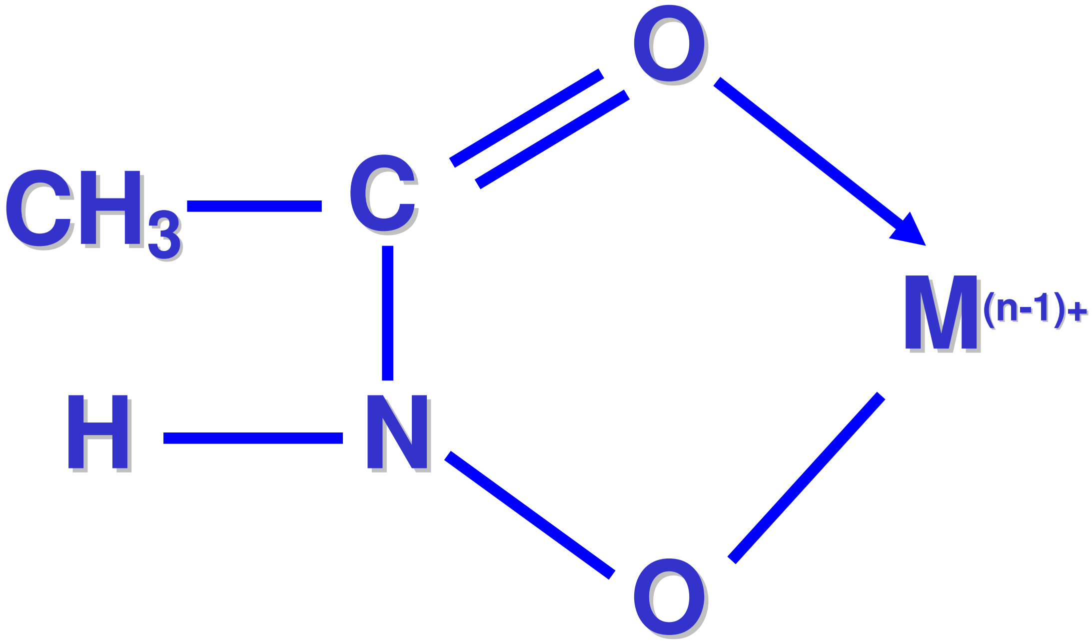


Fig. 1.3. Metal ion –AHA chelate complex [41]

2.b.ii. Reduction behaviour of AHA

AHA acts as a reductant also, involving two electron transfer [44], as shown by the reaction

$$CH_3CONHOH + 2H_2O \longrightarrow CH_3COOH + HN(OH)_2 + 2H^+ + 2e^- \quad (22)$$

Reaction (22) was confirmed by titration with Ce^{4+}. Each mole of AHA consumes 2 moles of Ce^{4+}. The onset potential of AHA was determined by cyclic voltammetry as + 0.55 V vs saturated calomel electrode in 0.1 M nitric acid and + 0.58 V in neutral 0.1 M KNO_3 [44]. The onset potential of + 0.861 V for AHA (vs Normal Hydrogen Electrode) obtained at a gold electrode in the cyclic voltammetric studies indicated that it is not chemically inert under acidic conditions [44].

2.b.iii. Hydrolysis of AHA in acid medium

In the presence of H^+ ions, AHA undergoes hydrolysis reaction to produce acetic acid and hydroxylamine.

$$CH_3CONHOH + H_2O \overset{H_+}{\leftrightarrows} CH_3COOH + NH_2OH \qquad (23)$$

Reaction (23) is assumed to follow pseudo-first order kinetics with respect to the reactant, AHA. The rate of reaction is given by following equation:

$$\begin{aligned} -d[AHA]/dt &= k\,[AHA]\,[H^+] \\ &= k'\,[AHA] \end{aligned} \qquad (24)$$

where $k' = k\,[H^+]$

The plot of log $[AHA]/[AHA]^o$ versus time gives a linear relation with the slope as k' at a constant acid concentration. This relationship indicates that the reaction is first order with respect to AHA [45]. The rate constant 'k' reported by different workers is not consistent. Taylor and May [44] reported that the reaction (23) follows pseudo first order kinetics with the rate constant k = 0.0025 L/mol.min. at 25°C. Chung and Lee [45] determined the value of k as 0.0015 L/mol.min. at 25°C. The value of k calculated from Fig. 1.4 (present work) is 0.003 L/mol.min. at 30°C.

The mechanism of hydrolysis reaction involves hydronium ion transfer in the transition state and therefore, the reaction is hydrogen ion catalysed [46]. In the first step, proton transfer takes place in the rapid pre equilibrium.

$$CH_3CONHOH + H_3O+ \xrightarrow{k1} CH_3COH^+NHOH + H_2O \qquad (25)$$

In the second step, water (nucleophile) attacks the carbonyl atom and forms tetrahedral intermediate. The carbonyl group is formed again by loss of a leaving group.

$$CH_3COH^+NHOH + H_2O \xrightarrow{k1} CH3COOH + NH_3OH^+ \qquad (26)$$

The temperature dependence of the hydrolysis reaction facilitated the calculation of activation energy, Ea. The value of 81.4 kJ/mol reported by Chung and Lee [45] is in good agreement with the value of 79.9 ± 2.9 kJ/mol obtained by Taylor and May [44].

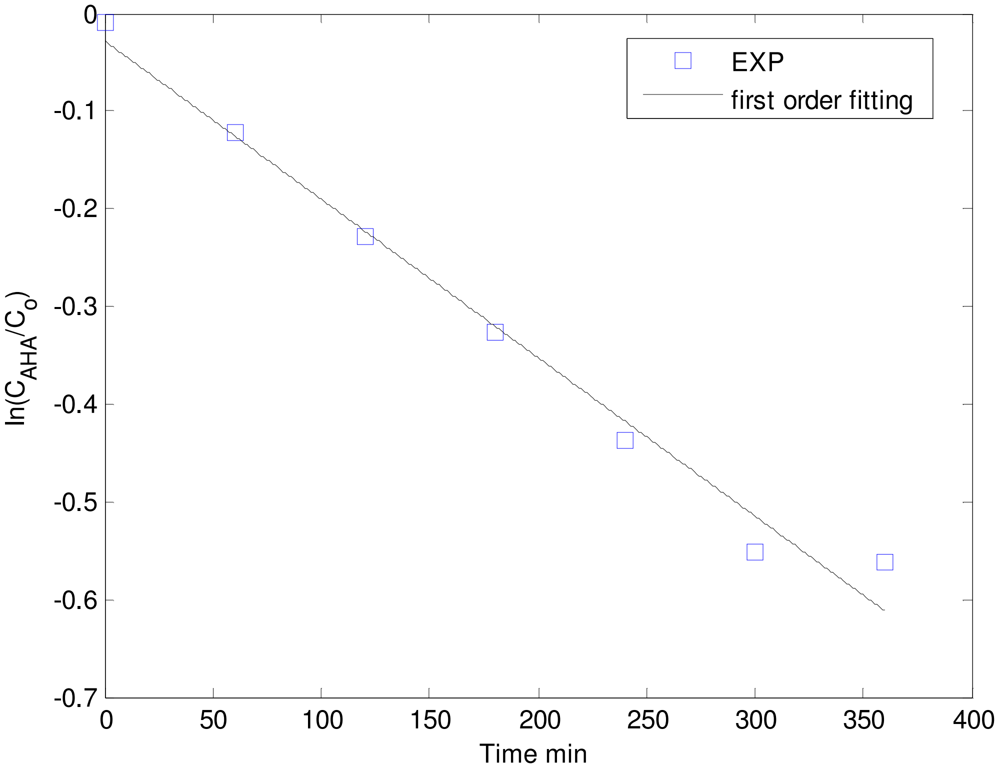


Fig. 1.4. Plot of log C_{AHA}/C_o vs time at 30°C (this thesis work); k = 0.003 L/mol.min.

2.b.iv. Radiolytic degradation of AHA

In the present study AHA was irradiated in a gamma chamber with ^{60}Co source at the dose rate of 0.3 kilogray/h. The results indicated that AHA did not undergo any degradation up to 28800 rads of gamma radiation.

2.c. Application of AHA in Spent Fuel Reprocessing

The application of AHA in nuclear solvent extraction operations was first reported by Grossi and Co-workers [47, 48]. But the usage of formo- and aceto hydroxamic acids in PUREX process conditions was proposed by Taylor et al. [39, 49] in late 90s only. The difference in the complexation and reduction behaviour of AHA towards plutonium and uranium has been exploited in utilizing AHA in the partitioning step of PUREX process. The stability constant of Pu^{4+}-AHA complex ($\log\beta1 = 14.2$) is six orders of magnitude higher than that of UO_2^{2+}-AHA complex ($\log\beta1 = 7.94$) [50, 51]. It is easier to reduce An^{4+} to An^{3+} rather than AnO_2^{2+} to actinides of lower valency [4]. The loaded organic obtained after co-decontamination cycle contains plutonium as Pu^{4+} and uranium as UO_2^{2+}. Therefore, reduction of Pu^{4+} to Pu^{3+} is easier than reducing UO_2^{2+} to U^{4+}. This fact had been verified by conducting preliminary reduction experiments using AHA in the present thesis work. Thus, the complexation and reduction properties of AHA facilitate the separation of plutonium from uranium.

2.c.i. Solvent extraction behaviour of uranium and plutonium in presence of AHA

The distribution coefficient of Pu(IV) at 2 M nitric acid with 30% TBP is around 8.05. In the presence of 0.3 M AHA, this value gets reduced to 0.41 [52]. AHA formed a brown-red coloured complex with Pu(IV) containing solution when it was equilibrated with TBP and the same colour with low intensity was observed in the organic phase (30% TBP) also [53]. However, further scrubbing with AHA in the presence of nitric acid resulted in stripping back plutonium to the aqueous phase. Plutonium concentration in the organic phase can be reduced to a few ppm level by further scrubbings [54].

As the extraction behaviour of uranium as uranyl nitrate into 30% TBP was reported to be unaffected in presence of AHA [43, 55, 56], uranium can be separated from plutonium using AHA. This behaviour of AHA in the partitioning step has been used in various processes which are briefly discussed below.

2.c.ii. Control of neptunium in PUREX process

In solutions, neptunium exists in different oxidation states from +3 to +7. Generally Np(VII) is stabilized in basic solution. Under the PUREX process conditions (acidic medium), neptunium is usually present as a mixture of Np(IV), Np(V) and Np(VI); Np(IV) and Np(VI) are the extractable species in PUREX process and Np(V) is inextractable. In the experiments conducted at Thorp miniature plant, Taylor et al. [57] observed that about 30 % of Np was lost to the high active raffinate and the remaining was extracted into the organic phase during the extraction process. The extracted neptunium was distributed to various product streams depending up on the nature of the process. Neptunium control in the PUREX process was achieved using different reagents and conditions. For example, conditioners at higher temperatures convert Np(IV) to inextractable Np(V), reaction of Np(VI) with hydroxylamine and complexation of Np(IV) by SO_4^{2-} ion followed by reduction using ferrous sulphamate, hydrazine and nitrous acid produce Np(V).

AHA and FHA were observed to reduce Np(VI) to Np(V) within a very short time [39]. Distribution coefficient value of 1.82 for Np(IV) in 1.75 M nitric acid with 30 vol % TBP was reduced to 0.2 in the presence of 0.1 M AHA [52]. Among FHA and AHA, the latter one is reasonably stable in nitric acid medium. Extraction studies in the presence of AHA confirmed the rejection of neptunium, which could be directed to the high active raffinate at acid concentrations below 1.5 M [50].

2.c.iii. UREX process

PUREX process, a matured solvent extraction process for the reprocessing of nuclear spent fuels [58] has been adopted for the separation of uranium and plutonium from fission products. In the Uranium Extraction Process (UREX), uranium alone is separated and plutonium will remain as such in the raffinate along with fission products. Technetium and neptunium are also separated in the UREX process. The simple flow chart of UREX process is given in Fig. 1.5.

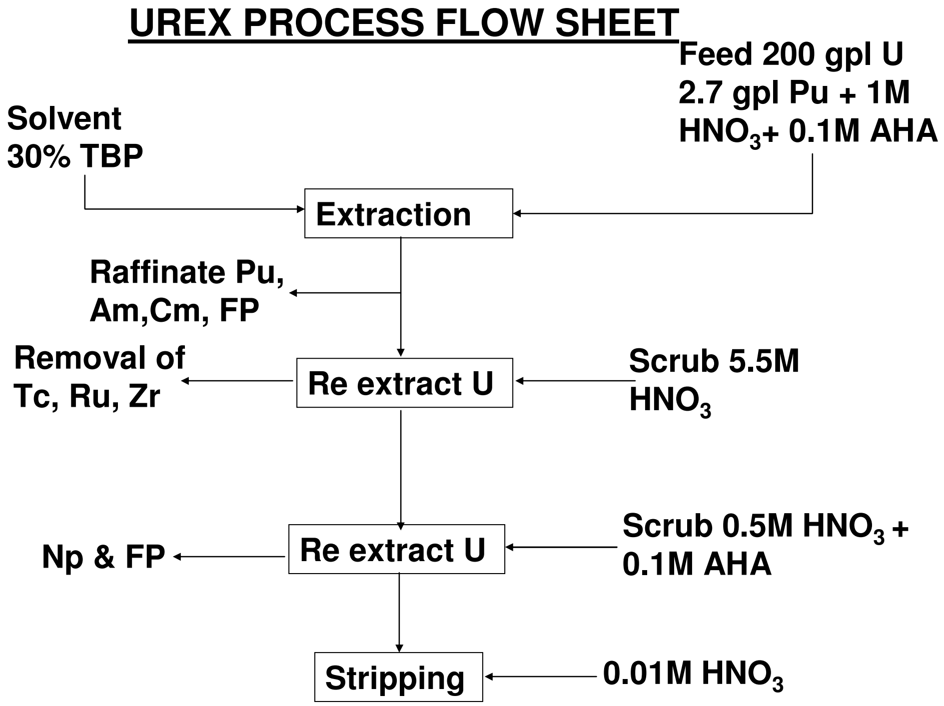


Fig. 1.5. Flow chart for UREX process

In the UREX process, 99.9 % of uranium is recovered with C level waste (uranium containing waste with gamma and alpha activity < 600 and 250 Bq/g respectively). Plutonium getting into the raffinate causes proliferation concerns. One way of eliminating plutonium is by burning it along with other minor actinides in accelerator-driven subcritical reactors. Technitium is recovered in a separate stream. Neptunium is recovered either in a separate stream or with the raffinate. The total uranium content in the raffinate, Np and technitium products must be less than 0.1 % for

UREX process requirement. AHA plays an important role in the UREX process by reducing Pu^{4+} to Pu^{3+} without affecting the extraction behaviour of uranium.

2.c.iv. UREX+ process

UREX+ process includes processes like UREX, CCD/PEG, NPEX, TRUEX and TALSPEAK. The outline of the UREX+ process is given in Fig. 1.6. It was developed by George vandegrift [59] in Argonne National Laboratory. UREX+ process gives a complete solution to the reprocessing of nuclear spent fuel by conducting a series of solvent extraction steps and one ion exchange process operation. AHA plays a vital role in the UREX+ process in extraction and stripping stages.

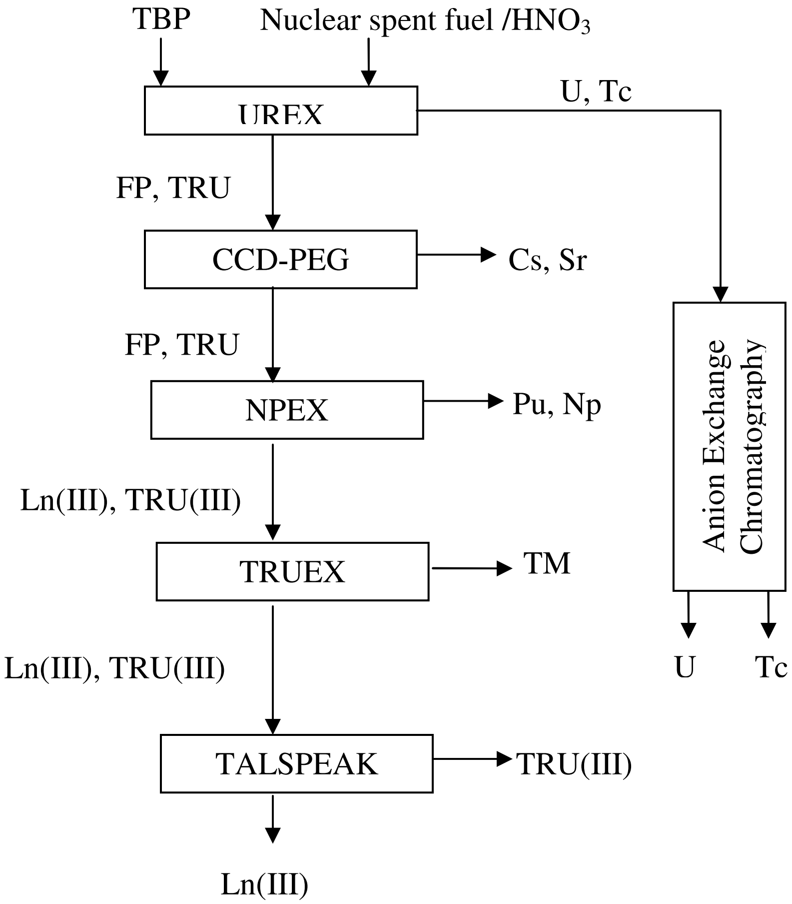


Fig. 1.6. Flow chart of the UREX+ process

The details of UREX+ process are listed in Table 1.2.

Table 1.2. Details of UREX+ process

Process name	Aqueous composition	Organic solvent composition	Elements recovered	Elements left out in the raffinate
UREX	U, Pu in 1 M nitric acid in the presence of 0.1 M AHA	30 % TBP	U and Tc	FP, TRU
CCD-PEG [60]	Aqueous raffinate from the UREX process	Chlorinated cobalt dicarbolide (CCD) and polyethylene glycol 400 (PEG-400) Diluent: phenyl trifluoromethyl sulfone	Cs, Sr	FP, TRU
NPEX	Aqueous raffinate from the CCD-PEG after conditioning to destroy AHA and Np by oxidation with vanadium(V)	30 % TBP in n-dodecane	Np, Pu	Ln(III), TRU(III)
TRUEX [61]	Aqueous raffinate from NPEX process	0.2 M CMPO and 1.4 M TBP in n-dodecane	TRU (An^{3+}) Ln^{3+}	Transition metals
TALSPEAK [62]	The product stream from TRUEX process was conditioned with lactic acid, ammonium lactate and aminopoly acetic acid (DTPA) which are dissolved in a 3-4 buffered solution	di-(2-ethylhexyl) phosphoric acid (HDEHP)	Ln^{3+}	An^{3+}

(a) CCD/PEG process

UREX+ process consists of a series of processes in which UREX process takes part in the first step. Subsequent to UREX process, CCD/PEG process, developed by Idaho National Laboratory is listed in the UREX+ process. In this process, cesium and strontium are separated from the raffinate obtained in UREX process. Cesium and strontium exist as ^{137}Cs and ^{90}Sr in the high active raffinate of UREX process. This raffinate is contacted with the organic phase comprising a mixture of chlorinated cobalt dicarbolide (CCD) and polyethylene glycol 400 (PEG), diluted in phenyl trifluoromethyl sulfone. CCD extracts cesium and PEG-400 extracts strontium into the organic phase. Any transuranic (TRU) element extracted into the organic phase is scrubbed with moderately concentrated nitric acid. Rubidium and barium are also extracted to the organic phase in significant levels. Cesium, strontium, rubidium and barium are stripped from the organic phase using a guanidine carbonate and diethylene triamine penta acetic acid (DTPA) as the stripping agent.

(b) NPEX process

The aqueous raffinate from CCD-PEG process is heated to destroy the AHA which was added during the UREX process. Acidity is also increased to facilitate the destruction of AHA. All the lower valencies of neptunium are oxidized to Np(VI) which is the readily extractable species by the addition of vanadium(V). The valency adjusted aqueous feed is contacted with 30 % TBP (v/v) in n-dodecane. The major elements extracted are neptunium and plutonium leaving TRU and fission products in the aqueous raffinate. Neptunium and plutonium are stripped from the organic phase using AHA in dilute nitric acid. Neptunium recovered can be used along with MOX fuel for power generation.

(c) TRUEX process

The raffinate from NPEX process contains TRU (Am^{3+} and Cm^{3+}), trivalent lanthanides and transition metals. TRUEX process was developed by Argonne National Laboratory for the purpose of partitioning TRU and trivalent lanthanides from transition metals. TRUEX process uses CMPO (Octyl (phenyl)-N,N- diisobutylcarbonylmethyl phosphine oxide) and TBP in n-dodecane diluent. Solvent of 1.4 mol/L TBP and 0.2 mol/L CMPO in n-dodecane diluent is contacted with aqueous raffinate from NPEX process. Three scrubbing sections are required to remove impurities. First scrub is with oxalic acid to remove transition metals. In second scrub, moderately concentrated nitric acid is used to remove any trace of oxalic acid present in the organic phase. Finally, in the third scrub, low nitric acid concentration is used. The aqueous phase resulting from all three scrubbings is combined, which contains oxalic acid, transition metals and trace amounts of An^{3+} and Ln^{3+}. An^{3+} and Ln^{3+} loaded in the TRUEX solvent can be stripped with strippants containing a weak complexant salt at high pH.

The limitation of TRUEX process is the formation of third phase; ie, the organic phase splits into two phases. TBP acts as a phase modifier to decrease the formation of third phase. But, it decreases the performance of extraction of Am^{3+} by CMPO in low nitric acid concentrations. This problem can be solved by increasing the acidity of extraction to greater than 2 M.

(d) TALSPEAK process

Trivalent Actinide Lanthanide Separations by Phosphorus reagent Extraction from Aqueous Komplexes (TALSPEAK), developed by Oak Ridge National Laboratory is the last process proposed among the UREX+ processes [62]. Dissimilarity in the property of Lewis acidity between the trivalent actinides and lanthanides is used in separating them. Even though lanthanides and TRU are in +3 oxidation state, lanthanides with smaller radii act as harder lewis acids than TRU(III). Feed solution is conditioned with lactic acid, ammonium lactate and DTPA present in a 3-4 buffered solution. DTPA, a soft lewis acid, forms complexes with trivalent actinides. The aqueous feed is extracted with HDEHP (di-(2-ethyl hexyl) phosphoric acid) dissolved in n-dodecane. The reaction of HDEHP with trivalent lanthanides is given below.

$$M^{3+}(aq) + 3H_2L_2(org) \leftrightarrows M(HL_2)_3\ org + 3H^+ \qquad (27)$$

The lanthanides extracted were stripped with high acidity containing fresh aqueous phase. Aqueous raffinate containing Am^{3+} and Cm^{3+} was recovered and transmuted in fast reactors or accelerator driven systems.

2.c.v. Basis for the selection of AHA as a salt-free reagent for the partitioning of U and Pu

AHA is a molecule possessing the combined chemical property of complexation and reduction. Its dual role is effective in the separation of plutonium in higher acidic medium also. The kinetics in plutonium reduction is fast. Therefore, it is compatible for contactors like centrifugal extractors. It decomposes into gases in 6 M nitric acid medium. The small organic backbone of AHA allows its limited solubility in TBP /hydrocarbon solvent system. This solubility enhances the reduction reaction.

Aquaphilic nature of AHA helps to remove traces of AHA-plutonium complex in the organic phase. AHA is also capable of scavenging nitrous acid; hence, stabilizing reagent such as hydrazine is unnecessary. However, AHA degrades into acetic acid and hydroxylamine under acidic conditions. Since, most of the operations in spent fuel reprocessing involves acidic conditions, the processes with AHA should be carefully controlled. Therefore, mixing of AHA and nitric acid, just before partitioning reaction is recommended.

3. OBJECTIVE OF THE PRESENT THESIS

The problems associated in the handling of large quantities of plutonium in the reprocessing of fast reactor spent fuels need to be addressed. In this case, reducing agents with metal ion origin are not desirable for the separation of uranium and plutonium, considering the burden in waste treatment. Hence, development of salt-free reagents is warranted for partitioning of uranium and plutonium. The present dissertation explores the possibility of AHA as the uranium/plutonium separation reagent. As the commercial availability of AHA is limited, a simple method of preparation of AHA was standardised. Prior to the application of AHA as the reducing agent in fast reactor spent fuel reprocessing, its reaction with uranium, plutonium and interfering fission products has been established. Govindan et al. [54] investigated the partitioning behaviour of AHA on simulated feeds. In the present dissertation, the performance of AHA in nitric acid medium has been demonstrated with uranous as well as with actual loaded organic resulted from the solvent extraction of U and Pu from the aqueous solution obtained by the dissolution of mixed carbide fuel discharged from Fast Breeder Test Reactor (FBTR) at IGCAR, Kalpakkam. Purification of plutonium contaminated uranium product using

AHA was also optimized and is included in this dissertation. For the estimation of AHA during its preparation and its application in process solutions, a spectrophotometric method was standardized.

CHAPTER II

MATERIALS AND METHODS

1. INTRODUCTION

The scope of the thesis work is to synthesise acetohydroxamic acid (AHA) and to separate uranium and plutonium using AHA. For this purpose, various analytical procedures and methods were employed, followed by conducting simulation studies and studies with actual plant solutions from CORAL reprocessing facility. The ratio of metal ion to ligand for Fe^{3+}:AHA complex using Job's variation procedure [63] was determined. Using the same method, metal:ligand ratio was also determined for Pu^{4+}:AHA complex. As solutions of various concentrations of AHA were used in the simulation studies and with actual plant solutions, monitoring the concentration of AHA was essential and hence, a spectrophotometric method was developed and standardized for the determination of AHA. The concentration of uranium (in g/L level uranium containing solutions) in each step was measured precisely by Davies and Gray method [64]. Uranium in ppm level concentration was determined by spectrophotometric method using pyridyl azo resorcinol as a chromogenic reagent [65]. Solutions of plutonium (g/L level concentration) were estimated by redox titrimetry after perchloric acid evaporation [66]. Plutonium in ppm level concentration was estimated by HTTA extraction and associated radiometric alpha counting [67].

AHA formation during its synthesis was ascertained by spectrophotometry from the absorbance of Fe^{3+}:AHA complex. Powder X ray diffraction method was used for identifying the intermediate product in the preparation of AHA. Synthesized AHA was characterized by UV-Visible spectrophotometry, FTIR and FTNMR methods. Estimation of moisture in the organic solvents used for the synthesis of AHA was carried out by coulometric Karl Fisher titration.

Chemicals and reagents used in the simulation studies and in analytical measurements were Analar Grade and were used as such without any purification. Double distilled water with conductivity 5-6 μS/cm was used for the preparation of all solutions and reagents. Extraction and scrubbing studies were carried out at 30 ± 0.2°C.

2. JOB'S VARIATION METHOD

Job's variation method is used to determine the following:

1. Stoichiometry of a chemical reaction experimentally
2. Chemical formula of a precipitate and
3. Oxidation state of an ion in solution.

In the present work, the stoichiometry of the coordination complex was determined experimentally. Reactions of AHA and metal ions (Fe^{3+} and Pu^{4+}) were studied. AHA forms a deep red colour with both Fe^{3+} and Pu^{4+} ions. By following the absorbance of the metal ion:AHA complex, one can find the stoichiometry of the complex [63].

2.a. Study with Fe^{3+} Ion

Various ratios of metal ions and ligand were mixed together. For each ratio of Fe^{3+}:AHA complex, absorbance was measured at 498 nm, which is the λ_{max} for Fe^{3+}:AHA complex. The results are given in Table 2.1. The absorbance values listed in Table 2.1 have been plotted against the concentrations of both Fe^{3+} (µmol) and AHA (µmol). From the plot, maximum value of absorbance could be obtained. The amount of metal and ligand corresponding to the peak value of absorbance can be read from the X axis. From the amount of metal and ligand, the metal:ligand ratio for a particular coordination complex can be found out. Job's variation plot for AHA and Fe^{3+} is given in Fig. 2.1.

Table 2.1. Absorbance measured for different combinations of metal and ligand

Fe^{3+} (μmol)	AHA(μmol)	Absorbance of Fe^{3+}-AHA complex at 498 nm
2	12	0.315
4	10	0.521
6	8	0.609
8	6	0.540
10	4	0.392
12	2	0.186

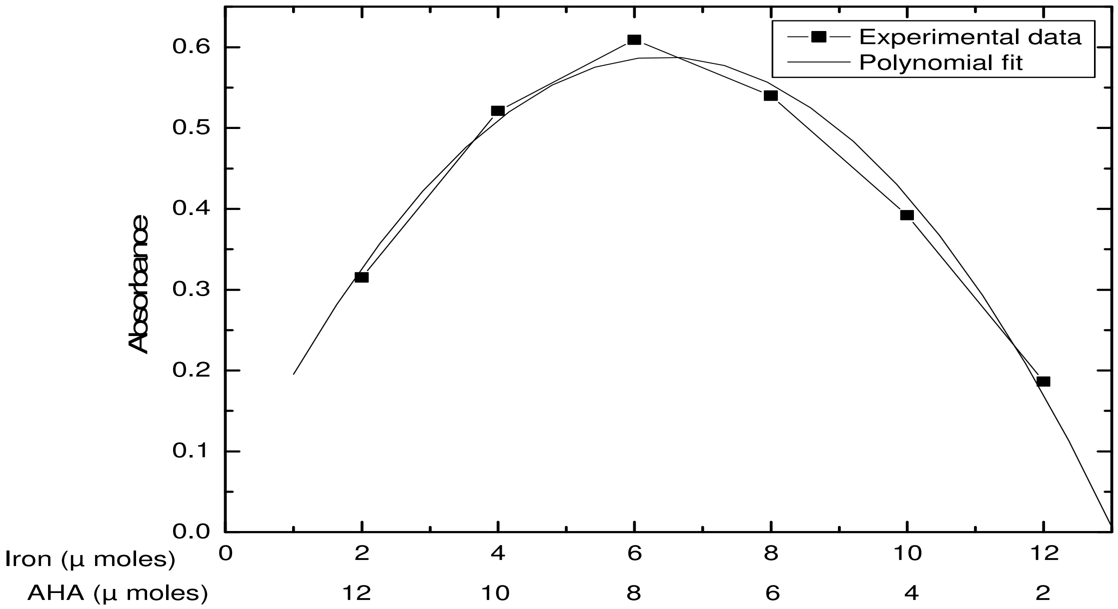


Fig. 2.1. Plot of Job's variation procedure for Fe^{3+} and AHA ligand

Figure 2.1 shows that Fe^{3+} and AHA form a 1:1 complex which was confirmed by measuring the absorbance of AHA:Fe^{3+} complex (in 1:1 ratio) independently.

2.b. Study with Pu^{4+}

Similar to the procedure followed for Fe^{3+}-AHA complex, various ratios of Pu^{4+} and AHA were mixed and absorbance was measured at 400 nm, which is the wavelength at which maximum absorbance is obtained in visible region. Table 2.2 gives the various concentrations of Pu^{4+} ions and AHA and the absorbance values.

Table 2.2. Various ratios of metal (Pu^{4+}) and ligand (AHA) and their absorbance

Pu^{4+} (μmol)	AHA (μmol)	Absorbance of Pu^{4+} - AHA complex at 400 nm
2	10	0.056
3	9	0.067
4	8	0.077
6	6	0.080
8	4	0.067
9	3	0.052
10	2	0.038

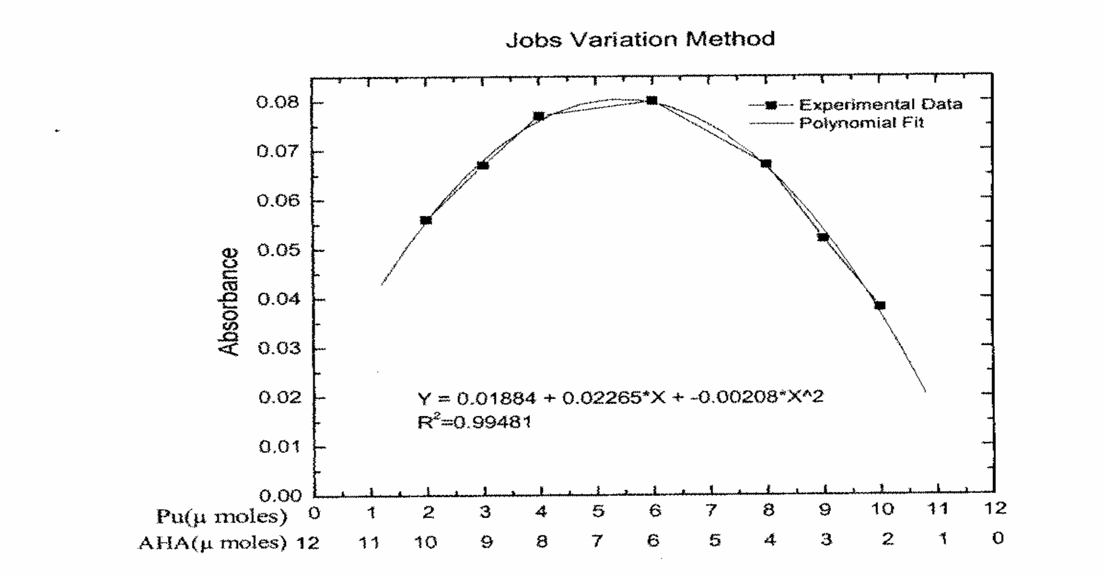


Fig. 2.2. Job's variation method for Pu^{4+} and AHA

Figure 2.2 reveals that Pu^{4+} forms a 1:1 complex with AHA.

3. SPECTROPHOTOMETRIC DETERMINATION OF AHA

Hydroxamic acids have been used as excellent spectrophotometric and gravimetric reagents owing to their reduction/complexation behaviour with metal ions [68, 69]. The O, O donor ligands have strong affinity for hard acids like Fe^{3+}, Pu^{4+}, Np^{4+} etc. As AHA is one of the lower homologues of hydroxamic acids, it forms a deep red coloured complex with Fe^{3+}, which is useful to analyse AHA spectrophotometrically.

3.a. Absorption Spectra

Absorption spectra recorded for AHA-Fe^{3+} complex is shown in Fig. 2.3.

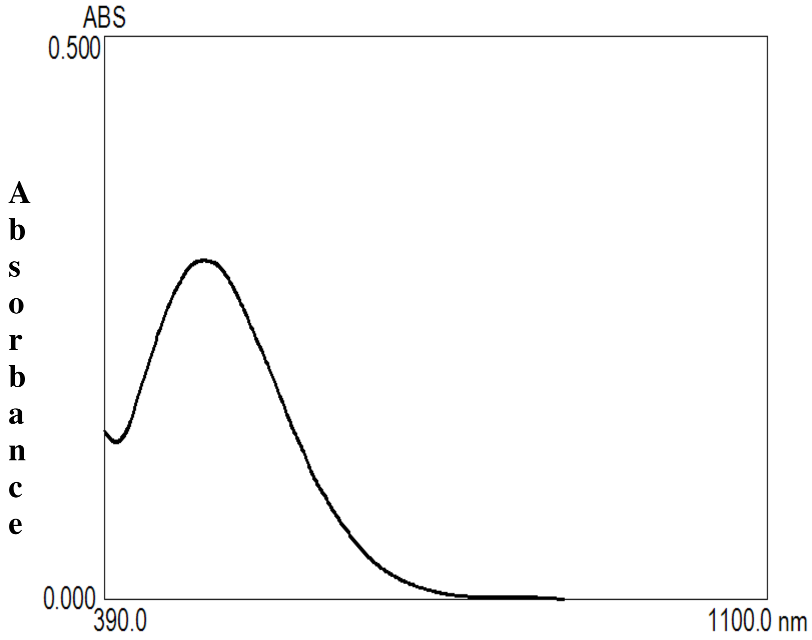


Fig. 2.3. Visible spectrum of Fe^{3+}-AHA complex

From Fig. 2.3, λ_{max} for Fe^{3+}-AHA complex was found to be 498 nm. Molal extinction coefficient (ε) of Fe^{3+}-AHA complex was determined as 865 $Lmol^{-1}cm^{-1}$.

3.b. Stability of the Complex with pH of the Medium

Investigation of the effect of pH on the stability of the complex (shown in Fig. 2.4) indicated that the absorbance values remain constant without any variation in the pH range 2.0-3.0. The pKa value of AHA is 7.397. Hence, with increase in pH of the solution, the free hydroxamate ion concentration increases (as per Henderson equation), facilitating the complexation of Fe^{3+} and AHA and increasing the absorbance.

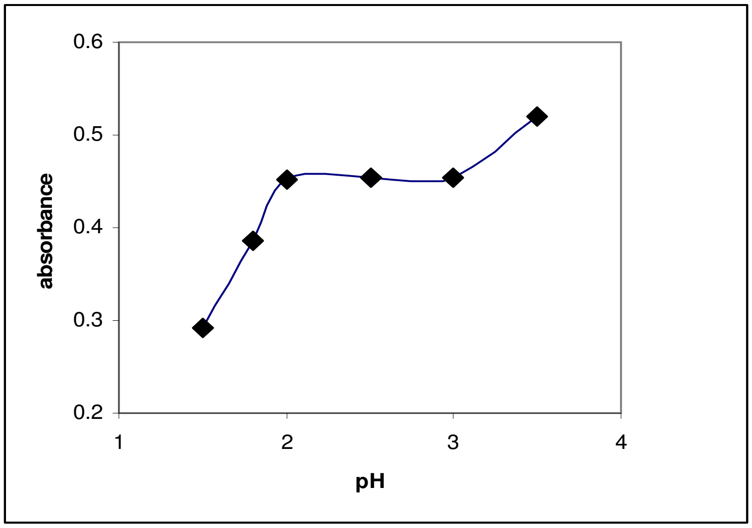


Fig. 2.4. Stability of complex as a function of pH

3.c. Stability of the Complex with Time

Stability of the Fe^{3+}-AHA complex was evaluated as a function of time just after the formation of the complex. After 15 minutes, absorbance started to decrease. Figure 2.5 shows that Fe^{3+}-AHA complex slowly degrades with time.

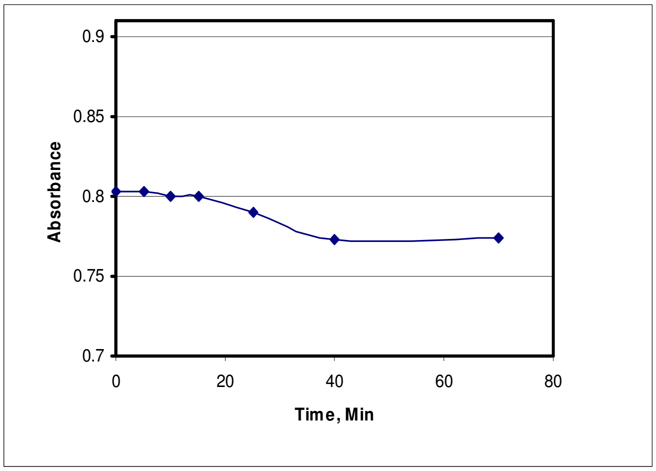


Fig. 2.5. Stability curve of Fe(III)-AHA complex

4. QUANTITATIVE ANALYSIS OF AHA, U, Pu AND WATER

4.a. Estimation of AHA

The following analytical procedure has been developed for the estimation of AHA. 0.1 mL of ferric nitrate from 8.0 g/l stock solution was taken in a 10 mL volumetric flask. 1 mL of the buffer solution (monochloro acetic acid and sodium acetate) with pH 2.8 was added to the flask. An aliquot of AHA in the aqueous sample containing 150 to 690 ppm was added and the contents in the volumetric flask was made up to the mark with double distilled water and the absorbance of the solution was measured at 498 nm within 15 minutes.

Range of analysis: 150 to 690 ppm; Precision: RSD = 3 % and $\varepsilon = 865$ L mol^{-1} cm^{-1}.

4.b. Analysis of Uranium

4.b.i. Davies and Gray method

This method is suitable for analyzing uranium in +6 oxidation state, which is called as uranyl ion (UO_2^{2+}). The concentration range for this method is 5-25 mg of uranium. Fe(II) ions reduce U(VI) to U(IV) in phosphoric acid medium. Excess Fe(II) in the solution is converted to Fe(III) ions in nitric acid medium using ammonium molybdate as the catalyst. Since, NO_2^- is deleterious to these reactions, sulphamic acid is used to scavenge nitrite ions. After diluting the reaction medium with 1 M H_2SO_4, U^{4+} is directly titrated with potassium dichromate. The end point is determined by using sodium diphenylamine sulphonate as the internal redox indicator. Statistical analysis has shown that the estimated values were within an accuracy of ± 1% and the precision of 0.6 %.

4.b.ii. PAR method

Uranium forms a stable 1:1 red coloured complex with pyridyl azo resorcinol (PAR) reagent at pH = 8.0. This method is applicable in the range 6 to 50 μg of uranium in 10 mL volume. Since the concentration of fission products in fast reactor spent fuels is higher than that in thermal reactor fuels, interfering fission product metal ions were masked by the complexing agent CyDTA (1,2-diamino cyclo hexane tetra acetic acid) combined with sodium fluoride. Triethanolamine (TEA) is used as a buffer to maintain the pH at 8.0. Organic samples also can be analysed using this method. For this purpose, ethanol is used to make up the reagent to 10 mL volume. The concentration range for organic samples is 20-200 μg of uranium in a 10 mL standard flask.

4.c. Plutonium Estimation

4.c.i. Redox titrimetry after perchloric acid evaporation

Pu present in the range of 3-10 mg can be analysed even in the presence of U and Fe, in this method. Pu(III) and Pu(IV) are oxidized to Pu(VI) by perchloric acid evaporation. Pu(VI) thus formed is reduced to Pu(IV) with excess ferrous sulphate solution in the presence of sulphuric acid. Excess Fe(II) ions can be titrated against standard dichromate with sodium diphenylamine sulphonate as the internal indicator.

Precision of this method is better than 0.8 %. U and Fe up to 50 and 10 mg respectively do not interfere. Anions like fluoride and acetate will not interfere since they will be removed during perchloric acid evaporation.

4.c.ii. Radiometric determination of Pu in aqueous samples

In the uranium product streams, plutonium will be present with large quantities of uranium. When this Pu is analysed by HTTA extraction procedure, even very small quantities of uranium extracted with plutonium will interfere in this method. Hence, lanthanum fluoride carrier precipitation is carried out to remove plutonium as fluoride precipitate from the bulk of uranium. The fluoride precipitate can be dissolved using aluminium nitrate. Plutonium separated from uranium is estimated by the HTTA extraction procedure. Relative standard deviation of this method is 5 %.

4.d. Coulometric Karl Fischer Titration

Coulometric Karl Fischer titration is the modified version of the classical method for the determination of water, developed by Karl Fischer. The traditional method utilizes a methanolic solution of iodine, sulphur dioxide and a base as buffer. Several reactions occur in the titration of a water containing sample, which could be summarized by the following overall equation:

$$H_2O + I_2 + [RNH]SO_3CH_3 + 2\ RN \rightarrow [RNH]SO_4CH_3 + 2\ [RNH]I \qquad (1)$$

According to reaction (1), iodine reacts quantitatively with water, which forms the basis for the determination of water. In the coulometric Karl Fischer titration, the iodine needed is generated directly in the electrolyte by electrochemical means. The end point is determined voltametrically by applying an alternating current of constant strength to a double Pt electrode. This results in a voltage difference between the Pt lead wires of the indicator electrode, which gets drastically lowered in the presence of minimal quantities of free iodine. This is the principle used to determine the end point of the titration.

5. INSTRUMENTAL METHODS OF ANALYSIS

5.a. X-ray powder diffraction (XRD) method

X-ray powder diffraction is a major analytical technique used for the phase identification of crystalline compounds. It can provide information on unit cell dimensions also. As the X-ray wavelength is similar to the spacing of planes in a crystal lattice, crystalline substances can act as three dimensional diffraction gratings for X-rays.

X-ray diffraction is based on the constructive interference of monochromatic X-rays on crystalline compounds. X-rays are generated by a cathode ray tube and further filtered to monochromatic radiation. X-ray produces constructive interference when conditions satisfy Bragg's law, $n\lambda = 2d \sin\theta$, where λ is the wavelength of electromagnetic radiation, d is the lattice spacing and θ the diffraction angle. Diffracted X-rays are detected, processed and counted. By scanning the sample through a range of 2θ angle, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d spacings allows identification of the material because each material has a set of unique d spacings. This is achieved by comparison of d spacings with standard reference patterns.

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder and a X-ray detector. X-rays are generated in a cathode ray tube and using filters, monochromatic X-ray will be produced for X-ray diffraction. Monochromatic X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then sent as output to a device such as a printer or computer monitor. The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates an angle of 2θ. Different X-ray transitions from the same element are shown in Fig. 2.6. The instrument used to maintain the angle and rotate the sample is termed as goniometer. For the thesis work XRD patterns were recorded using INTEL XRG 3000 Model equipped with curved position sensitive CPS590 detector. The target was Cu-$K_{\alpha1}$ with the radiation wavelength of 1.54056 A° and the peak analysis was carried out using JCPDS-2003 software.

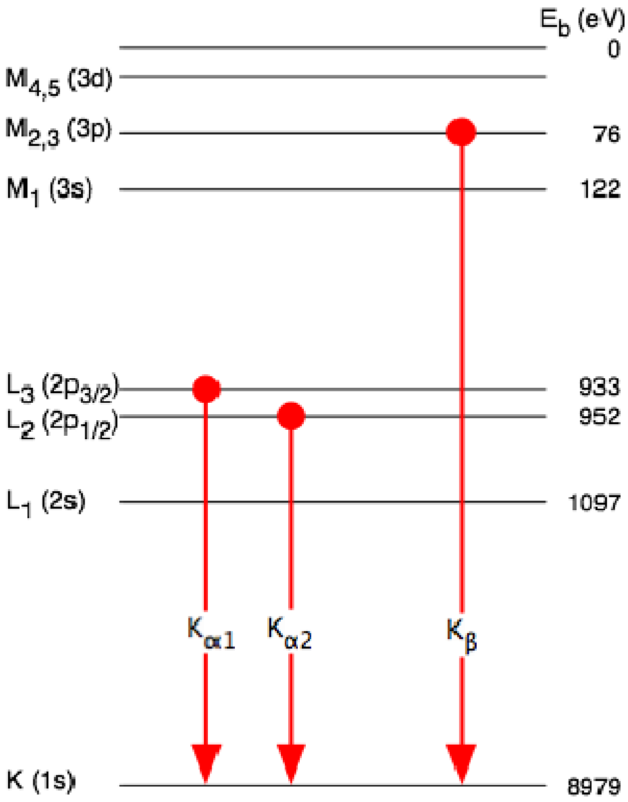


Fig. 2.6. Different X-ray transitions ($K_{\alpha1}$, $K_{\alpha2}$, K_β etc.) from the same element

5.b. UV-Visible Spectrophotometry

The difference in energy among molecular bonding, non-bonding and anti-bonding orbitals is in the range 125 – 650 kJ/mol. This energy corresponds to electromagnetic radiation in the ultraviolet and visible regions of the spectrum. Therefore, UV-Visible spectroscopy deals with the measurement of energy absorbed when electrons are promoted to higher energy levels. UV-Visible spectroscopy is useful in two ways. One is in identifying functional groups in molecules and the other is in determining the concentration or quantity. Wavelength maximum or λ_{max} is the wavelength (in nm) of UV-Visible region at which molecules of our interest absorb more. Since wavelength maximum or λ_{max} depends on the nature of a particular environment of the molecule, λ_{max} facilitates the identification of a particular compound, functional group or oxidation state. After fixing the λ_{max}, the amount of the compound can be estimated by measuring the absorbance at λ_{max}. Estimation can also be done at a wavelength other than λ_{max}, where Beer- Lambert law is obeyed.

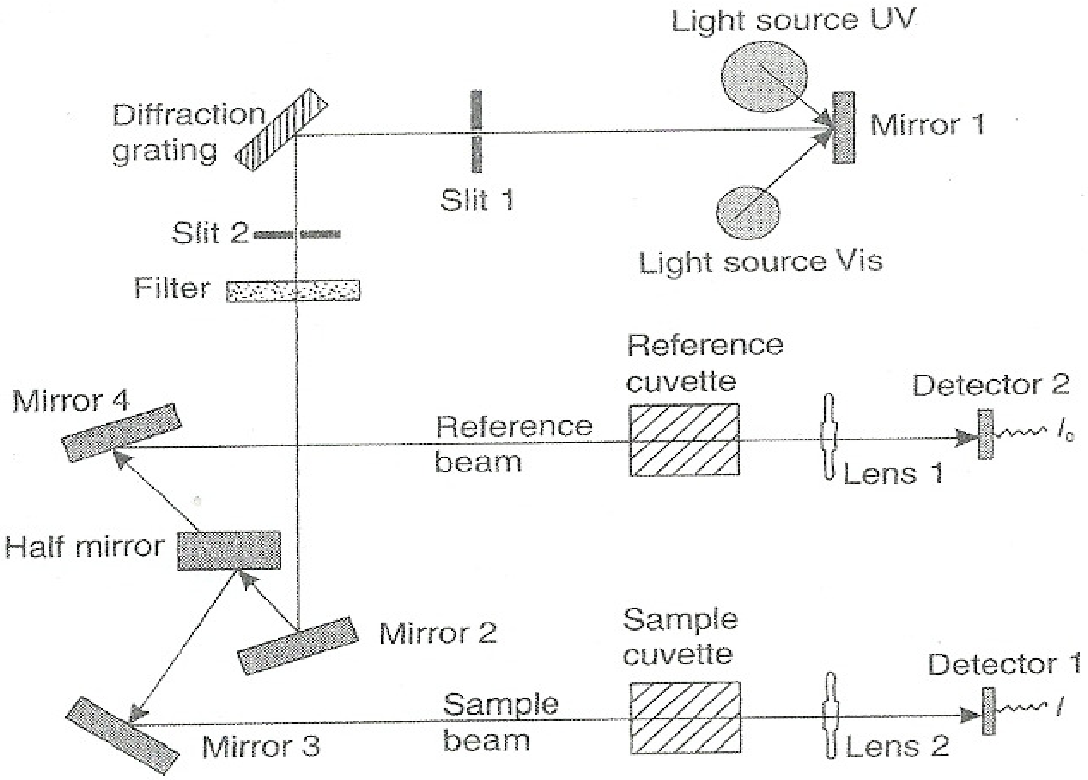


Fig. 2.7. Schematic of a double beam spectrophotometer

5.c. Fourier Transform Infrared spectroscopy (FTIR)

5.c.i. Introduction

Infrared (IR) spectrum covers the range of electromagnetic spectrum between 0.78 and 1000 µm. Usually, in infrared spectroscopy wavelength is measured in 'wave number'.

Wave number = 1/wavelength (in cm) = cm^{-1}

IR region is divided into the three sections: near, mid and far infrared. The wave length/wave number range of the three regions is listed in Table 2.3.

Table 2.3. Wave length/wave number range of IR regions

Region	Wavelength range (μm)	Wave number range (cm^{-1})
Near	0.78-2.5	12800-4000
Middle	2.5-50	4000-200
Far	50-1000	200-10

The region of interest to the analytical chemist lies between 4000 and 670 cm^{-1}. Infrared spectroscopy explains the vibrational motion of chemical bonds and dipole moment change due to the vibrational motion. Dipole moment change of the molecule due to this vibrational motion results in the absorption of electromagnetic radiation in IR region. A typical dispersive IR spectrometer consists of a radiation source, monochromator and detector.

Radiation source is an inert solid heated to 1000-1800ºC (e.g.) Nernst glower (consisted of rare earth oxides), Globar (consisted of SiC) and nichrome coil. Monochromator comprises a prism or gratings with combination of variable slit mechanisms, mirrors and filters. Detector can be thermal or photon detectors.

A block diagram of dispersive spectrometer is given in Fig. 2.8

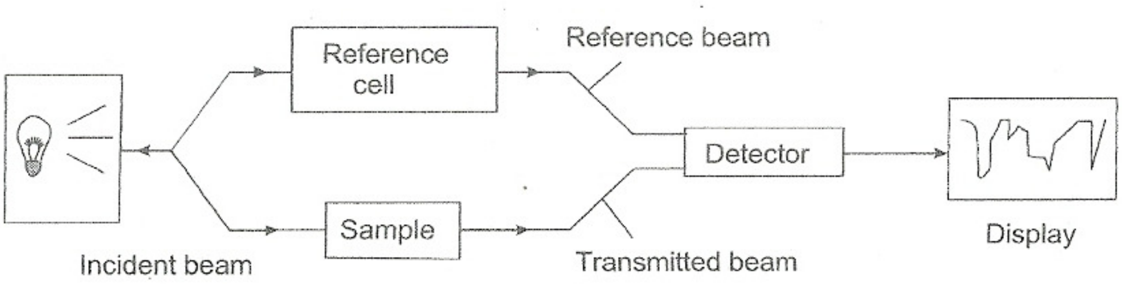


Fig. 2.8. Dispersive IR spectrometer

5.c.ii. Fourier Transform Infrared (FTIR) spectrometer

In FTIR, the spectrum is stored in the form of intensity vs time. Fourier transform is the mathematical process that converts the information from intensity and time to intensity and frequency. FTIR spectrometer records an entire spectrum within a few seconds. The block diagram of a typical FTIR spectrometer is given in Fig. 2.9.

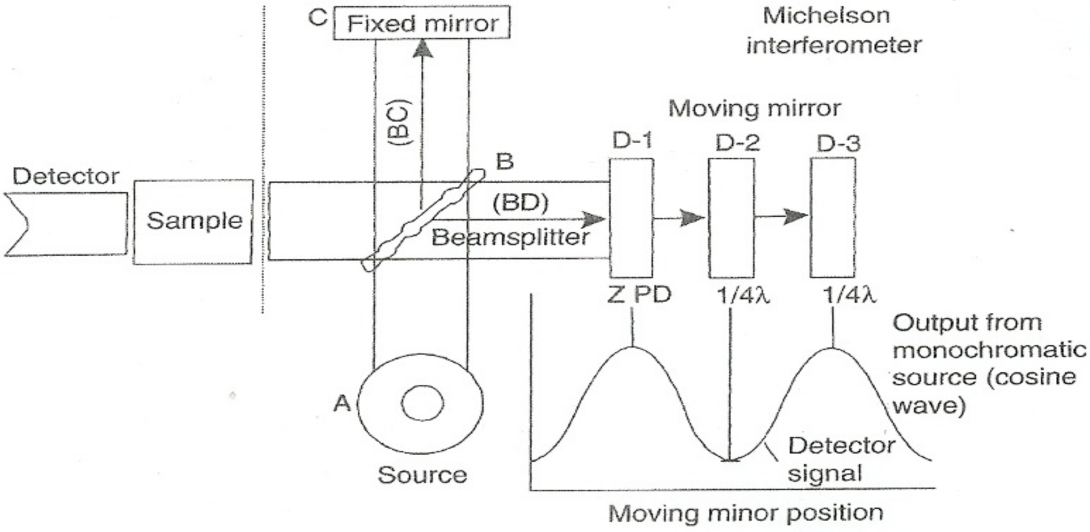


Fig. 2.9. Fourier Transform IR spectrometer

FTIR is different from dispersive IR spectrometers. In FTIR the monochromator is replaced by an interferometer, which divides radiant beams, generates an optical path difference between the beams and recombines them in order to produce repetitive interference signals which are measured as a function of optical path difference by a detector. Commonly used interferometer is a Michelson interferometer. It consists of three components namely beam splitter, moving mirror and fixed mirror. The two mirrors are perpendicular to each other. Beam splitter is a partial reflecting device and is made by depositing a thin film of germanium on to a flat KBr substrate. The radiation from broadband IR source is collimated and directed into the interferometer, which falls on the beam splitter. At the beam splitter, half of the IR beam is transmitted to the fixed mirror and the remaining half is reflected by the moving mirror. After the beams are reflected from the two mirrors, they are recombined at the beam splitter. An interference pattern will generate, due to the changes in the relative position of the moving mirror and the fixed mirror. Differences in the optical paths of the single frequency between the components of two split beams are created by varying the relative position of the moving mirror to the fixed mirror. If the two arms of the interferometer are of equal length, the two split beams travel through the same path length. The two beams are totally in phase with each other; thus, they interfere constructively and lead to a maximum detector response. This position of the moving mirror is called the point of zero path difference (ZPD). When the moving mirror travels in either direction by a distance equal to $\lambda/4$, the optical path is changed by $2(\lambda/4)$ or $\lambda/2$. When the two beams are out of phase with each other, they interfere destructively. As the moving mirror travels another $\lambda/4$ distance, the optical path difference is $2(\lambda/2)$ or λ. The two beams are now in phase with each other and they interfere constructively.

When the mirror is moved at a constant velocity, sinusoidal response is obtained in the detector which is called as interferogram. It is in the time domain. The sinusoidal wave is reduced by an amount proportional to the amount of the sample in the beam. The extension of this procedure to three component frequencies would result in a more complex interferogram, which is the summation of three individual modulated waves. When the IR beam is directed through the sample, the amplitude of a set of waves is reduced by absorption if the frequency of this set of waves is the same as the one which is the characteristic frequencies of the sample. A mathematical operation known as Fourier transformation converts the interferogram to the final IR spectrum which is the familiar frequency domain spectrum showing intensity versus frequency. The detector signal is sampled at small, precise interval during the mirror scan. The sampling rate is controlled by an internal, monochromatic beam from helium-neon laser focused on a separate detector. The common detectors in FTIR spectrometers are deuterated triglycine sulphate (DTGS) and mercury cadmium telluride (MCT).

5.d. Fourier Transform Nuclear Magnetic Resonance Spectroscopy (FTNMR)

Radio waves are the lowest energy form of electromagnetic radiation that is useful in analytical chemistry. But the energy in radio frequency (RF) is sufficient to affect the nuclear spin of atoms that make up the molecule. As a result, the spinning nuclei of atoms in a molecule can absorb RF radiation and change the direction of spinning axis. However, this phenomenon requires the presence of an external magnetic field. This is the principle of nuclear magnetic resonance spectroscopy (NMR). The block diagram of a continuous wave NMR spectrometer is shown in Fig. 2.10.

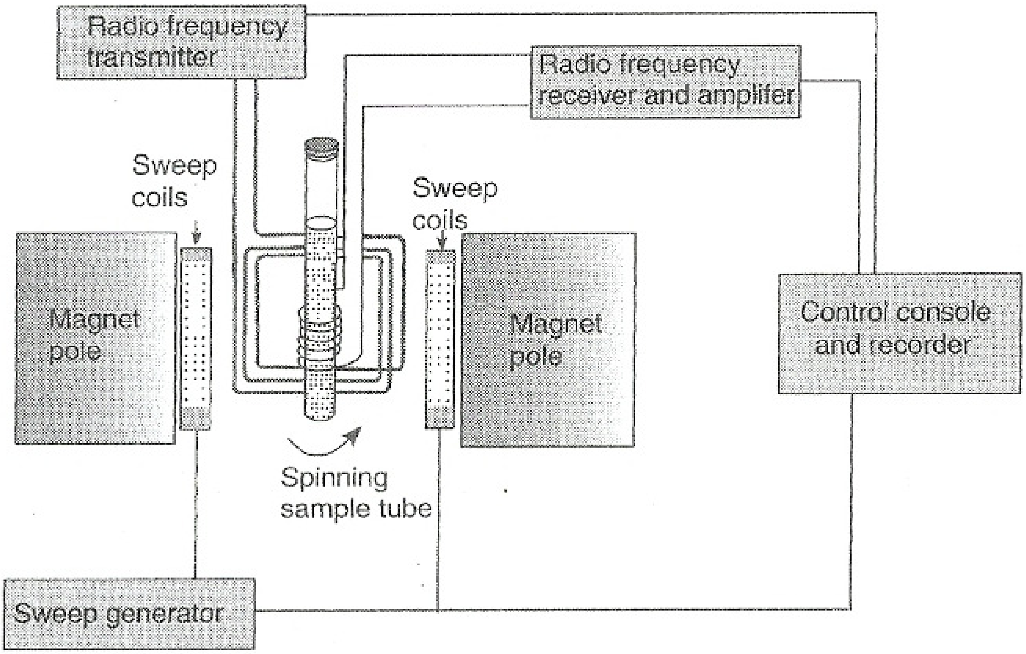


Fig. 2.10. Continuous wave NMR spectrometer

In pulsed Fourier transform NMR, the resonances are not measured one after another, but all nuclei are excited at the same time by a radiofrequency pulse. The excited spins emit the absorbed radiation after the pulse. The emitted signal is a superposition of all excited frequencies. Its evolution in time is recorded. The intensities of several frequencies, which give the observed signal in their superposition are calculated by Fourier transformation, which translates the time data in to frequency domain. The resulting NMR spectrum looks like an ordinary continuous wave NMR spectrum, but its resolution is several orders of magnitudes better. For the thesis work, both ^{1}H and ^{13}C NMR spectra were obtained from 500 MHz NMR spectrometer, Model Bruker AV III.

CHAPTER III

SYNTHESIS OF ACETOHYDROXAMIC ACID

1. INTRODUCTION

Hydroxamic acids and their derivatives have been widely used as bioactive compounds [70-73]. Hydroxamic acid derivatives are antibacterial [74-76], antifungal [77-79] and anticancer agents [77-80] as well as specific enzyme inhibitors [81, 82]. Hydroxamic acid and especially its siderophores are employed as carriers in the development of broad-spectrum and species-selective antibiotics for invitro application [75, 76]. Acetohydroxamic acid is reported to be a good chelating agent for heavy metals. AHA and its alkali metal salts form complexes with metal ions like copper, iron, cobalt, nickel, chromium, manganese, uranium, etc. It has been suggested as a partitioning agent for the separation of uranium and plutonium in the spent nuclear fuel reprocessing [43, 54, 83], owing to the advantage of its complete incinerable property. In view of its complexing ability, which is exploited in the partitioning of uranium and plutonium in nuclear industry, the preparation of AHA economically with simple process steps is essential for its effective use.

2. GENERAL METHODS OF PREPARATION OF HYDROXAMIC ACIDS

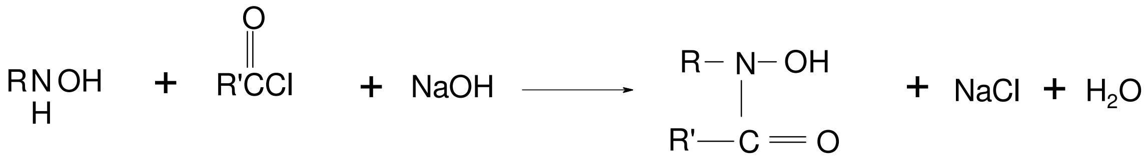
Blatt's method [84] has been the basic procedure for preparing hydroxamic acids for a long time. In this procedure, the ester, RCO_2Et (R = alkyl or aryl) reacts with hydroxylamine in the presence of an alkali. In the second step, free acetohydroxamic acid is generated as per equation (1), by the addition of calculated quantity of the acid, HX to the cold reaction mixture.

$$CH_3CO_2Et + H_2NOH{\cdot}HCl \xrightarrow[2.H_3O^+]{1.KOH} CH_3CONHOH \qquad (1)$$

The following modifications have been made in Blatt’s procedure by different researchers [85 – 88, 42] for the synthesis of hydroxamic acids.

(a) Sodium ethoxide was employed by Dutta [85, 86] in Eq. (1) instead of alkali.

(b) Tandon & Co-workers [87, 88] prepared n-aryl hydroxamic acids using the reactants n-phenyl hydroxylamine (RNHOH) and acetyl chloride in the presence of dilute alkali.



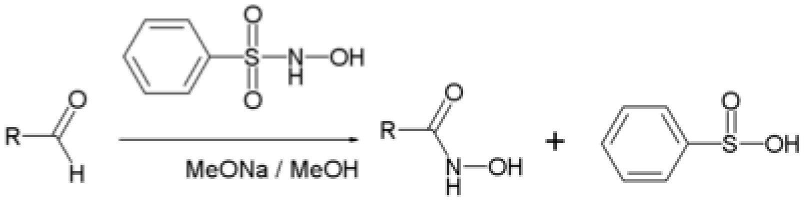
$$RNHOH + R'\overset{O}{\overset{\|}{C}}Cl + NaOH \longrightarrow \underset{R'-C=O}{\overset{R-N-OH}{|}} + NaCl + H_2O \qquad (2)$$

(c) Wise and Brandt [42] had reported a different procedure for the regeneration of AHA. Methanolic solution of a metal hydroxamate was converted to the acid form by cation exchange method using the cation exchanger (R’-H)

$$RCONHOK + R'\text{-}H \longrightarrow RCONHOH + R'\text{-}K \qquad (3)$$

In all these methods, the purity of the product could not be ascertained owing to the presence of salt as an impurity. In addition, the extraction of AHA (prepared by the above methods) into organic solvents was observed to be hindered due to its preference for aqueous medium to exist as alkali metal salts.

Hydroxamic acid has also been prepared by Angeli-Rimini reaction. In this reaction, an aldehyde and sulfonamide (n-hydroxy benzene sulfonamide) react in the presence of a weak base such as methoxide to produce hydroxamic acid [89, 90] according to equation 4.



(4)

When primary nitro compounds are treated with sulfuric acid without previous conversion to the conjugate bases, carboxylic acids are formed. Hydroxamic acids are intermediates in this reaction. They can be isolated under stringent conditions and this is also a method for their preparation [91, 92].

$$CH_3CH_2NO_2 \xrightarrow{H_2SO_4} [CH_3CONHOH] \xrightarrow[H+]{H_2O} CH_3CO_2H + H_2NOH$$

(5)

Since the product obtained in the last two methods has corrosive ions like SO_4^{2-} and SO_3^{2-} as impurities, they may not be ideal for the preparation of AHA.

3. IMPROVED METHOD PROPOSED FOR AHA PREPARATION

3.a. Reagents and Reaction Mechanism

In the present thesis, a modified procedure has been developed for the synthesis of AHA. The chemicals used for the preparation of AHA are (a) Hydroxylamine solution (minimum assay: 50 %) of concentration: 16.954 M, procured from M/s. Himedia Chemicals Pvt Ltd, Mumbai, (b) AR grade ethyl acetate after moisture removal with Na_2SO_4 and (c) acetic anhydride of concentration 9.44 M (AR grade).

Hydroxylamine hydrate reacts with acetic anhydride to produce acetohydroxamic acid and acetic acid as per reaction (6). As this reaction does not involve any alkali salt, purification of the resulting AHA is very easy. AHA thus formed from reaction (6) was purified by solvent extraction followed by crystallization.

$$(CH_3CO)_2O \quad + \quad H_2NOH \longrightarrow CH_3CONHOH \quad + \quad CH_3CO_2H \tag{6}$$

3.b. Selection of Solvent for the Extraction of AHA

In the present study, various organic solvents were tested for their extractability of AHA using 1.33 M AHA feed prepared from 98 % pure commercial AHA compound (M/s. Sigma Aldrich). The concentration of AHA was chosen as 1.33 M because it is the typical concentration of AHA produced from the reaction mixture (hydroxylamine hydrate and acetic anhydride) proposed for the thesis work. 50 mL feed of 1.33 M AHA was transferred to 250 ml separating funnel. To this 50 ml of the organic solvent was added. Aqueous and organic phases were equilibrated for 10 minutes and were separated. The organic and aqueous phases were analysed spectrophotometrically for AHA concentration. The results are given in Table 3.1.

The two solvents, ethyl acetate and 2-butanone showed some extractability of AHA. Among these two solvents, 2-butanone has shown better extractability for AHA. But, it was found to be completely soluble with the AHA formed from the reaction mixture according to Eq. (6). This may be due to the formation of micelle with acetic acid. Therefore, organic and aqueous phase separation was not observed with the actual reaction mixture. In addition, 2-butanone has higher solubility with water itself (27.5 g per 100 ml of water). Hence, ethyl acetate was chosen as the solvent for AHA extraction (solubility of ethyl acetate in water = 8.3 g per 100 ml water).

Table 3.1. Extractability of AHA into various solvents at 30°C

Solvent	Extracted AHA (mol/L)	Remarks
n- Hexane	BDL	No trace of solubility
Benzene	BDL	No trace of solubility
Xylene	BDL	No trace of solubility
Tetra chloromethane	BDL	No trace of solubility
Diethyl ether	0.010	Extraction was insignificant
chloroform	0.010	Extraction was insignificant
Ethyl acetate	0.027	Low extractability
Hexone or methyl isobutyl ketone	0.017	Low extractability
2- Butanone or methyl ethyl ketone	0.182	Very good extractability

BDL- Below Detectable Limit

3.c. Ethyl Acetate as the Solvent for AHA Extraction

After ascertaining the extractability of AHA by ethyl acetate, the effect of pH on the extractability of AHA into ethyl acetate was investigated. The pH of the 1.33 M AHA feed was adjusted with ammonium hydroxide and hydrochloric acid for alkaline and acidic medium respectively. The results are given in Table 3.2.

Table 3.2. The effect of pH on the extractability of AHA in ethyl acetate solvent

pH of extraction	Extracted AHA (mol/L)
1.5	0.025
2.5	0.026
3.5	0.026
4.5 (actual pH of reaction mixture)	0.027
6.0	0.026
8.0	0.025

This Table indicated that there was no change in the extraction of AHA into ethyl acetate due to the change in pH of the medium. Since there was no change in the extraction of AHA with change in pH, the effect of temperature was studied on the extractability of AHA into ethyl acetate solvent by measuring the extractability at various temperatures (from room temperature (30°C) to nearly the boiling temperature of ethyl acetate (77°C). The results are given in Table 3.3.

Table 3.3. Effect of temperature of the medium on the extractability of AHA in to ethyl acetate

Temperature of the reaction mixture (°C)	Concentration of extracted AHA (mol/L)
30	0.027
40	0.055
50	0.106
60	0.156
70	0.236

It could be observed that the extractability was about an order of magnitude higher at 70°C compared to room temperature (30°C). However, vapourisation of ethyl acetate will be high at 70°C, because this temperature is very close to the boiling temperature of ethyl acetate and handling the vapour will be difficult. Hence, alternate reaction path should be identified in which AHA extraction into ethyl acetate will be high at room temperature.

3.d. Preparation of AHA

To 25 mL of a 50 % solution of hydroxylamine hydrate (0.42 mol) taken in a beaker, 25 mL of water was added. This beaker was kept over a magnetic stirrer and the contents were stirred. To this solution under stirring, 45 ml of acetic anhydride (0.42 mol) was added slowly. The temperature of the reaction mixture rose to 80º during the addition. After the addition of acetic anhydride, the reaction mixture was allowed to cool to room temperature with continued stirring and was equilibrated with ethyl acetate (4 x 70 mL). The combined extracts were concentrated in vacuum to a volume of 90 mL and cooled to 0ºC for 16 h. The resulting precipitate (20 g, 88 % pure) was collected and recrystallized from acetone to give 17 g (yield: 55 %) of 98 % pure product.

3.e. Solvent Extraction of AHA from the Reaction Medium

The formation yield of AHA was estimated to be 89.3 %, by measuring the absorbance of Fe^{3+}-Hydroxamate complex at 498 nm. Acetic acid formed in the reaction was found to be 0.56 mol, which was estimated by titrating with standardized NaOH. The amount of acetic acid expected from the reactants was 0.42 mol. The higher amount of acetic acid in the reaction mixture, which is contradictory to the stoichiometric coefficient of the reactants, is attributed to the hydrolysis of acetic anhydride. AHA produced was extracted into ethyl acetate, for purifying it from the reactants and the results are given in the Table 3.4.

Table 3.4. Extraction of AHA by ethyl acetate (organic phase)

Extraction stage	Feed		After extraction		Amount of AHA		% extracted in each stage
	Aqueous phase volume mL	Organic phase volume mL	Aqueous phase volume mL	Organic phase volume mL	Aqueous phase g	Organic phase g	
Feed	83	---	---	---	28	---	---
1	83	80	81	79	18.73	9.65	34.46
2	82	80	53	110	5.66	13.07	46.68
3	53	50	44	56	4.96	0.70	2.5
4	44	44	40	47	4.50	0.44	1.57
5	40	40	36	43	4.10	0.39	1.39

The data presented in Table 3.4 indicates that 34 and 47 % of AHA could be extracted into the organic phase in the first contact and second contact respectively, whereas the AHA extraction was nearly constant beyond 4th contact. Hence, further extraction was not carried out. The AHA extracted in all the stages was determined quantitatively. In the first contact, the volume of 80 mL of the aqueous became 81 mL, because about 1 mL of the organic phase dissolved in the reaction mixture. The percentage of extraction of AHA from the total amount formed was 34.5 % in the first contact. In the second contact, volume of the organic phase increased to 110 mL from 80 mL. Increased miscibility of aqueous phase reaction mixture in the organic phase is attributed to the formation of micelle by dissolved ethyl acetate with acetic acid and water system. Owing to this miscibility, AHA extraction increased to 46.7%. AHA extraction decreased drastically in further contacts. Extraction percentage of AHA plotted against contact number in Fig. 3.1 indicates that from third contact onwards, extractability of AHA into the organic phase was almost equal in further contacts. As further contacts would increase the organic volume and dilute the extracted product, equilibration contacts up to four numbers is sufficient to extract 85 % of AHA. The remaining 15 % of AHA was retained in the mother liquor. This trend of extraction in different contacts was confirmed by five iterations. In all the five iterations, similar trend as in Fig. 3.1 was observed.

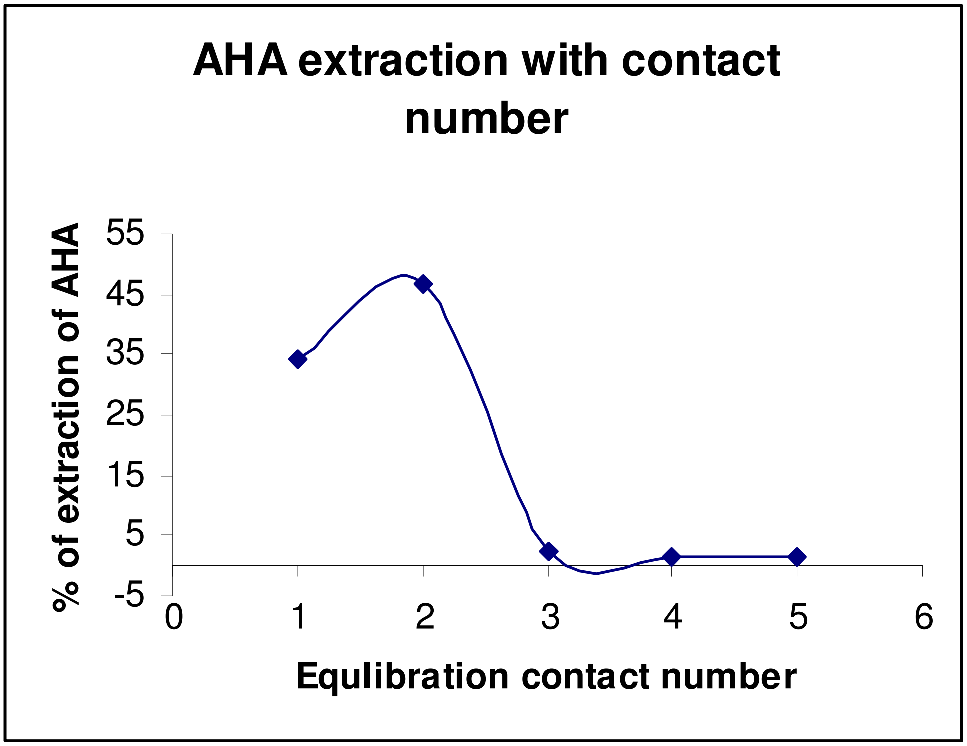


Fig. 3.1. Extraction percentage of AHA with contact number

3.f. Crystallisation of AHA from Ethyl Acetate Extract

Acetohydroxamic acid in ethyl acetate (≈ 240 mL) was concentrated in a Rotary evaporator under reduced pressure. The volume was reduced to 90 mL. Moisture content of ethyl acetate product in the reduced volume was estimated by (coulometric)

Karl Fischer titration to be 10.5 %. The concentrated product was refrigerated with AHA seed for 16 h. 20.02 g of AHA crystals were formed leaving behind 4.1 g of AHA in the organic phase. This 4.1 g of AHA in the organic phase can be recovered by further concentration and crystallisation by refrigeration. The AHA crystals thus formed were characterized by different methods.

4. CHARACTERISATION OF AHA

4.a. FTIR Spectral Study

FTIR spectra of the synthesized AHA were recorded using Bomem MB FTIR spectrometer at the resolution of 4 Wave Numbers. The spectra recorded for the synthesized compound has been compared with a similar IR spectrum obtained for a commercially available AHA sample of purity 98 %, procured from M/s. Sigma-Aldrich in Fig. 3.2. Absorption peaks of commercial and synthetic AHA are given in Table 3.5 along with their assignment. The vibrational spectrum of AHA mainly consists of amide I, amide II and amide III bands [93]. Amide I band is due to the $\nu_{C=O}$ stretch. Amide II band is caused as a result of vibrational coupling of $\delta_{(N-H)}$ bend and $\nu_{(C-N)}$ stretch. Amide III band resulted from the combination of $\nu_{(C-N)}$ stretching and $\delta_{(N-H)}$ rocking character. $\nu_{(N-O)}$ (oxime) stretch, $\delta_{(CH3)}$ and $\delta_{(NOH)}$ bending modes were also observed. These vibrations are in the wave number range of 900-1700 cm^{-1}.

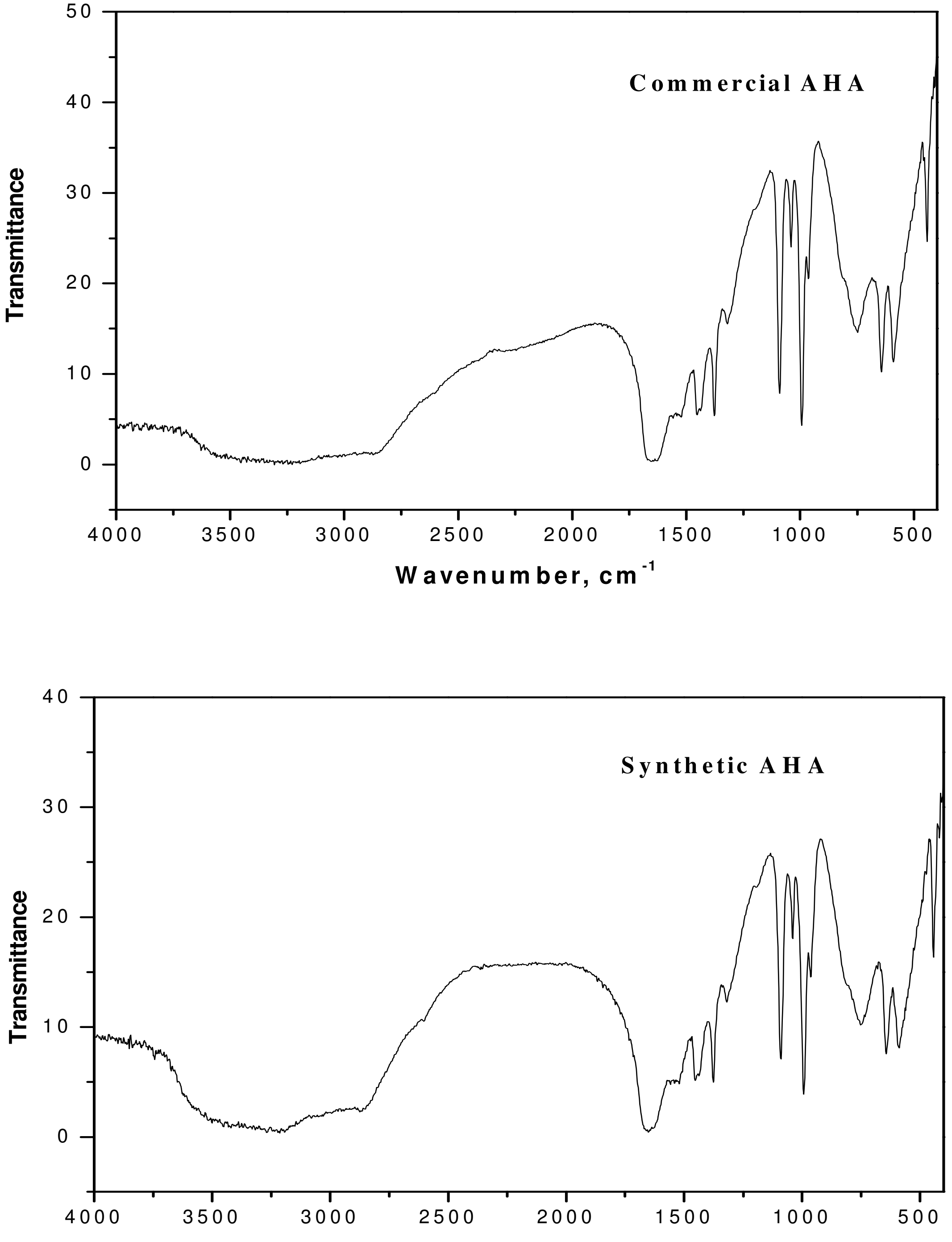


Fig. 3.2. FTIR spectra of commercial and synthetic AHA

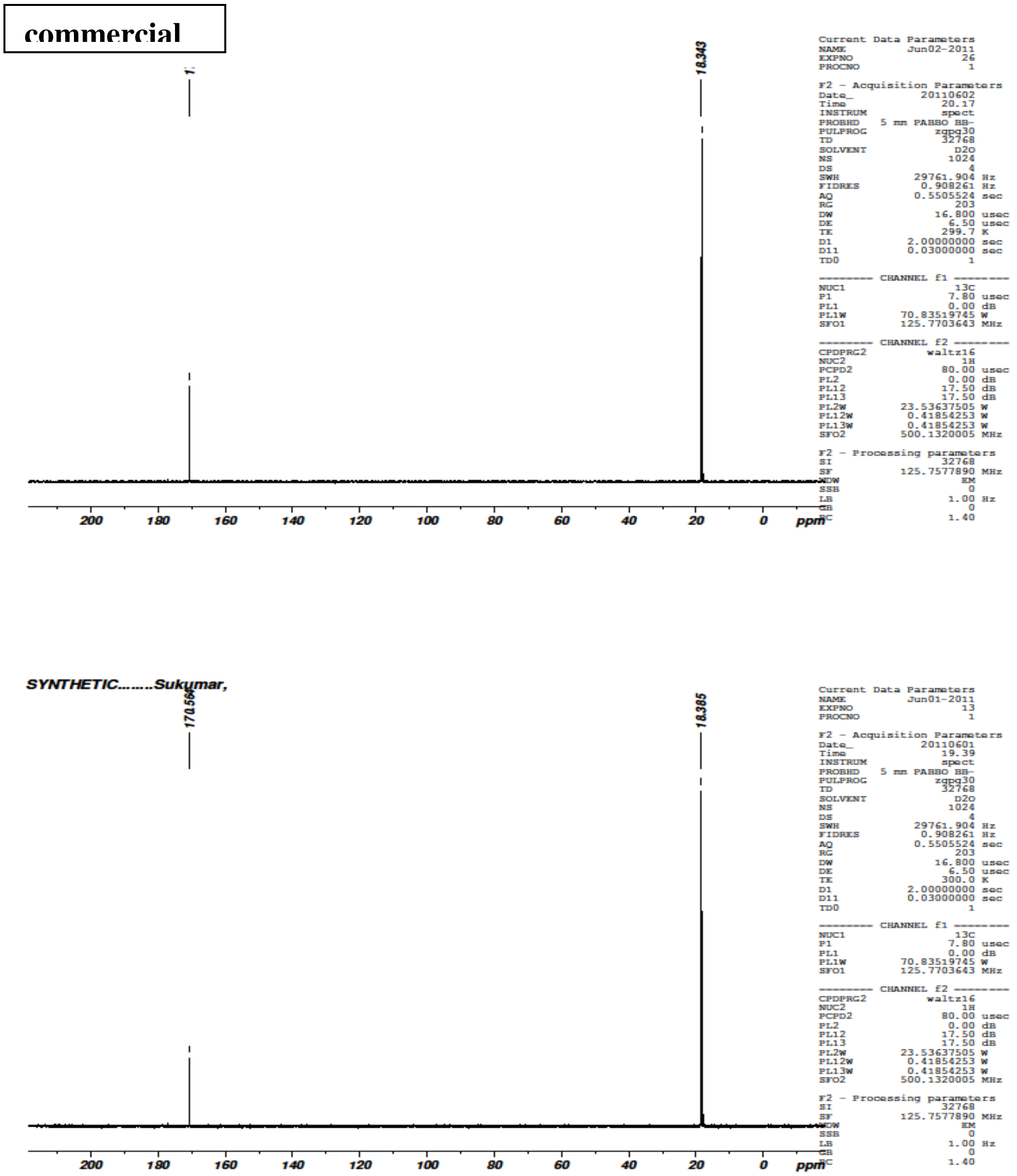
Table 3.5. Comparison of FTIR spectral analysis of commercial and synthesized AHA

Sl. No.	Peaks of Commercial AHA (Wave number in cm^{-1})	Peaks of synthesized AHA (Wave number in cm^{-1})	Assignment
1	1642.6	1643.4	Amide I $\nu_{C=O}$
2	1438.9	1439.76	Amide II δ_{CH3} adef δ_{CH3} rock
3	1374.6	1375.4	Amide II δ_{CH3} sdef
4	1321.0	1321.85	Amide III ν_{C-N} δ_{N-H} ν_{N-O}
5	1085.2	1086.03	Amide III ν_{N-O} ν_{CH3} rock
6	1044.8	1044.8	Amide III ν_{CH3} rock
7	999.4	1000.2	Amide III ν_{CH3} rock ν_{N-O} ν_{C-C}

4.b. NMR Spectral Study

Both ^{1}H and ^{13}C NMR spectra recorded for the synthesized as well as commercial (98 % pure) AHA compounds are reproduced in Figs. 3.3 and 3.4 respectively. In ^{13}C NMR spectra, methyl carbon (18.343 ppm) and carbonyl carbon (170.55 ppm) were observed for both samples. In ^{1}H NMR only methyl proton (1.7 ppm) could be observed for both samples. Since, the protons attached to nitrogen atom and oxygen atom exchange themselves with the solvent (D_2O) very rapidly, they did not appear in the peaks. In proton NMR, the peak at around 4.8 ppm corresponded to D_2O.

The NMR studies confirmed that the synthesized AHA compound is similar to the commercially available AHA.



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PROCNO                 1

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PULPROG          zgpg30
TD                32768
SOLVENT              D2O
NS                 1024
DS                     4
SWH            29761.904 Hz
FIDRES          0.908261 Hz
AQ             0.5505524 sec
RG                   203
DW                16.800 usec
DE                  6.50 usec
TE                 299.7 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.80 usec
PL1                 0.00 dB
PL1W         70.83519745 W
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               17.50 dB
PL13               17.50 dB
PL2W         23.53637505 W
PL12W         0.41854253 W
PL13W         0.41854253 W
SFO2         500.1320005 MHz

F2 - Processing parameters
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FIDRES          0.908261 Hz
AQ             0.5505524 sec
RG                   203
DW                16.800 usec
DE                  6.50 usec
TE                 300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.80 usec
PL1                 0.00 dB
PL1W         70.83519745 W
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
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NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               17.50 dB
PL13               17.50 dB
PL2W         23.53637505 W
PL12W         0.41854253 W
PL13W         0.41854253 W
SFO2         500.1320005 MHz

F2 - Processing parameters
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LB                  1.00 Hz
GB                     0
PC                  1.40
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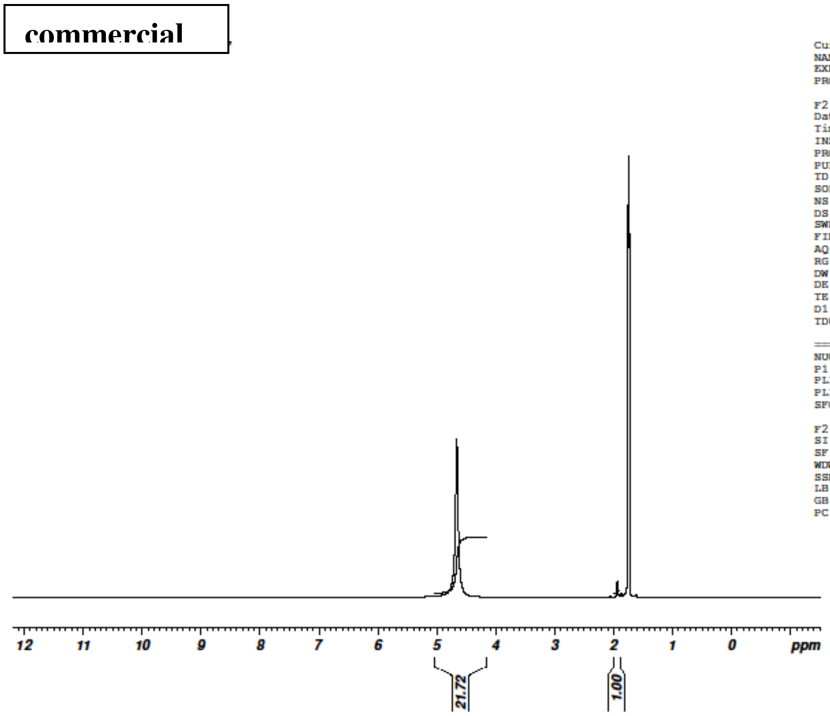
Fig. 3.3. ^{13}C NMR spectra of commercial and synthetic AHA



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AQ             1.5860212 sec
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TE                 297.8 K
D1            1.00000000 sec
TD0                    1

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PL1W         23.53637505 W
SFO1         500.1330885 MHz

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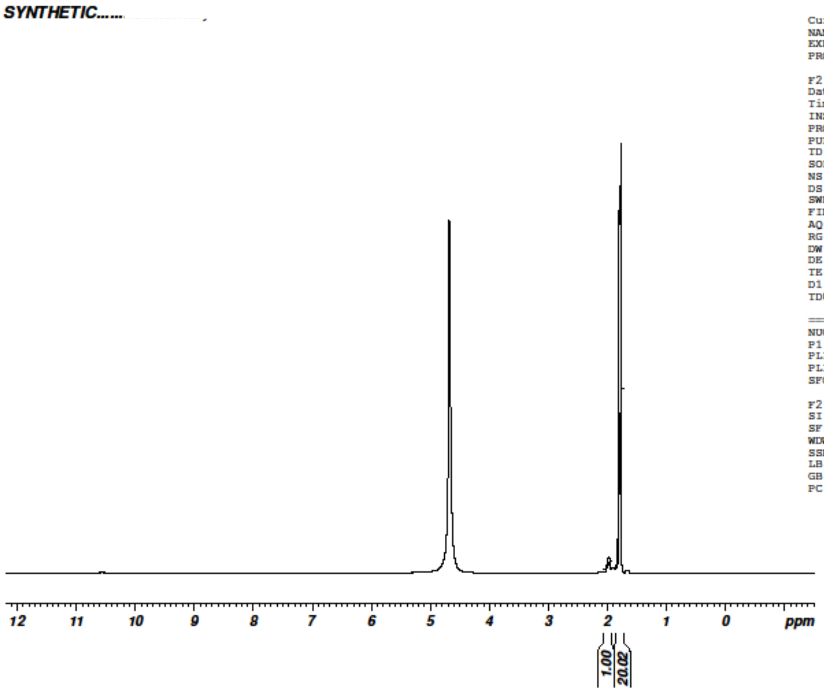

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TD                 32768
SOLVENT              D2O
NS                    32
DS                     2
SWH            10330.578 Hz
FIDRES          0.315264 Hz
AQ             1.5860212 sec
RG                  45.2
DW                48.400 usec
DE                  6.50 usec
TE                 298.5 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.65 usec
PL1                 0.00 dB
PL1W         23.53637505 W
SFO1         500.1330885 MHz

F2 - Processing parameters
SI                 32768
SF           500.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

Fig. 3.4. ^{1}H NMR spectra of commercial and synthetic AHA

4.c. Purity Check of AHA Crystals by UV- Visible Spectrophotometry

Vibrational spectra/NMR studies confirmed that the synthesized AHA compound does not have other functional groups. In order to ascertain the applicability of AHA in complexing Pu(IV), the synthesized AHA was tested with Fe^{3+}, whose reduction behaviour would represent the behaviour that would be exhibited by Pu(IV) and thus, indicating the applicability of AHA in the partitioning of uranium and plutonium. For this purpose, aqueous solution of the synthesized AHA was complexed with Fe^{3+} and the absorption spectra of the complex was recorded and shown in Fig. 3.5. The absorption spectral study indicated that the purity of AHA was 88.7 %. In view of the lower purity as compared to commercial AHA, the synthesized AHA was further purified by recrystallizing from acetone medium. The purity of the recrystallised AHA was enhanced to 98 %, which was ascertained by Fe^{3+}-AHA complex formation studies. The purity achieved by this method was confirmed by cross checking the purity of commercial AHA by the same method. The flow sheet for the preparation of AHA by the method of synthesis proposed in the present thesis is given in Fig. 3.6.

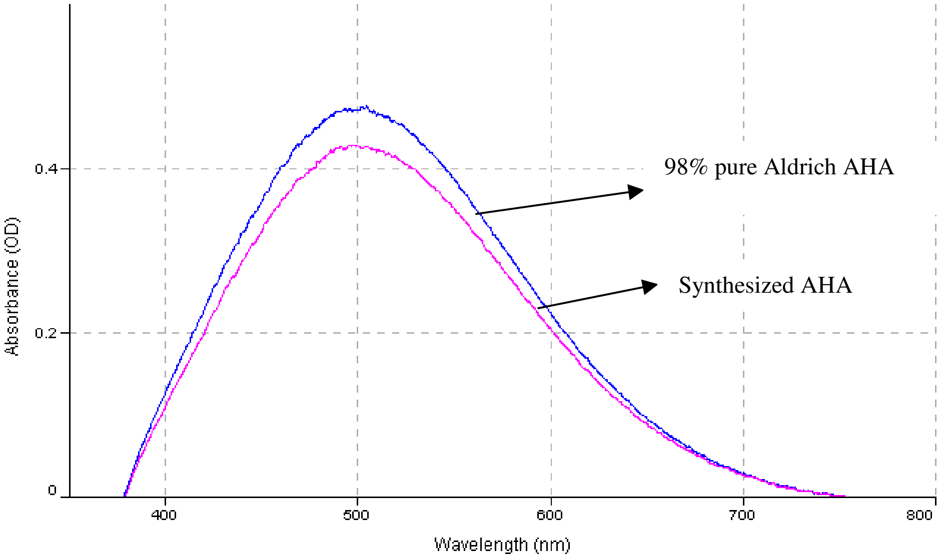


Fig. 3.5. UV visible spectra of commercial and synthesised AHA:Fe^{3+} complex

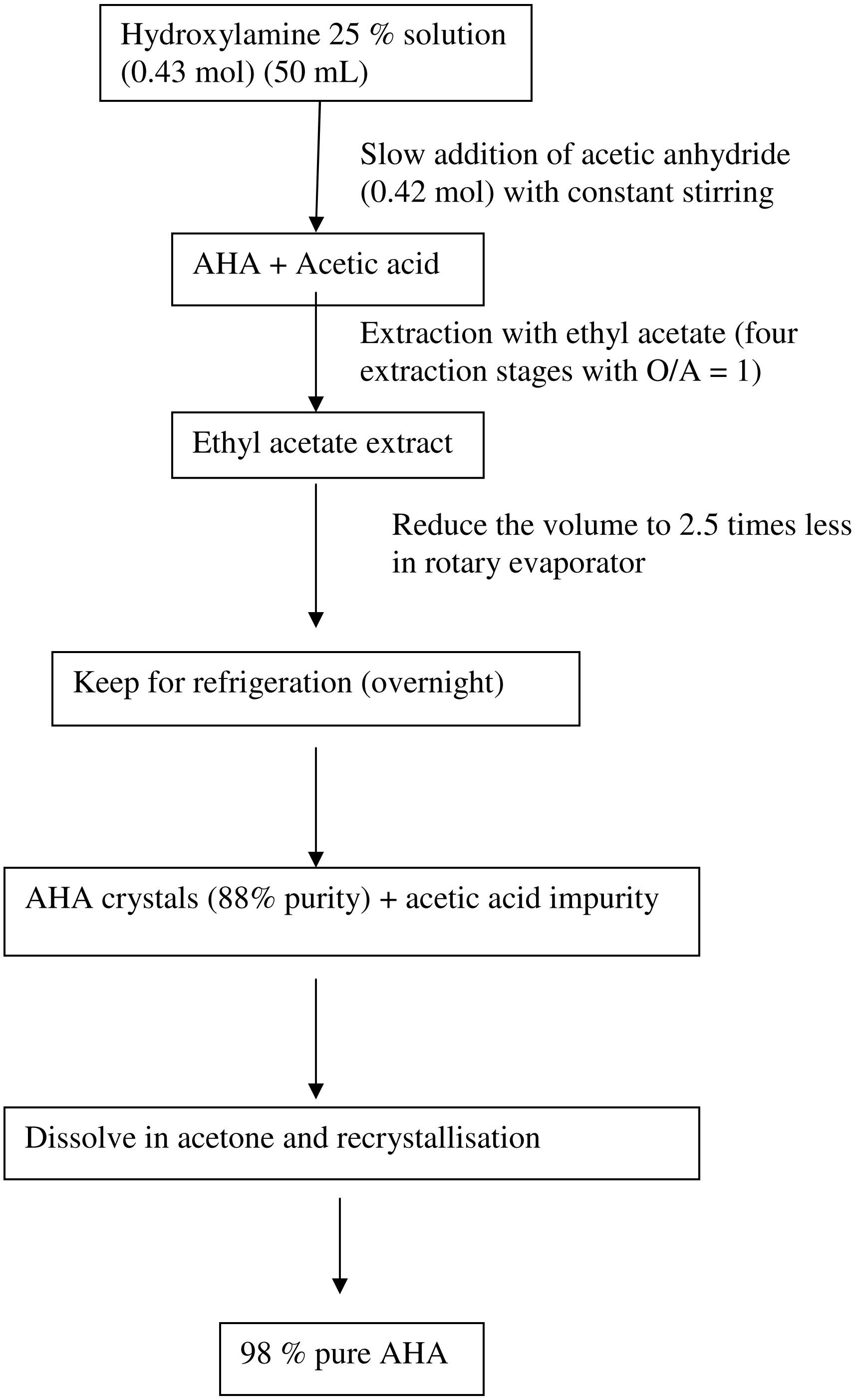


Fig. 3.6. Flowsheet of AHA preparation

5. CONCLUSION

A simple method for the preparation of AHA has been identified by acylation of hydroxylamine with acetic anhydride. Generally, hydroxylamine hydrochloride is used as the precursor material. If hydroxylamine hydrochloride is used, removal of chloride is required before solvent extraction step; otherwise, it interferes in the solvent extraction in addition to introducing corrosive ions. In the proposed method, hydroxylamine hydroxide was chosen instead of hydroxylamine hydrochloride. The reaction product from the acylation of hydroxylamine hydroxide using acetic anhydride does not involve any salt content. Hence, with two contacts of solvent extraction, most of the AHA in the reaction medium could be extracted into the solvent, ethyl acetate. Ethyl acetate was selected as the solvent for extraction based on its extraction behaviour compared to other solvents. The ethyl acetate extract was concentrated and AHA was crystallised out from the ethyl acetate extract upon refrigeration. The crystals were further purified by recrystallisation in acetone medium. Purity of the synthesized product was found to be nearly the same as that of the commercial product. Feasibility studies performed with Fe^{3+}-AHA complex confirmed that the synthesized AHA compound could be employed for the separation of U and Pu.

CHAPTER IV

REDUCTION AND COMPLEXATION OF METAL IONS BY ACETOHYDROXAMIC ACID – POSSIBLE MECHANISM

1. INTRODUCTION

Acetohydroxamic acid (AHA) has the potential application in the single cycle solvent extraction flowsheets for Advance Fuel Cycles (AFCs) [83]. AHA has been used as a reduction/complexation reagent to separate uranium from plutonium and other metallic impurities in the popularly called UREX process [43]. AHA is used as colorimetric and gravimetric reagent for many years [94]. The current interest on AHA is focused towards investigating the reduction/complexation behavior of AHA with metal ions. Acetohydroxamic acid exists in two tautomeric forms. One is keto form and the other is enol form (viz. Fig. 1.2).

Keto form has one replaceable hydrogen atom, but in the enol form two replaceable hydrogen atoms are present. In acid medium, the keto form predominates and in alkaline medium hydroxamic acids exist as enol form. Carbonyl oxygen acts as a donor centre in the metal chelate based on the hydroxamide structure. Therefore, electron withdrawal from carbonyl group takes place. As a consequence, electron density in C-N bond increases. Owing to the metal chelation, lowering of carbonyl frequency and an increase in C-N frequency of hydroxamic acid will occur in the Infra Red spectrum. Hydroxamic acids (RCONR’OH) are in general a weak donor and the pKa value varies from 7.05 to 11.33 depending on the substituents in nitrogen atom (R’) and alkyl groups (R). pKa value of AHA is 7.397 [42].

2. THE COMPLEXING ABILITY OF AHA

Most of the literature reviews on the stability constants and metal complexation properties have been focused on benzohydroxamic acid. Fe(III), Ru(III), U(VI), Zr(VI), Th(VI), Pu(IV), rare earths and Al(III) are some of the metals investigated with benzohydroxamic acid [41, 47, 95]. The stability constants of selected cations with AHA [43] are listed in Table 4.1.

Table 4.1. Stability constants of some metal ions with AHA

Meal ion	$\log\beta_1$	$\log \beta_2$	$\log \beta_3$
Fe(III)	11.42	21.10	28.33
Al(III)	7.95	15.29	21.47
Ce(III)	5.45	9.79	12.80
La(III)	5.16	9.33	11.88
Ca(II)	2.4	---	---

β_1= [ML]/[M] [L]; β_2= [ML_2]/[ML] [L] and β_3 = [ML_3]/[[ML_2] [L]

The trend in the stability constants of metal chelate of AHA with actinide ions is as follows [43].

$\beta(U(VI)) < \beta(H+) < \beta(U(IV)) < \beta(Np(IV)) < \beta(Pu (IV))$

3. REDUCTION BEHAVIOUR OF ACETOHYDROXAMIC ACID

The earlier work on measuring the onset potential of AHA by cyclic voltammetry was by Taylor and May [44], who have reported the value as 0.55V vs saturated calomel electrode in 0.1 M nitric acid and 0.58 V in neutral 0.1 M KNO_3. A recent estimate of the onset potential for the oxidation of AHA is reported to be 0.861 V [96]. The value of

0.55 V has been accepted as reasonable and it was confirmed by other researchers. Karraker et al. [52] reported the possible oxidation of AHA to give 2 e^-. The oxidation reaction is given in Eq. (1).

$$\text{R-CONHOH} + 2\text{H}_2\text{O} \leftrightarrows \text{R-COOH} + \text{HN(OH)}_2 + 2\text{H}^+ + 2\ e^- \qquad (1)$$

Carrot et al. [96] indicated the following mechanism for the reduction of Pu^{4+} ion in a recent study:

$$Pu^{4+} + n\text{AHA} \overset{\text{Fast}}{\leftrightarrows} Pu(\text{AHA})_n{}^{4-n} \overset{H^+,\ \text{slow}}{\leftrightarrows} Pu^{4+} + \text{AHA} + NH_3OH^+ + CH_3COOH \overset{\text{AHA}/NH_3OH^+}{\leftrightarrows} Pu^{3+} \qquad (2)$$

Reaction (2) indicates that the initial hydrolysis of AHA to hydroxylamine and acetic acid occurs in a fast manner, and subsequently the metal ion is reduced by hydroxylamine. Qualitative analytical tests have reported that Pu(IV) forms an intense red colour with AHA solution [52]. When allowed to stand for a long time, the colour turns to blue. Hence, the following reaction (Eq.(3)) will favour the formation of NH_3OH^+ which in turn will react with Pu^{4+} to produce Pu^{3+}.

$$CH_3CONHOH + H_2O \overset{H^+}{\leftrightarrows} CH_3COOH + NH_3OH^+ \qquad (3)$$

4. PRESENT STUDY ON THE MECHANISM OF AHA REACTION WITH PLUTONIUM IONS IN NITRIC ACID

4.a. Study with Iron (Fe^{3+} and Fe^{2+})

4.a.i. Study with Fe^{3+}

Ferric nitrate solution (0.1 mL) from 8.0 g/L stock solution was mixed with 500 µg of AHA in a 10 mL standard measuring flask. The absorbance spectra was recorded using HITACHI U2800 Model spectrophotometer (vide Fig. 2.3). From the absorption spectra, λ_{max} value was found to be 498 nm for Fe^{3+}-AHA complex. The metal ion (Fe^{3+}): ligand ratio was estimated by Job's variation method (Chapter II. 2.a). In Job's variation method, various permutation combinations of metal and ligand were added to each other and the metal and ligand concentrations are plotted in the X axis against the absorbance in Y axis. From the plot, one can get peak value of absorbance. The corresponding metal and ligand quantities from the X axis for the peak value of absorbance are noted. From the metal and ligand quantities, one can find the metal: ligand ratio for a particular coordination complex. Job's variation plot for AHA and Fe^{3+} ion has been shown in Fig. 2.1. From the Job's variation procedure, the metal/ligand ratio for Fe^{3+}-AHA complex was found to be 1:1. The structure of the intense deep red coloured complex was presented in Fig. 1.2.

4.a.ii. Study with Fe^{2+}

Ferrous (Fe^{2+}) ions were produced by the reduction of ferric ions with hydroxylamine in order to investigate the complexation behaviour of AHA with ferrous ions. The Fe^{2+} ions thus produced were made to react with AHA and the absorbance spectrum was recorded for Fe^{2+}-AHA complex using Hitachi U2800 spectrophotometer. Neither red colour formation nor peaks could be observed.

4.b. Complexation of AHA with Plutonium

Plutonium mainly exists as Pu(III), Pu(IV) and Pu(VI) in aqueous solutions of nitric acid. AHA complexation studies were carried out with all the three oxidation states of Pu.

4.b.i. Study with Pu(IV) ion

A solution of plutonium(IV) nitrate was prepared by dissolving PuO_2 powder in 12 M nitric acid containing 0.1 M HF. The fluoride ions were eliminated from plutonium(IV) nitrate solution by solvent extraction using 30% TBP and subsequent stripping with 0.1 M nitric acid. This solution was conditioned with $NaNO_2$ and its concentration was estimated using alpha scintillation counter. The absence of other oxidation states of Pu was confirmed by measuring the absorbance spectrum of plutonium.

Plutonium(IV) nitrate feed was prepared with [Pu] = 5 g/L and $[HNO_3]$ = 0.4 M. To this feed, slight excess to the stoichiometric requirement of AHA was added. Intense deep red colour formation was observed. Absorbance spectra of the complex recorded with fibre optics spectrophotometer is shown in Fig. 4.1.

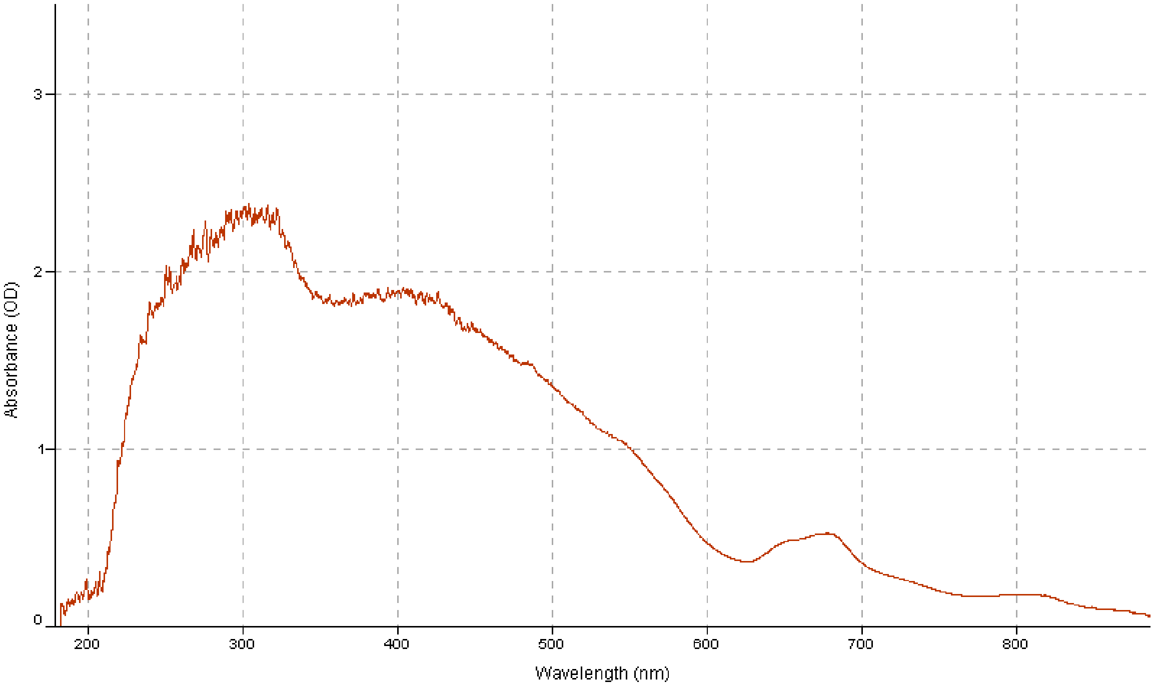


Fig. 4.1. Absorbance spectra of Pu^{4+}-AHA complex

In this figure the nitrate peak was observed at 300 nm. In the visible region of the spectrum, a gradual decrease in absorbance from 400 to 630 nm was observed, followed by a broad peak at 675 nm. In the visible region, 400 nm was chosen as the λ_{max} for the study of Job's variation method to find out the metal: ligand ratio of Pu^{4+}: AHA complex. The plot of Pu^{4+}:AHA complex (shown in Fig. 2.2) reveals the Pu^{4+}:AHA ratio to be 1:1 by Job's variation method.

4.b.ii. Study of AHA reaction towards Pu(III) ion

To 2 mL of $Pu(NO_3)_4$ solution consisting of 5 g/L plutonium in 0.5 M nitric acid ascorbic acid was added with a little excess of the stoichiometric requirement to convert Pu^{4+} to Pu^{3+}. The blue coloured $Pu(NO_3)_3$ solution formed was characterized by recording its absorbance spectra using fibre optics spectrophotometer. The absorbance spectrum of Pu^{3+} is shown in Fig. 4.2.

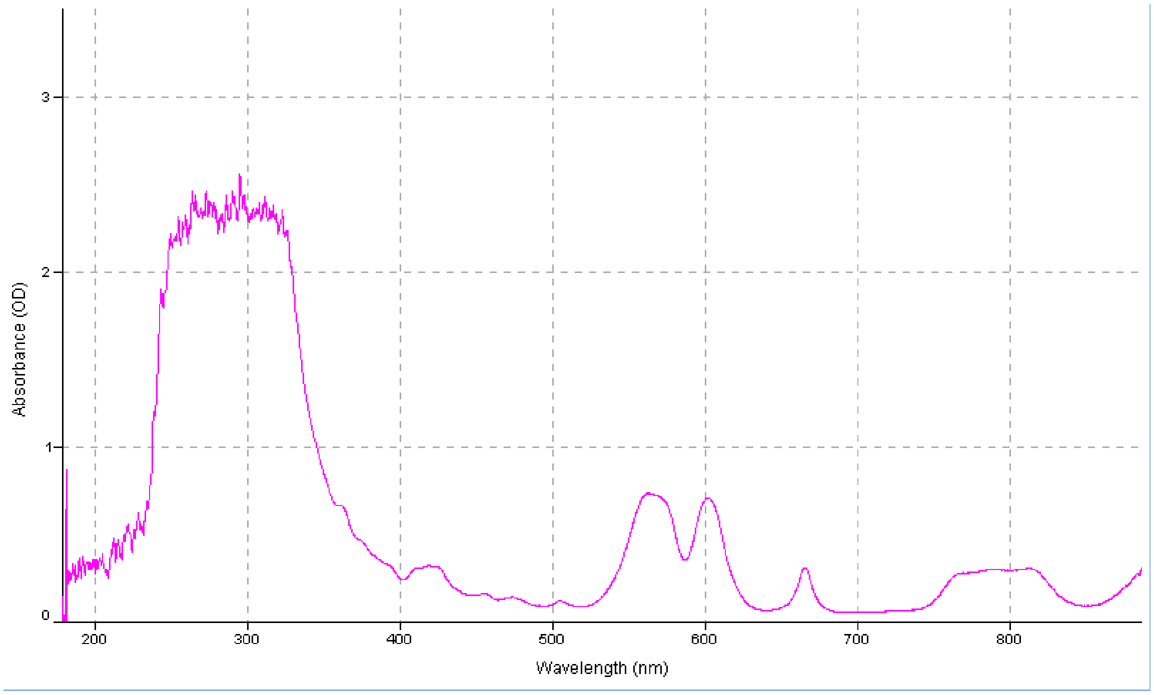


Fig. 4.2. Absorbance spectrum of Pu^{3+} ion in 0.5 M nitric acid

There was no change in blue colour when 1 mL of 0.3 M AHA in double distilled water was added to the above $Pu(NO_3)_3$ solution. The absorbance spectrum recorded for $Pu(NO_3)_3$ solution after adding AHA is given in Fig. 4.3.

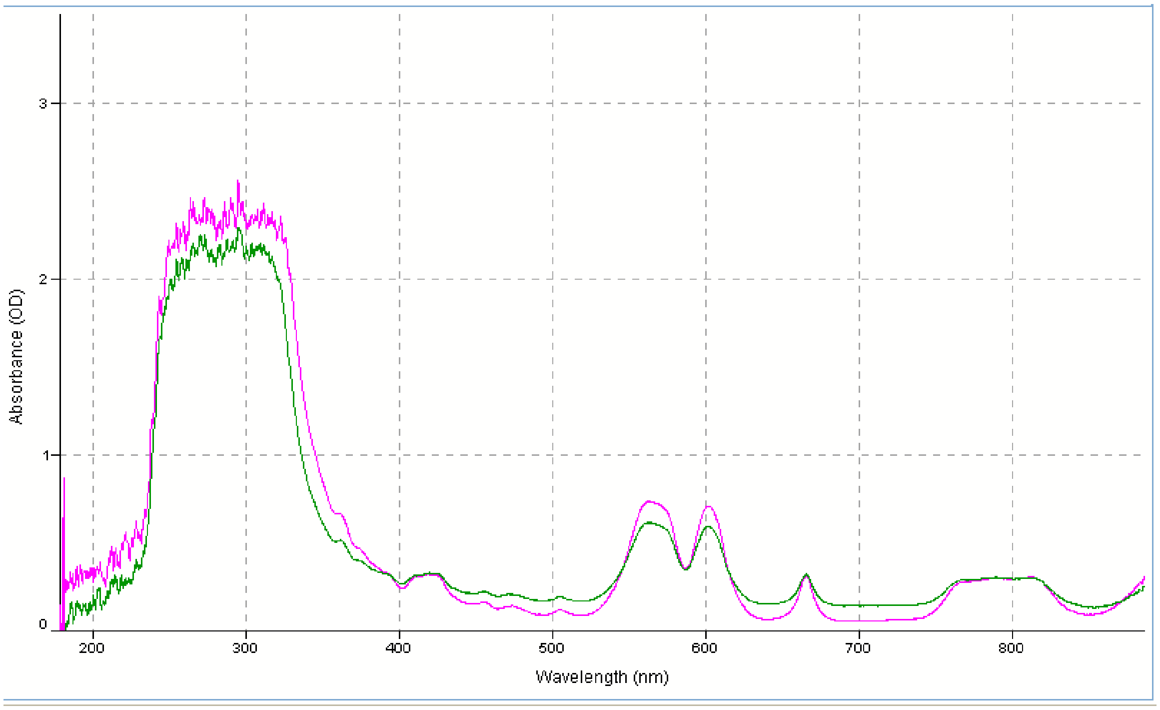


Fig. 4.3. Absorbance spectra of Pu^{3+} in 0.5 M nitric acid, after the addition of 1 mL of 0.3 M AHA

Two overlapped spectra are presented in Fig. 4.3. The spectrum which is displayed as the upper curve corresponds to $Pu(NO_3)_3$ solution before adding AHA. The lower curve resulted after the addition of AHA to $Pu(NO_3)_3$ solution. The marginal decrease in the absorbance is due to the dilution of the sample. Otherwise, no change could be observed in the peak positions in the spectrum of $Pu(NO_3)_3$ solution due to the addition of AHA. Visual examination also indicated that there was no change in blue colour of $Pu(NO_3)_3$ solution due to AHA addition.

4.b.iii. Study of AHA reaction with Pu(VI)

Plutonium in its +6 oxidation state (PuO_2^{2+}) was produced by treating $Pu(NO_3)_4$ solution with perchloric acid and evaporating the mixture to dryness. This PuO_2^{2+} solution was dissolved in 0.75 M nitric acid. The feed solution of Pu as $PuO_2(NO_3)_2$ was estimated for its concentration of plutonium by α counting in ZnS(Ag) scintillation counter. The concentration of the feed solution was [Pu] = 2.9 g/L and $[H^+]$ = 0.75 M in a volume of 2 mL. The absorbance spectrum given in Fig. 4.4 was recorded for the feed solution using fibre optic spectrophotometer.

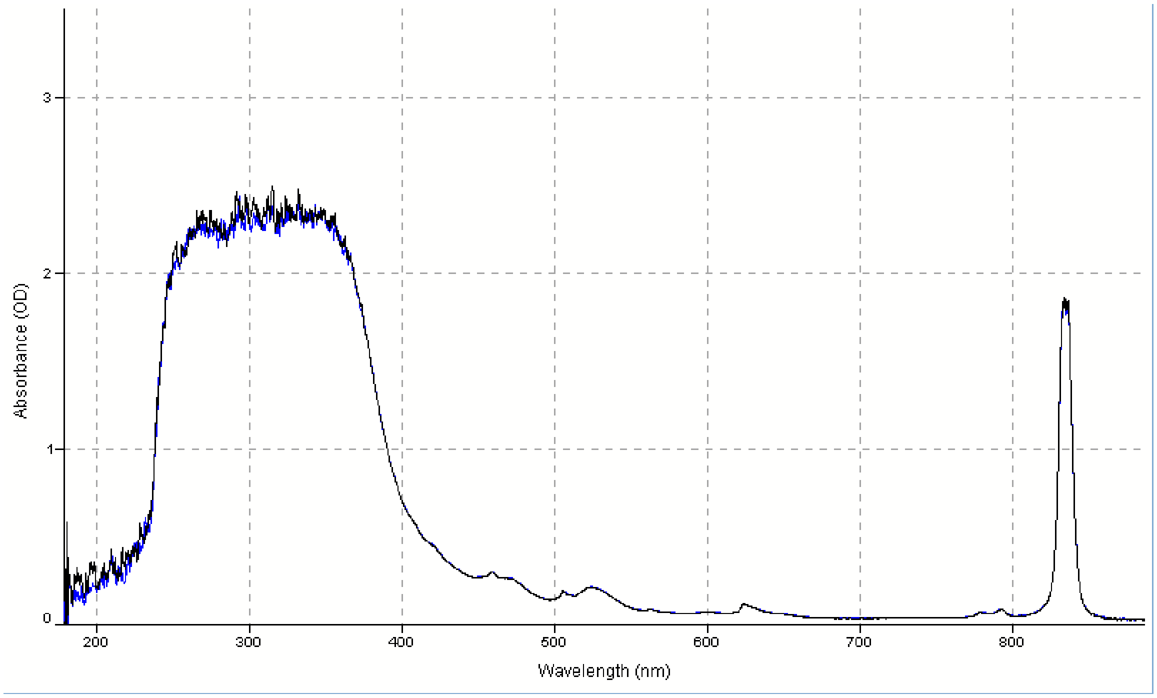


Fig. 4.4. Spectrum of PuO_2^{2+} ([Pu] = 2.9 g/L) in 0.75 M nitric acid

Figure 4.4 clearly shows the +6 valency peak at around 834 nm. To the same feed solution, 1 mL of 0.3 M AHA was added and the absorbance spectrum was taken which is given in Fig. 4.5.

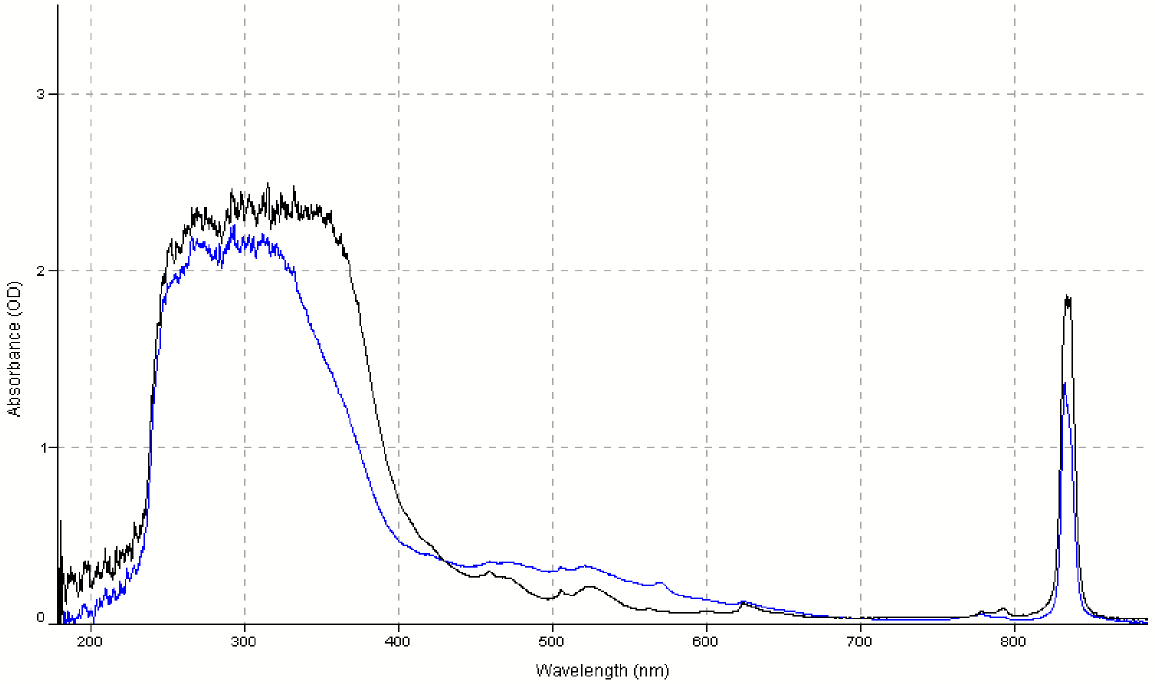


Fig. 4.5. Absorbance spectra of PuO_2^{2+} ([Pu] = 2.9 g/L) and PuO_2^{2+} after the addition of AHA

In the two overlapped spectra shown in Fig. 4.5, the upper curve with the peak at 834 nm corresponds to +6 valence state. The lower curve with the peak at 834 nm is the one resulted after the addition of 0.3 M AHA. Here again, the marginal decrease in the absorbance in the 2 peaks from 1.9 to 1.4 at 834 nm after the addition of AHA was due to the dilution of the sample. It should be noted that red colour did not appear up on the addition of AHA to PuO_2^{2+} ions, which is an indication of the ring structure or metal-ligand chelation. Figure 4.6 shows the absorbance spectrum recorded one day after the addition of AHA to PuO_2^{2+} ions. In this case, no distinct or sharp peak could be observed at 834 nm. However, a sharp peak appeared at 475 nm which corresponds to Pu^{4+} peak. This implies that the reduction kinetics of PuO_2^{2+} to Pu^{4+} by AHA is slow. The reduction reaction is attributed to the formation of hydroxylamine due to the degradation of AHA.

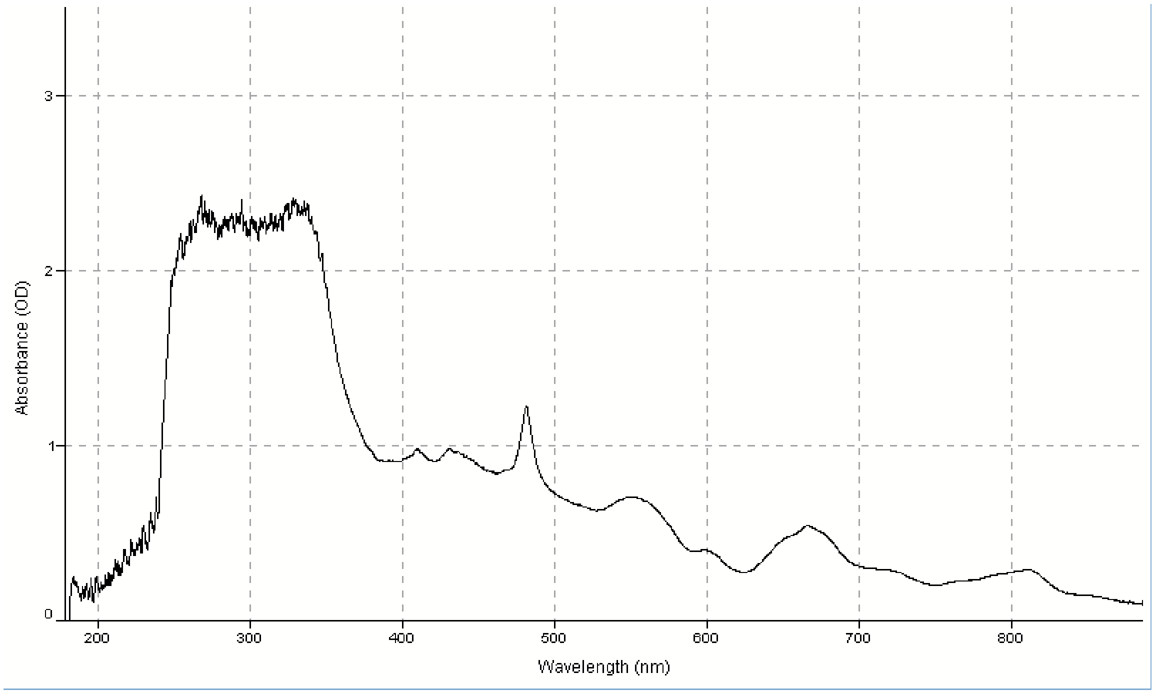


Fig. 4.6. PuO_2^{2+}-AHA spectrum recorded after 24 h

4.c. Complexation of AHA with Cerium Metal Ions

4.c.i. Study with Ce^{4+}

Using ammonium ceric nitrate ($(NH_4)_2Ce(NO_3)_4$), 0.1 M Ce^{4+} solution was prepared and 1 mL of this solution was taken in a cuvette. 1 mL of 0.3 M AHA was added to this solution and absorbance spectrum was taken using fibre optics spectrophotometer. 0.05 M ammonium ceric nitrate was the blank. The obtained spectrum is reproduced in Fig. 4.7. This figure shows the broad peak starting from around 400 to 600 nm with wavelength maximum at 475 nm, which corresponds to the absorbance peak of the five membered metal chelate ring. Appearance of red colour was observed in this solution.

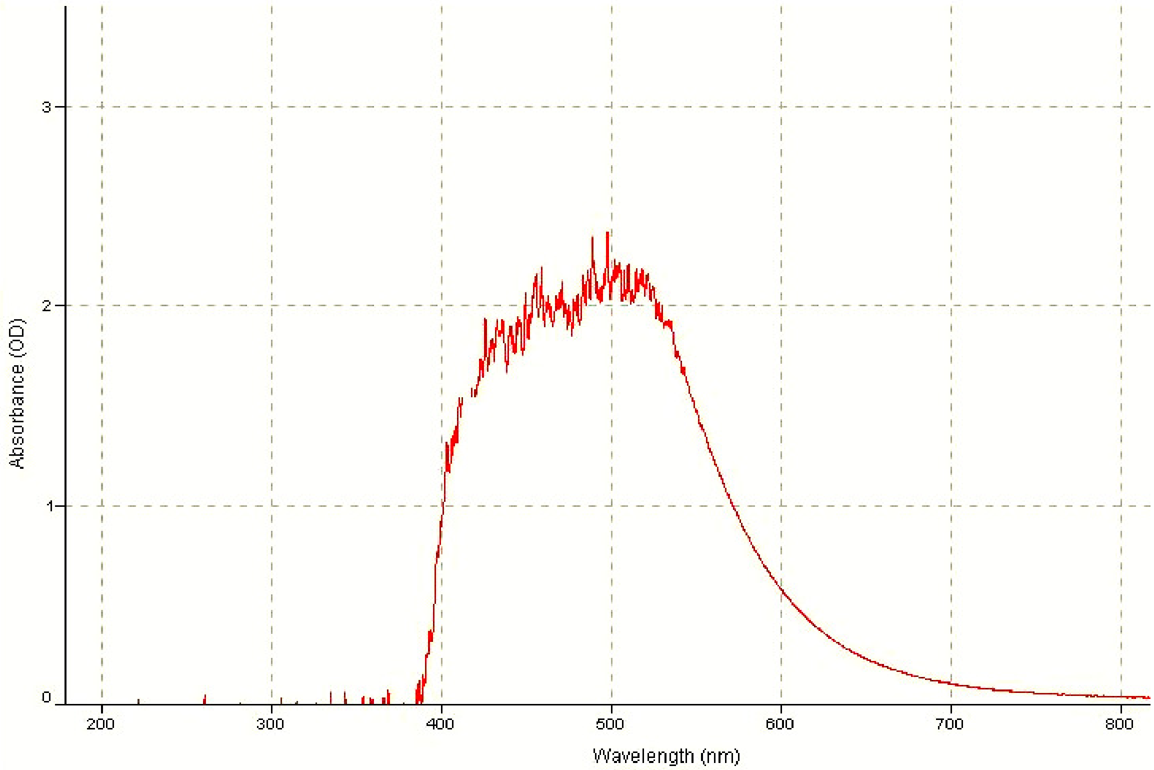


Fig. 4.7. Ce^{4+}-AHA spectrum (1 mL of 0.1 M Ce^{4+} and 1 mL of 0.3 M AHA)

4.c.ii. Study with Ce^{3+}

0.1 M solution of Ce^{3+} ion was prepared from $Ce(NO_3)_3$ crystals. To 1 mL of this Ce^{3+} solution taken in a cuvette, 1 mL of 0.3 M AHA was added. Figure 4.8 shows the spectrum scanned using fibre optics spectrophotometer and 0.05 M $Ce(NO_3)_3$ as blank. It is evident that there was no complexation between Ce^{3+} ion and AHA because no peak could be observed in Fig. 4.8.

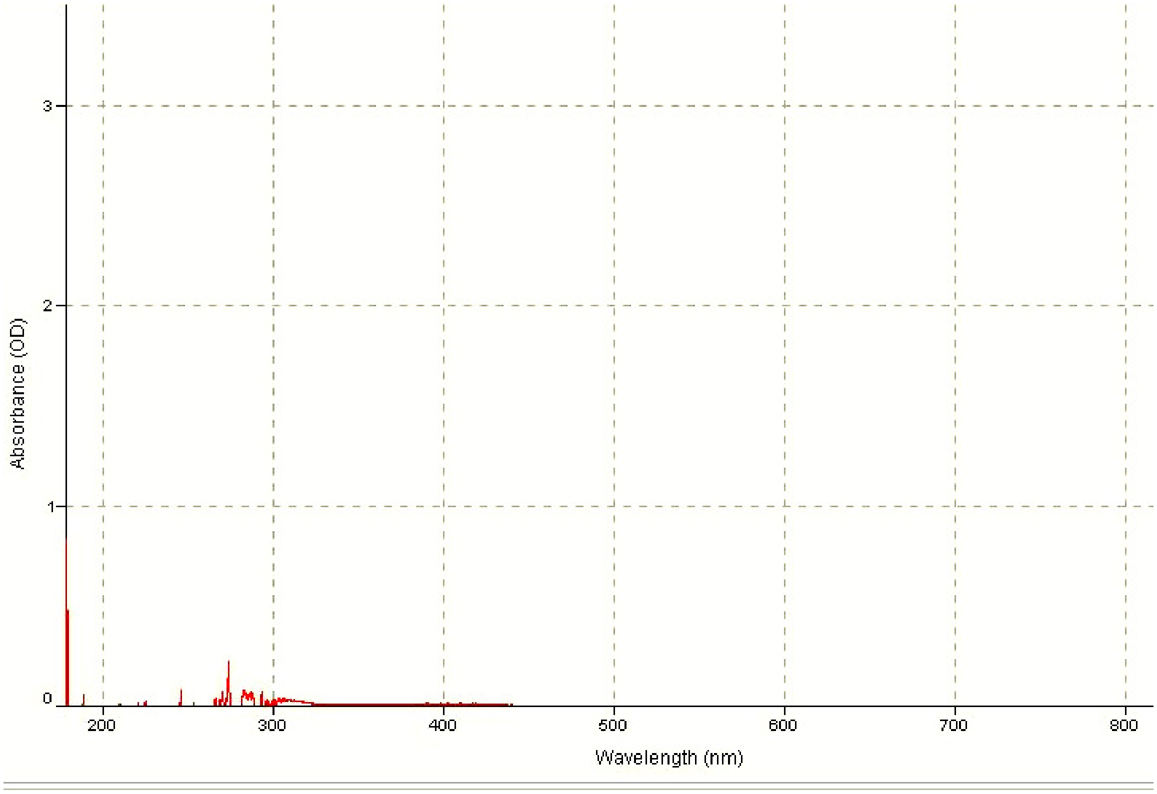


Fig. 4.8. Ce^{3+}-AHA spectrum (1 mL of 0.1 M $Ce(NO_3)_3$ and 1 mL of 0.3 M AHA)

4.d. Solubility of Pu(IV) and Pu(III) Oxalates with AHA in Nitric Acid

4.d.i. Solubility of Pu(IV) oxalate

Plutonium nitrate solution was prepared by dissolving PuO_2 powder in 12 M nitric acid containing 0.1M HF. The valency of plutonium was adjusted to +4 using $NaNO_2$ and the nitrate solution was purified from fluoride ions by solvent extraction using 30 % TBP followed by stripping. Plutonium(IV) oxalate solid was prepared from the $Pu(NO_3)_4$ solution. It was washed with acetone and air dried.

Pu(IV) oxalate (containing 100 mg of Pu) was equilibrated with the following reagents of 10ml volume for 20 minutes:

(1) 3.5 M nitric acid containing 0.1 M oxalic acid (Blank)

(2) Blank with 0.1 M AHA

(3) Blank with 0.2 M AHA

(4) Blank with 0.3 M AHA

The solubility data obtained for the above solutions are listed below in Table 4.2.

Table 4.2. Solubility of Pu(IV) oxalate with different concentrations of AHA

Solvent	Solubility of Pu, ppm	Remarks
3.5 M HNO_3 containing 0.1 M oxalic acid (Blank)	89.5	---
Blank with 0.1 M AHA	289.5	Deep red colour appeared in the equilibrated solution
Blank with 0.2 M AHA	290.5	Deep red coloration in equilibrated solution
Blank with 0.3 M AHA	300.3	Deep red coloration

Pu^{4+} complexation with AHA resulted in deep red colouration. The absorbance spectrum of this equilibrated solution was similar to that of Fig.4.1.

4.d.ii. Solubility of Pu(III) oxalate

Calculated quantity of hydroxylamine was added to the purified $Pu(NO_3)_4$ solution for the purpose of converting Pu(IV) to Pu(III). Pu(III) oxalate solid was prepared by the addition of oxalic acid to $Pu(NO_3)_3$ solution and the precipitate of plutonium(III) oxalate was washed with acetone and air dried. The oxalate solid was contacted with the following reagents for 20 minutes:

(1) 3.5 M HNO_3 containing 0.1 M oxalic acid (Blank) and (2) Blank solutions with 0.1, 0.2 and 0.3 M AHA

The solubility of plutonium(III) oxalate in these solvents is listed in Table 4.3.

Table 4.3. Solubility of plutonium(III) oxalate

Solvent	Solubility of Pu, ppm	Remarks
3.5 M HNO_3 containing 0.1 M oxalic acid (Blank)	22	
Blank with 0.1 M AHA	23	There was no deep red coloration
Blank with 0.2 M AHA	23.2	“
Blank with 0.3 M AHA	23	“

4.d.iii. Solubility of plutonium oxalate formed from AHA partitioned Pu solutions

A feed solution consisting of [Pu]: 2.5 g/L; [H+]: 1.5 M and [AHA]: 0.3 M was subjected to oxalate precipitation by adding oxalic acid directly without any conditioning. The observations are listed in Table 4.4. Plutonium loss in the oxalate supernatant indicates that the precipitation process is similar to the oxalate precipitation of Pu^{3+} ions. Pu oxalate obtained was subjected to solubility test with the following reagents:

1. 3.5 M HNO_3 containing 0.1 M oxalic acid (Blank)
2. Blank with 0.3 M AHA

The results are tabulated in Table 4.5. Plutonium oxalate obtained from AHA partitioned solutions did not show higher solubility of Pu as was the case with the solubility of Pu(IV) oxalate in the presence of AHA.

Table 4.4. Oxalate precipitation of AHA partitioned Pu solution

Feed: [Pu]: 4.0 g/L; $[H^+]$: 1.5 M; [AHA]: 0.3 M

No. of precipitation	Pu present in oxalate supernatant (ppm)
1	29.14
2	28.70
3	29.50
4	25.20
5	26.10
6	29.10

Table 4.5. Solubility of Pu from Pu oxalate obtained in the presence of AHA

Solvent	Solubility of Pu, ppm	Remarks
3.5 M HNO_3 containing 0.1 M oxalic acid (Blank)	22 .1	Solubility behavior was similar to the Pu(III) oxalate solubility
Blank with 0.3 M AHA	22.5	Similar to the Pu(III) oxalate solubility. There was no red coloration.

4.e. SOLVENT EXTRACTION STUDIES WITH THORIUM (Th^{4+})

Thorium is present in +4 oxidation state in dilute nitric acid medium. It has a comparable ionic potential as that of Pu^{4+}. Hence, its complexation behaviour with AHA was analysed by stripping thorium from 30 % TBP in n-dodecane. In order to avoid the interference by acetic acid, $NaNO_3$ was chosen as the ionic medium. 30% TBP loaded with 22.1 g/L of Th as $Th(NO_3)_4$ was equilibrated with the two reagents: (a) 1.5 M $NaNO_3$ and (b) 0.3 M AHA in 1.5 M $NaNO_3$ .The results are given in Table 4.6.

Table 4.6. Equlibration studies of Th^{4+} ion with AHA

Organic feed: 30% TBP loaded with 22.1 g/L of Th

Aqueous feed: (1) 1.5 M $NaNO_3$ and (2) 1.5 M $NaNO_3$ with 0.3 M AHA

Aqueous phase composition	Concentration of Th(g/L) after equilibration		D_{Th}
	Organic phase	Aqueous phase	
1.5 M $NaNO_3$	20.61	1.5	13.74
1.5 M $NaNO_3$ with 0.3 M AHA	20.56	1.5	13.71

Table 4.6 reveals that there is no change in the distribution coefficient between 1.5 M sodium nitrate and 0.3 M AHA in 1.5 M sodium nitrate. But in the case of plutonium, the D_{Pu} value decreased from 8.1 to 0.4 in the presence of 0.3 M AHA.

5. MECHANISM PROPOSED FOR THE REACTION OF AHA WITH Pu IN ACIDIC MEDIUM

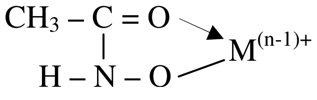
The reaction of AHA with Fe^{3+} and Fe^{2+} ions was discussed in the Section 4.a of this Chapter. This study revealed that AHA forms complexes with Fe^{3+} whose absorption lies in the visible range of electronic spectrum. Nevertheless, AHA does not form any complex with Fe^{2+} ion, which has been confirmed by the absence of absorption peaks in the electronic spectrum. Similarly, among Pu^{4+} and Pu^{3+} ions, AHA forms an intense red colour chelate complex with Pu^{4+} ions only, which shows some signature of absorbance in the visible range of electronic spectrum. No change was observed in the Pu^{3+} ion spectrum after the addition of AHA. In the case of PuO_2^{2+} spectrum also, there was no change after the addition of AHA. In the case of Ce^{4+} and Ce^{3+} ions, AHA showed absorption signatures only with Ce^{4+} and not with Ce^{3+}. Solubility study with Pu(IV) oxalate revealed that the solubility of Pu increased in the presence of AHA. However, Pu(III) oxalate did not have any effect of AHA on its solubility. Oxalate precipitation of AHA partitioned plutonium solutions resulted in the formation of plutonium oxalate which was characteristic of Pu(III) oxalate. Pu loss in the oxalate filtrate was also less, which behavior was similar to that observed in the Pu(III) oxalate precipitation. The distribution studies of Th^{4+} ion in 30 % TBP indicated that there was no change in the distribution ratio in the presence of AHA, implying that AHA does not form a complex with Th^{4+}. These observations reveal that AHA reduces those metal ions which have variable valency and forms a chelate complex instantaneously. This behaviour could be explained by the following mechanism:

In the reduction reaction of AHA with the metal ion in its higher oxidation state, **nascent metal ion** with its lower oxidation state is formed initially, which readily reacts with AHA to form a five membered chelate ring. This chelate complex absorbs in the visible range of electronic spectrum. Reactions (4) to (12) explain the mechanism proposed for the formation of chelate complex between the metal ion M^{n+} (Fe^{3+}, Pu^{4+} and Ce^{4+}) and AHA.

$$2M^{n+} + CH_3CONHOH + 2H_2O \longrightarrow CH_3COOH + HN(OH)_2 + 2H^+ + \underset{\text{(nascent metal ion)}}{2M^{(n-1)+}} \quad (4)$$

$$HN(OH)_2 \longrightarrow H_2N_2O_2 \text{ (hyponitrous acid)} \longrightarrow N_2O + H_2O \quad (5)$$

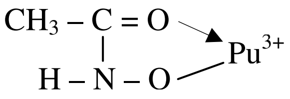
$$\underset{\text{(Nascent metal ion)}}{M^{(n-1)+}} + CH_3CONHOH \longrightarrow$$



(6)

In the case of Pu^{4+}

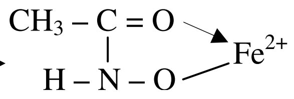
$$2Pu^{4+} + CH_3CONHOH + 2H_2O \longrightarrow 2Pu^{3+} + CH_3COOH + NH(OH)_2 + 2H^+ \tag{7}$$

$Pu^{3+} + CH_3CONHOH \longrightarrow$  $+ H^+$

(8)

For the reaction with Fe,

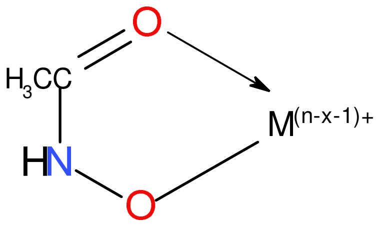
$$2Fe^{3+} + CH_3CONHOH + 2H_2O \longrightarrow 2Fe^{2+} + CH_3COOH + NH(OH)_2 + 2H^+ \tag{9}$$

$Fe^{2+} + CH_3CONHOH \longrightarrow$  $+ H^+$

(10)

In general, the metal ion, M^{n+} will be reduced to the stable lower oxidation state (i.e.) $M^{(n-x)+}$ by AHA. For example, in the redox couple Fe^{3+}/Fe^{2+}, x is 1.

$$M^{n+} + AHA \longrightarrow \underset{\text{(nascent reduced metal ion)}}{M^{(n-x)+}} \quad \text{where } x=1,2,3 \text{ etc.} \tag{11}$$

$M^{(n-x)+} + AHA \longrightarrow$ 

(12)

The oxidation state of metal ion after reduction is +(n-x). Owing to the covalent bond between oxygen and metal ion, the oxidation state of metal ion is mentioned as +(n-x-1) in the ring structure.

6. CONCLUSIONS

The formation of a five membered chelate ring by the reaction of metal ions with acetohydroxamic acid occurs, subsequent to the reduction reaction of the metal ion to lower oxidation states. Therefore, AHA reacts first to reduce the metal ion to lower valency state and subsequently forms the complex with the nascent metal ion formed from the reduction reaction.

CHAPTER V

PERFORMANCE OF URANOUS NITRATE AND AHA IN THE PARTITIONING OF PLUTONIUM FROM URANIUM AND IN THE DISTRIBUTION OF Ru AND Cs

1. ABSTRACT

The performance of uranous nitrate and acetohydroxamic acid (AHA) in the partitioning of plutonium from uranium was studied with actual loaded organic resulted from CORAL reprocessing facility. Aqueous feeds containing 7 g/L uranous nitrate with 0.5 M hydrazine nitrate in 1 M nitric acid and 0.3 M AHA in 1.5 M nitric acid were used as partitioning agents. Volume ratio of organic to aqueous was maintained as one. Two aqueous contacts for uranous and five contacts for AHA were required for quantitative stripping of plutonium from the loaded organics. Gamma spectrum was taken for the lean organic and strip product to study the behaviour of Ru and Cs distribution during partitioning. As a partitioning agent, uranous was found to be more effective in stripping plutonium, but it was always accompanied by significant amount of uranium in the strip product. AHA on the other hand, required more number of stages for effective partitioning, but provided plutonium with minimum uranium content in the strip product. Uranous stripped ruthenium significantly in the second contact but cesium was intact in the lean organic. AHA was found to strip cesium from the loaded organic quantitatively.

2. INTRODUCTION

Among the reagents for the partitioning of uranium and plutonium, uranous/hydrazine mixture is commonly used in many countries because ferrous sulphamate and sulphuric acid introduce corrosive ions and the kinetics of reduction by hydroxylamine/hydrazine is rather slow [98-102]. Uranous/hydrazine reagent stripped solutions require extensive conditioning to convert the unused U(IV) to U(VI) ions. Otherwise, it may lead to uranium contaminated plutonium oxide product owing to the co-precipitation of unconverted uranous ions. Partitioning by uranous also results in extra metal ion loading to the reprocessing plant. Hence, the salt-free reagent, Acetohydroxamic acid was considered as the reducing agent and its performance in uranium and plutonium partitioning had been studied with simulated uranium and plutonium loaded organics [54]. Nevertheless, its performance on actual loaded organic from the reprocessing plant is to be established. In this Chapter, the performance of uranous/hydrazine and AHA in partitioning uranium and plutonium from the actual loaded organic from CORAL (Compact Reprocessing of Advanced fuel in Lead cells) reprocessing facility at IGCAR is compared. Distribution of the troublesome fission products Cs and Ru during partitioning with uranous and AHA is also investigated because Cs and Ru are the fission products which are co-extracted with U and Pu in significant quantity as compared to other fission products and increase the total β,γ activity in the UO_2 and PuO_2 product, as these are long lived fission products.

3. EXPERIMENTAL DETAILS

Uranous nitrate was prepared from uranyl nitrate by electro-reduction using titanium cathode and platinum anode. Sigma Aldrich brand acetohydroxamic acid (purity 98 %) and AR grade nitric acid were used in all the experiments.

Analysis of uranium in both aqueous and organic phases was done by spectrophotometric method using PAR (Pyridyl Azo Resorcinol) as the chromogenic reagent [65]. Analysis of plutonium was carried out radiometrically using Para electronics made alpha scintillation counter. Fission product gamma spectra of the organic and aqueous phases resulted during the partitioning by uranous and AHA were recorded using coaxial HPGe detector.

One of the loaded organics received from CORAL facility was taken as the organic feed. The loaded organic feed was divided into two equal parts. One part was used for partitioning with uranous-hydrazine and the other part was used with AHA as the partitioning agent.

The concentrations of U, Pu and H^+ and the activity levels of the organic feed are as follows:

[U]: 9.29 g/L; [Pu]: 6.88 g/L; [H^+]: 0.76 M

β activity: 3.358 mCi/L; γ activity: 1.568 mCi/L

3.a. Partitioning with U(IV)–Hydrazine Mixture

The concentration in the aqueous feed was

[U^{4+}]: 7.0 g/L; [N_2H_4]: 0.5 M; [H^+]: 1.0 M; [UO_2^{2+}]: 5.33 g/L

To a known volume of organic feed, equal volume of uranous/hydrazine reagent was added in an extraction vial and equilibrated for five minutes in a vortex shaker. After settling, the organic and aqueous phases were centrifuged and the concentration of uranium and plutonium were analysed in both phases. The aqueous phase was separated and one more contact was given with fresh uranous reagent to the organic phase for the purpose of quantitative stripping of plutonium. Fission product spectrum was also recorded in each stage.

3.b. Partitioning Study with AHA

Partitioning experiments were carried out with 0.3 M AHA in 1.5 M nitric acid as the aqueous feed. Using the procedure described in Section 3.a, five contacts were given for the quantitative stripping of plutonium. In each contact, both organic and aqueous phases were analysed for uranium and plutonium. Fission product spectrum was also obtained using HPGe detector.

4. PERFORMANCE OF U(IV) AND AHA AS PARTITIONING REAGENTS

4.a. Partitioning with U(IV)

U(IV) reduces Pu(IV) to Pu(III) as follows:

$$U^{4+} + 2Pu^{4+} + 2H_2O \longrightarrow 2Pu^{3+} + UO_2^{2+} + 4H^+ \quad (1)$$

Since the distribution coefficient of Pu(III) is low in 30 % TBP-n-dodecane system, Pu is back extracted into the aqueous phase. The values of uranium and plutonium distributed in the lean organic and strip product are given in Table 5.1.

Table 5.1. Distribution of U and Pu in the partitioning by uranous ions

Contact No.	Lean organic		Strip product	
	U (g/L)	**Pu (g/L)**	**U (g/L)**	**Pu (g/L)**
1	22.54	0.066	0.100	6.800
2	24.40	0.007	10.46	0.058

Organic feed: [U]: 9.29 g/L; [Pu]: 6.88 g/L; $[H^+]$: 0.76 M; β activity: 3.358 mCi/L; γ activity: 1.568 mCi/L

Aqueous feed: $[U^{4+}]$: 7.0 g/L; $[N_2H_4]$: 0.5 M; $[H^+]$: 1.0 M; $[UO_2^{2+}]$: 5.33 g/L

No. of aqueous contacts: 2

In the first contact, concentration of plutonium reduced from 6.88 g/L to 66 ppm in the organic phase. In the second contact, Pu concentration got reduced to 7 ppm. But, uranium in the loaded organic increased from 9.29 to 22.54 g/L. In the second contact, uranium concentration in the organic phase increased to 24.40 g/L only. Remaining uranium went along with the strip product.

The activity levels of Ru and Cs in the lean organic and strip product resulted from the partitioning experiments using uranous ions are given in Table 5.2.

Table 5.2. Activity levels of Ru and Cs in lean organic and strip product in the partitioning using uranous ions

Description of Sample	Activity (mCi/L)	
	^{106}Ru	^{137}Cs
Feed	1.974	0.237
Lean organic (1 contact)	1.752	0.219
Strip product (1 contact)	0.22	BDL
Lean organic (2 contact)	1.015	0.218
Strip product (2 contact)	0.740	BDL

BDL: Below Detectable Limit

It could be observed that Cs is not stripped by uranous reagent. However, ruthenium is quantitatively stripped in the second contact. Typical gamma spectrum of lean organics after first and second contact with uranous are shown in Figs. 5.1 and 5.2 respectively.

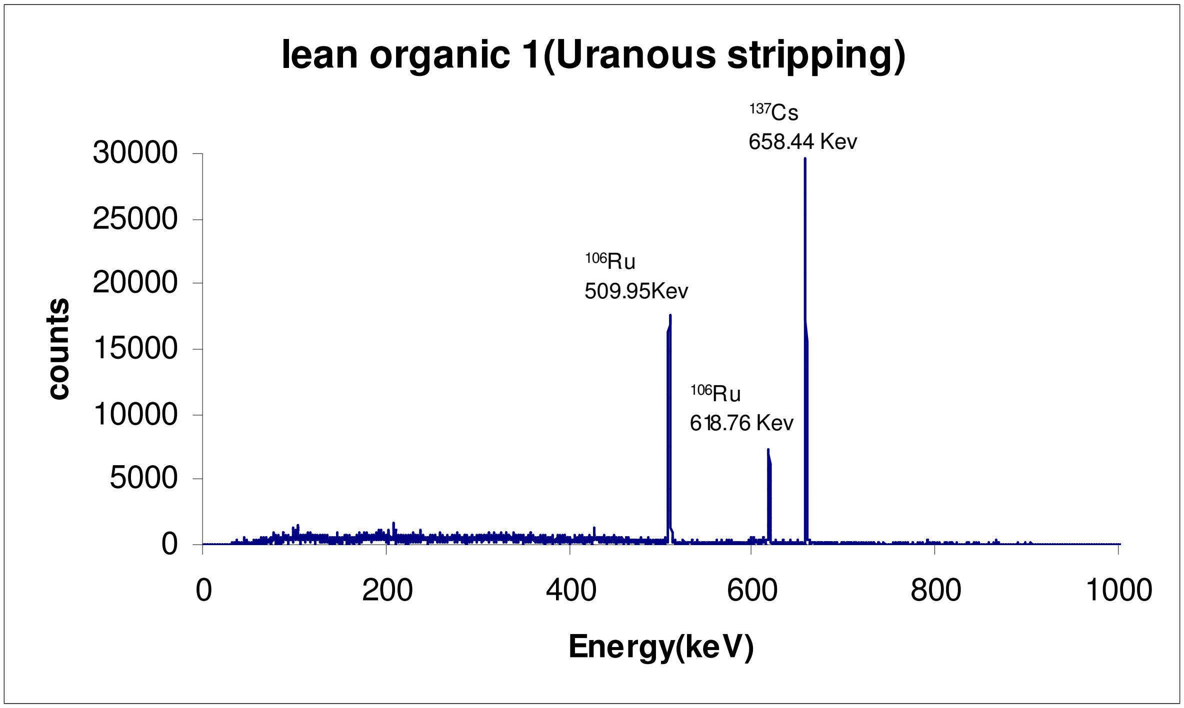


Fig. 5.1. Gamma spectrum of lean organic resulted from first uranous contact

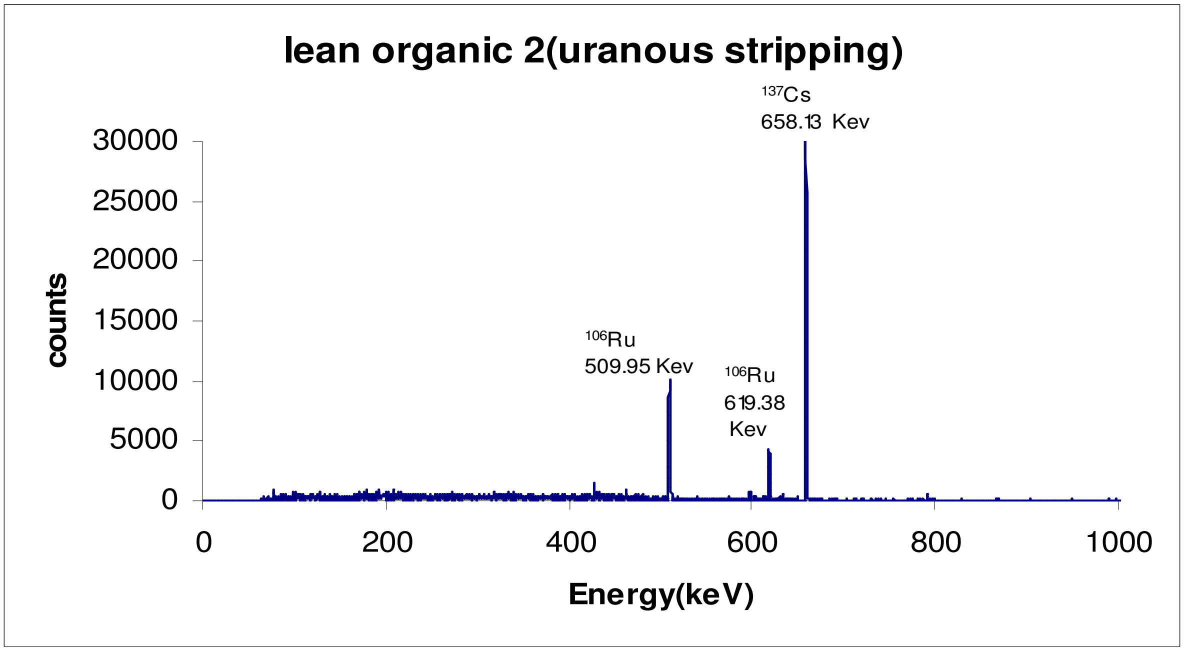


Fig. 5.2. Gamma spectrum of lean organic resulted from second uranous contact

4.b. AHA Partitioning

AHA reduces Pu(IV) to Pu(III) as follows:

$$2Pu^{4+} + CH_3CONHOH + 2H_2O \longrightarrow 2Pu^{3+} + CH_3COOH + NH(OH)_2 + 2H^+ \qquad (2)$$

From the results reported earlier [56], the optimum composition of AHA as partitioning reagent has been chosen as 0.3 M in 1.5 M nitric acid. Hence, the second part of loaded organic received from CORAL reprocessing facility was contacted with 0.3 M AHA in 1.5 M nitric acid. The distribution values of uranium and plutonium in the lean organic and strip product are given in Table 5.3.

Table 5.3. Distribution of U and Pu in AHA partitioning

Contact No.	Lean organic		Strip product	
	U (g/L)	Pu (g/L)	U (g/L)	Pu (g/L)
1	9.23	2.16	0.08	4.76
2	8.54	0.97	0.69	1.18
3	7.95	0.51	0.58	0.48
4	NA	0.25	NA	0.24
5	NA	0.12	NA	0.11

NA: Not analysed

Organic feed: [U]: 9.29 g/L; [Pu]: 6.88 g/L; [H^+]: 0.76 M; β activity: 3.358 mCi/L;

γ activity: 1.568 mCi/L
Aqueous feed: 0.3 M AHA in 1.5 M nitric acid
No. of aqueous contacts: 5

Table 5.3 reveals that in the first two contacts with AHA reagent, concentration of plutonium in the organic phase decreased from 6.88 to 0.97 g/L only. Concentration of plutonium requires to be decreased further in the organic phase. So, three more contacts with AHA reagent were given. Even after five contacts, Pu concentration decreased to 0.12 g/L only (solvent disposal limit <10 ppm of Pu). Since the feed organic used in these experiments is the actual loaded organic from the plant, it also contained the degradation products of solvent and diluent. Analysis of the lean organic showed the presence of 1.6 g/L of dibutyl phosphate (DBP), which is the degraded product of TBP. Since the reduction of Pu(IV):TBP solvated complex is kinetically faster than Pu(IV):DBP complex, more number of stages are required for the quantitative stripping of plutonium using AHA reagent. The distribution ratio of Pu against contact number is plotted in Fig. 5.3.

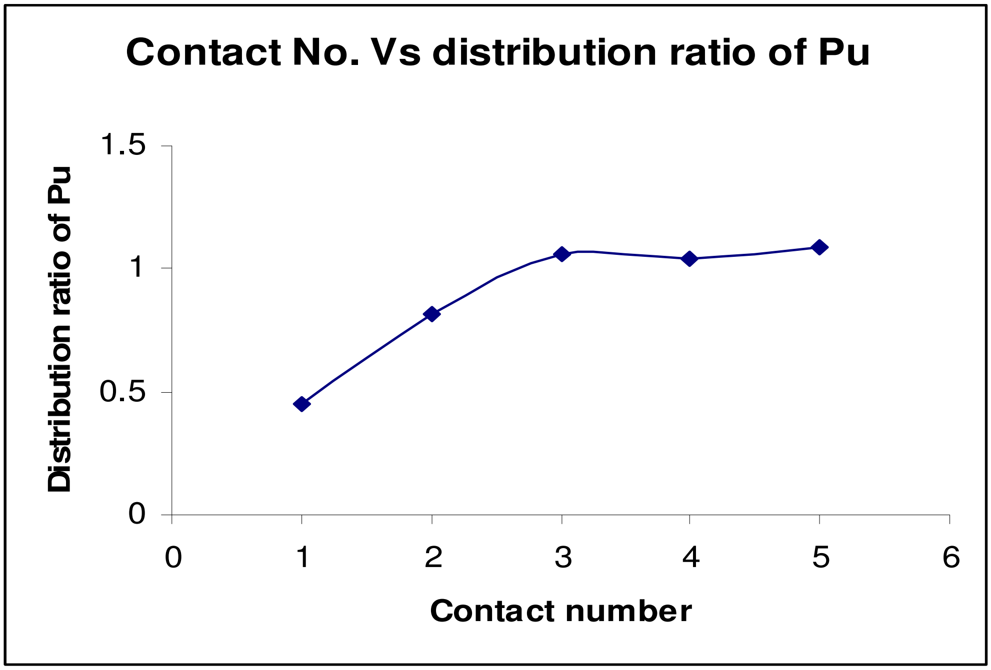


Fig. 5.3. Contact number against distribution ratio of plutonium in AHA partitioning

From the graph it is evident that the value of distribution ratio increases with increase in the contact number and reaches a saturation value of almost 1 after third contact. This observation is contradictory to the behaviour of plutonium partitioning using AHA in simulated feeds reported previously [54]. In the experiments conducted with simulated feed, distribution ratio of plutonium was almost constant in the range 0.12-0.25. Karraker et al. [52] reported the distribution ratio of plutonium using 0.3 M AHA in 1.71 M nitric acid equilibrated with 30 % TBP to be 0.167. Carrot et al. [50] had extensively studied the distribution of plutonium with varying initial concentration of plutonium, AHA and acidity. They obtained a value of 0.082 as the distribution ratio for 11.48 g/L of Pu in the presence of 0.25 M AHA in 1 M nitric acid at 298 K. The high distribution ratio of plutonium in this thesis work, with actual plant feed, could be due to the presence of DBP.

The radioactivity levels of Ru and Cs in the lean organic and strip product in the first and second contacts resulted from partitioning experiments using AHA are listed in Table 5.4. Cesium was stripped quantitatively by AHA reagent in the 1st contact. Cesium stripping by AHA can be explained by the formation of the salt ($CH_3CONHOCs$) from AHA and Cs^+ ion and not by the formation of a chelate complex. In the case of ruthenium, about 19 % was stripped in the first contact and further stripping was not significant.

Table 5.4. Activity levels of Ru and Cs in the lean organic and strip product in AHA partitioning

Description of Sample	Activity (mCi/L)	
	^{106}Ru	^{137}Cs
Feed	1.974	0.237
Lean organic (1 contact)	1.379	0.065
Strip product (1 contact)	0.375	0.162
Lean organic (2 contact)	1.153	BDL
Strip product (2 contact)	0.054	BDL

BDL: Below detectable Limit

The gamma spectra of lean organic after first and second contact with AHA are shown in Figs .5.4 and 5.5 respectively.

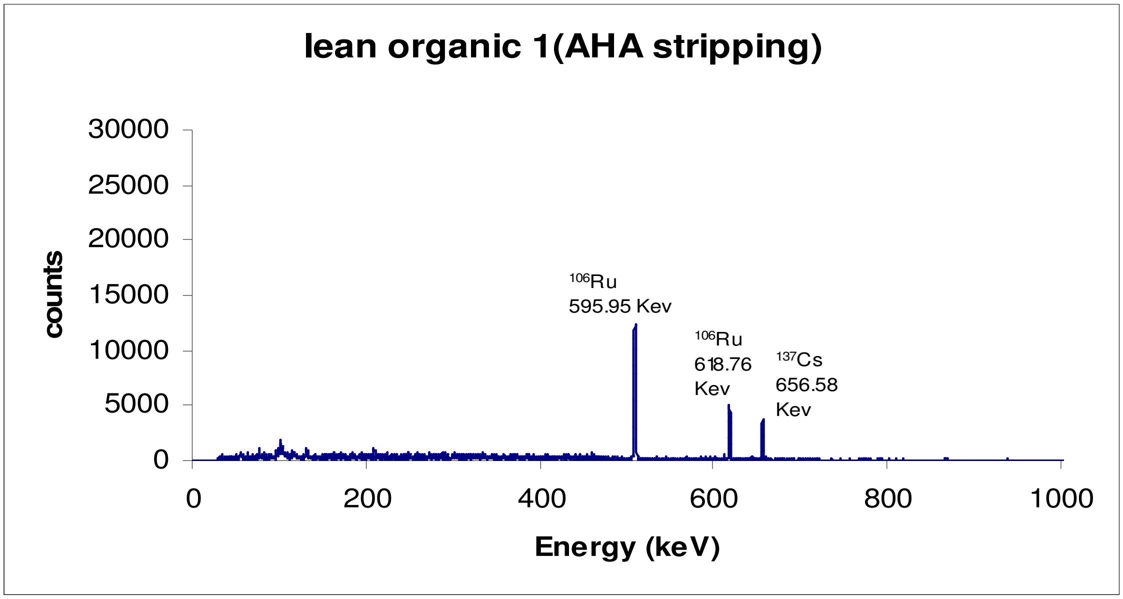


Fig. 5.4. Gamma spectrum of lean organic after 1st contact with AHA

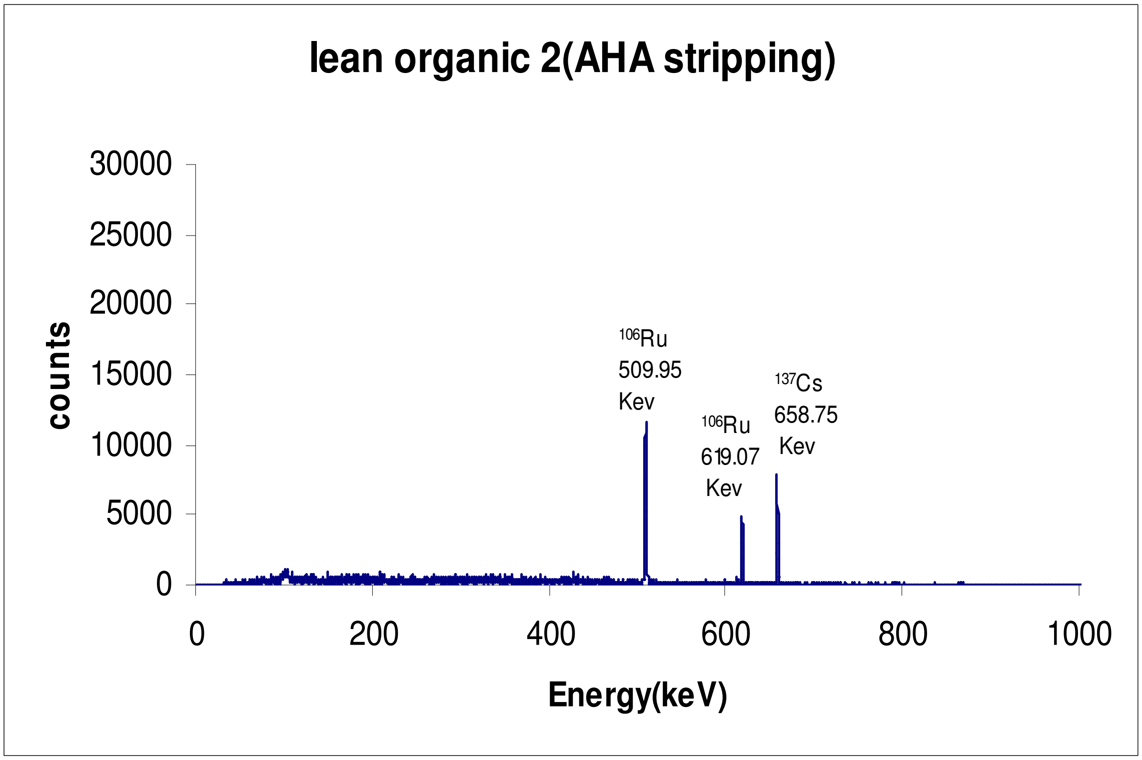


Fig. 5.5. Gamma spectrum of lean organic after 2nd contact with AHA

5. CONCLUSIONS

While comparing the performance of uranous-hydrazine and AHA as partitioning agents, uranous is undoubtedly more effective than AHA in stripping plutonium from loaded organics even in the presence of solvent degradation products. However, it has the disadvantage of higher uranium loading in the partitioning cycle and the additional step required for converting U(IV) to U(VI). AHA on the other hand, requires more number of stages than uranous reagent owing to the presence of solvent degradation products, but the plutonium product is devoid of uranium. While comparing the decontamination factor (DF) due to Ru and Cs in the strip product, uranous was found to be less effective in decontaminating Ru whereas, AHA was less effective in decontaminating Cs. Nevertheless, for obtaining pure PuO_2 (uranium: <0.5 %), the salt free reagent AHA is a superior partitioning agent than uranous reagent.

CHAPTER VI

PURIFICATION OF URANIUM PRODUCT FROM PLUTONIUM CONTAMINATION USING AHA BASED PROCESS

1. ABSTRACT

Acetohydroxamic acid based purification process for uranium product from plutonium was optimized. For this purpose, equilibrium data had been generated to optimize the concentration of AHA and acidity of stripping agent/scrubbing agent. Two options namely (i) plutonium complexation in aqueous phase followed by extraction and scrubbing and (ii) Extraction followed by scrubbing with AHA were investigated. Results of these studies indicated that the uranium product obtained from the purification process involving AHA was close to the table top specification (≤0.4 ppm of plutonium wt/wt) and quantitative recovery of plutonium from the AHA strip product was possible by oxalate precipitation.

2. INTRODUCTION

CORAL is a mini hot cell experimental facility located at Indira Gandhi Centre for Atomic Research, Kalpakkam to reprocess the mixed carbide fuel discharged from FBTR (Fast Breeder Test Reactor). In this facility, spent fuel of different burn-ups (25, 50, 100 and 155 GWd/t) have been reprocessed successfully employing the modified PUREX process [97] which involves codecontamination cycle, partitioning and reconversion of uranium and plutonium to their respective oxides. In the partitioning cycle, uranium and plutonium are separated from each other by selective oxalate precipitation. The uranium oxide obtained from the reprocessing campaign in CORAL contains significant amount of plutonium (up to 1 % wt/wt), which is higher than the uranium product specification for table top handling. Therefore, it is essential to purify the uranium product from plutonium. Different methods of purification such as the use of uranous (U^{4+}) and the use of inorganic ion exchangers like stannic phosphate are reported in the literature for uranium product [103]. The disadvantage in the use of uranous (U^{4+}) is the increase of uranium load to the plant. In the inorganic ion exchanger method, immediate break-thorough was observed with the uranium feed containing higher plutonium. Hence, an alternate method of purification of Pu contaminated uranium product is to be developed using a reagent which does not add salt load to the plant.

It has been reported that AHA is a salt-free reagent and the stability constant of Pu-AHA ($\log\beta = 14.2$) complex is 10^6 times greater than UO_2^{2+}-AHA ($\log\beta = 8.22$) complex [55, 56]. The extraction behavior of uranium and plutonium from nitric acid in the presence of AHA by 30 % TBP has been studied in detail and reported elsewhere [54]. The results of this study indicated that uranium and plutonium can be separated using AHA. A detailed study on the extraction of uranium from nitric acid by 30 % TBP in the presence of AHA has been reported by Tkac et al. [104]. These authors have investigated the effect of nitric acid and $HNO_3/LiNO_3$ on the percentage extraction of uranium as well as the complex formation tendency. However, study of the purification of uranium product from plutonium by solvent extraction employing 30 % TBP in the presence of AHA has not been reliably reported. In this study, the salt-free reagent, AHA has been exploited for the purification of uranium product by way of minimizing the extraction of plutonium while extracting uranium from nitric acid medium by 30 % TBP. Systematic studies have been carried out to optimize the process parameters to purify uranium product from plutonium. Counter current studies by batch mode was also performed with natural uranium to optimize the number of stages required for purification of uranium.

3. EXPERIMENTAL DETAILS

3.a. Materials and Methods

U_3O_8 powder obtained from the CORAL plant was dissolved in HNO_3 and the feed solutions of required U/Pu ratio were prepared using this solution. The concentration of plutonium was determined by α counting after HTTA extraction [67]. Uranium concentration in each stage was determined by Davies and Gray method [64].

For computing McCabe-Thiele diagrams [105], U_3O_8 powder obtained from natural uranium was dissolved in nitric acid and feed solutions with the acidities 1.5 and 3.0 M were prepared from this solution.

3.b. Extraction Experiments

To the feed solution taken in an extraction vial, AHA was added to obtain the desired concentration of AHA. 30% TBP was added to the aqueous feed, equilibrated for 5 minutes and the phases were separated after settling. The concentrations of uranium and plutonium in the organic and aqueous phases were determined. Similar extraction experiments were carried out without AHA and the organic phases obtained were subjected to scrubbing using AHA.

3.c. Scrubbing Studies

The organic phase obtained from the extraction experiments was scrubbed with AHA in nitric acid by equilibrating the organic phase with AHA for 5 min., allowing the phases to settle, separating them and analyzing the concentrations of U and Pu.

4. OPTIMIZING THE CONCENTRATION OF AHA AND ACID FOR STRIPPING /SCRUBBING

Uranium and plutonium get extracted into the organic phase in the extraction process with 30 % TBP from HNO_3; hence, decontamination of plutonium from uranium extracted into the organic phase is essential. Partitioning of uranium and plutonium using AHA for the typical feed concentration encountered in the CORAL plant was demonstrated by Govindan et al. [54]. For the purpose of purifying uranium from plutonium, variation in the distribution ratio of plutonium (D_{Pu}) as a function of AHA was studied in detail and the results are given in Table 6.1.

Table 6.1. Equilibration study of Pu with AHA

[AHA] in aqueous phase	**Distribution ratio of Pu (D_{Pu})**
0.0	8.05
0.1	0.25
0.2	0.20
0.3	0.16
0.4	0.15

Organic phase: [Pu]: 4.0 g/L in 30 % TBP in NPH
Scrubbing agent: 0 to 0.4 M AHA in 1.5 M HNO_3
No. of iterations: 2

It is evident from this Table that beyond 0.1 M AHA concentration, D_{Pu} remains more or less the same value. Hence, AHA concentration of 0.2-0.4 M can be considered for the conversion of Pu(IV) to Pu(III). The concentration of AHA chosen for the present study was 0.3 M, taking into account of the loss of AHA, owing to the degradation of AHA in nitric acid medium.

The variation of distribution ratio for uranium extraction was determined as a function of [HNO_3]/[AHA] for the purpose of optimizing the feed concentration, and that of scrubbing/partitioning agent. The effect of concentration of AHA on the extraction of uranium, for a given strength of HNO_3 is given in Fig. 6.1.

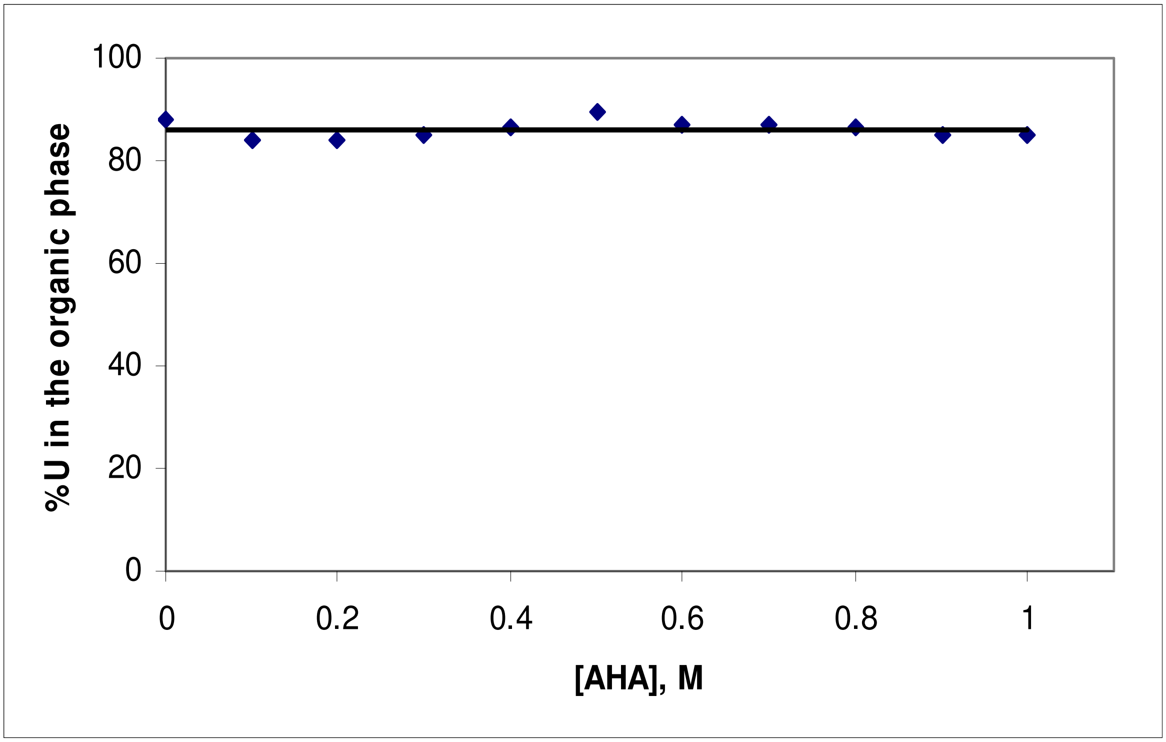


Fig. 6.1. Retention of U(%) in the organic phase for various concentrations of AHA

Feed organic: [U]: 41.76 g/L; [H^+]: 0.5 M in 30 % TBP in NPH

Scrubbing agent: 0.1-1.0 M AHA in 1.5 M nitric acid; O/A: 1

No. of iterations for each point: 3

It was observed that the bulk of uranium was extracted into the organic phase. The extraction of uranium is attributed to the fact that uranium does not have a strong tendency to form a complex with AHA as compared to TBP; hence, uranium prefers to be in the organic phase rather than in the aqueous phase. Similar results have been reported for the extraction of uranium with AHA [43, 55].

The extraction of uranium has also been studied as a function of concentration of HNO_3 for a given concentration of AHA and the results are plotted in Fig. 6.2. It is evident from this figure that the percentage of uranium extraction increases with increase in nitric acid concentration in the feed which is due to the salting out effect of nitrate ions even in the presence of AHA [55]. It was also observed that the uranium extraction percentage increased steeply up to 1.5 M and became independent of nitric acid concentration beyond this acidity, as expected.

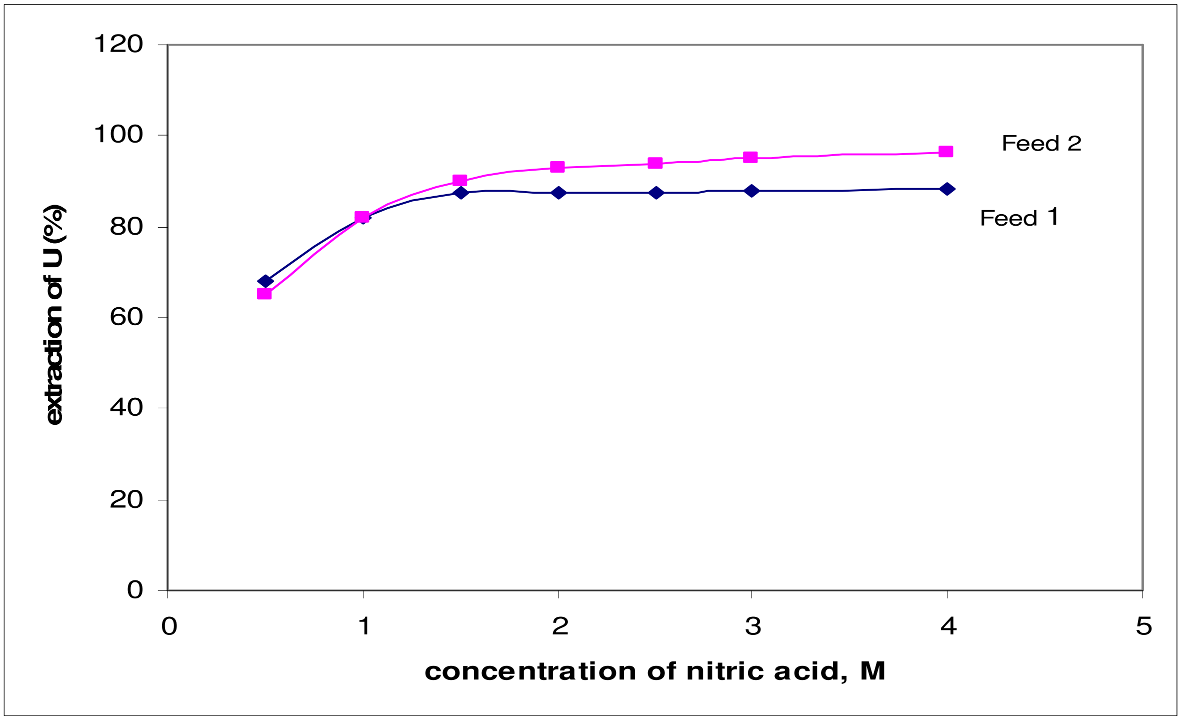


Fig. 6.2. Extraction percentage of uranium with nitric acid concentration in the presence of 0.3 M AHA

Feed 1: [U]: 44.00 g/L; $[H^+]$: 0.5 M in 30 % TBP in NPH;

Feed 2: [U]: 65.28 g/L; $[H^+]$: 0.5 M in 30 % TBP in NPH;

Scrubbing agent: 0.5 - 4.0 M nitric acid in the presence of 0.3 M AHA

No. of iterations for each point: 3

Uranium concentration in the aqueous phase plays a vital role in the presence of AHA during extraction or scrubbing for reconverting plutonium to PuO_2; hence, the acidity of the scrub solution is important. The effect of scrub acidity on uranium concentration in the aqueous phase, shown in Fig. 6.3 reveals that an acidity higher than 1.5 M is suitable for retaining uranium in the organic phase.

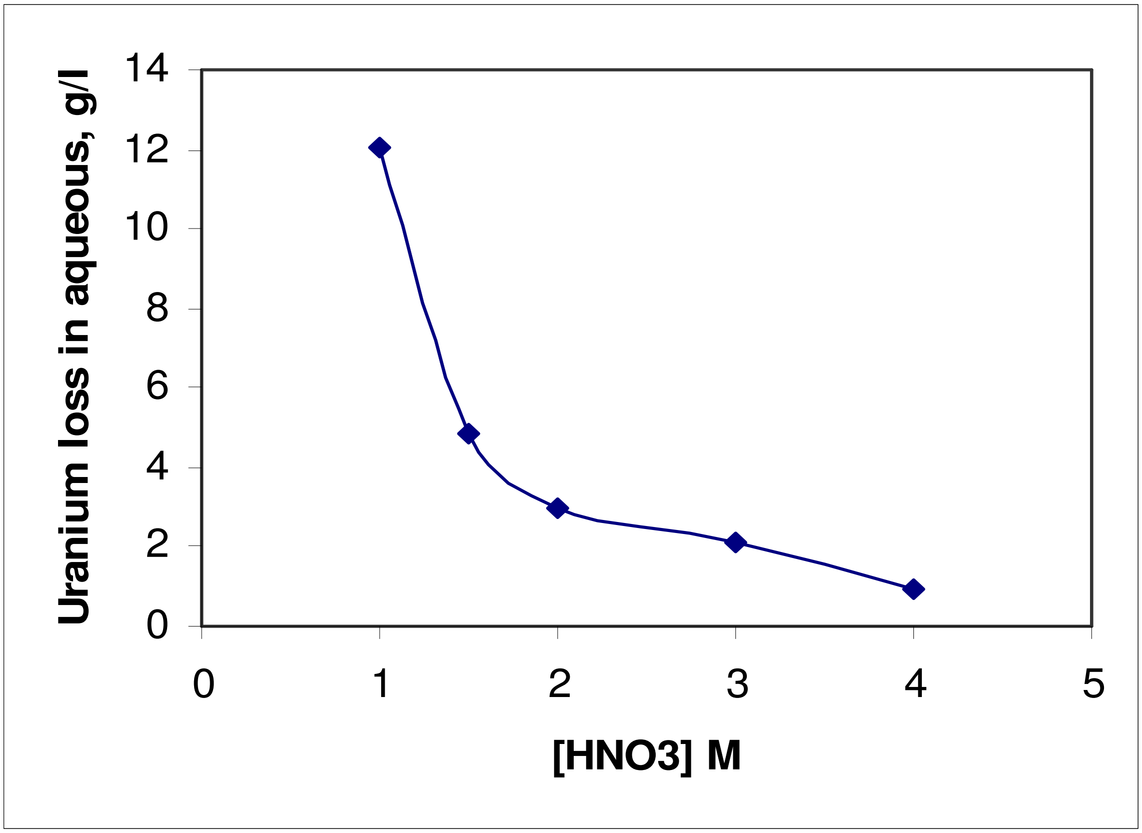


Fig. 6.3. Effect of nitric acid concentration on the loss of uranium in the aqueous phase
Feed : U: 65.276 g/L; H^+: 0.5 M in 30 % TBP in NPH;
Scrubbing agent: 0.5-4.0 M nitric acid in the presence of 0.3 M AHA
No. of iterations for each point: 3

5. McCabe-Thiele DIAGRAMS FOR URANIUM EXTRACTION WITH AND WITHOUT AHA

McCabe-Thiele diagrams have been computed to compare the extraction process of uranium in the presence and absence of AHA. The scheme for solvent extraction to draw McCabe-Thiele diagram is given in Fig. 6.4.

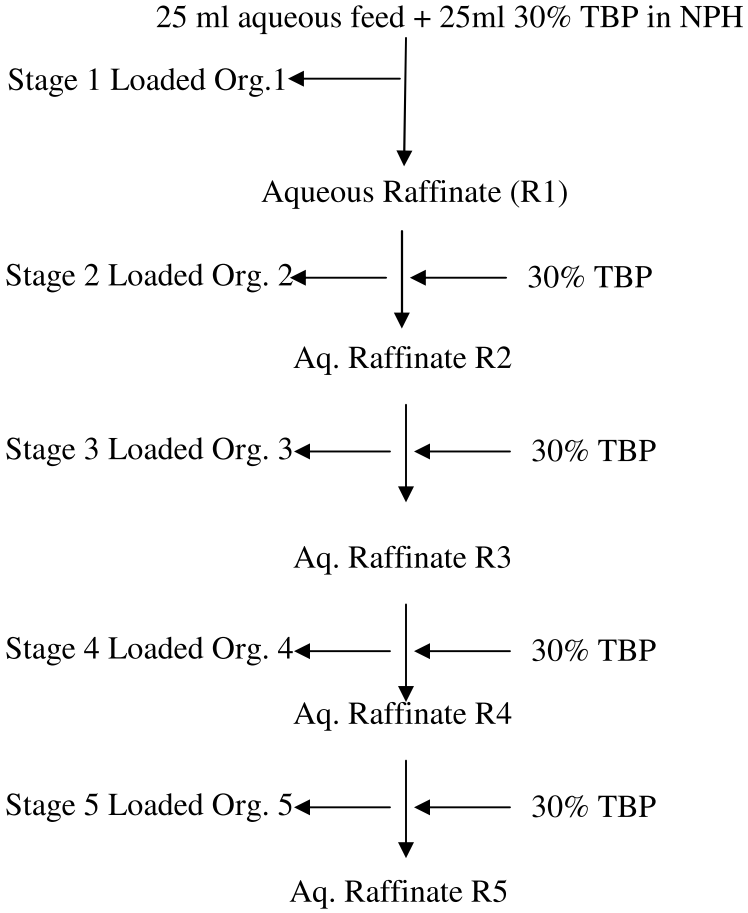


Fig.6.4 **.** The scheme for Solvent extraction to draw McCabe-Thiele diagram

5.a. McCabe-Thiele Diagram for the Extraction of Uranium Without AHA

Tables 6.2 and 6.3 give the results of solvent extraction studies for uranium with 1.5 and 3.0 M acidity in the absence of AHA.

Table 6.2. Solvent extraction study-1 for uranium

Stage number	$[H^+]$/M		[U]/g/L		D_{H+}	D_U
	Loaded organic	Raffinate	Loaded organic	Raffinate		
Stage 1	0.544	1.056	95.72	131.52	0.52	0.73
Stage 2	0.360	0.640	64.80	66.68	0.56	0.97
Stage 3	0.190	0.432	36.71	30.06	0.44	1.22
Stage 4	0.156	0.334	14.81	13.15	0.47	1.12
Stage 5	0.083	0.305	6.38	6.57	0.27	0.97

Aqueous feed: [U]: 235 g/L; $[H^+]$: 1.596 M; Organic feed: 30 % TBP in NPH; A/O: 1

Table 6.3. Solvent extraction Study-2 for uranium

Stage number	$[H^+]$/M		[U]/g/L		D_{H+}	D_U
	Loaded organic	Raffinate	Loaded organic	Raffinate		
Stage 1	0.88	2.37	104.14	131.40	0.37	0.79
Stage 2	0.63	1.81	82.20	49.8	0.35	1.65
Stage 3	0.33	1.53	41.38	9.99	0.21	4.18
Stage 4	0.30	1.20	8.21	2.0	0.25	4.10
Stage 5	0.27	1.05	1.88	0.20	0.26	9.4

Aqueous feed: [U]: 235.3 g/L; $[H^+]$: 3.3 M; Organic feed: 30 % TBP in NPH; A/O: 1

Using Matlab program, McCabe-Thiele diagrams were drawn for the data listed in the Tables 6.2 and 6.3 and are shown in Figs. 6.5 and 6.6 respectively.

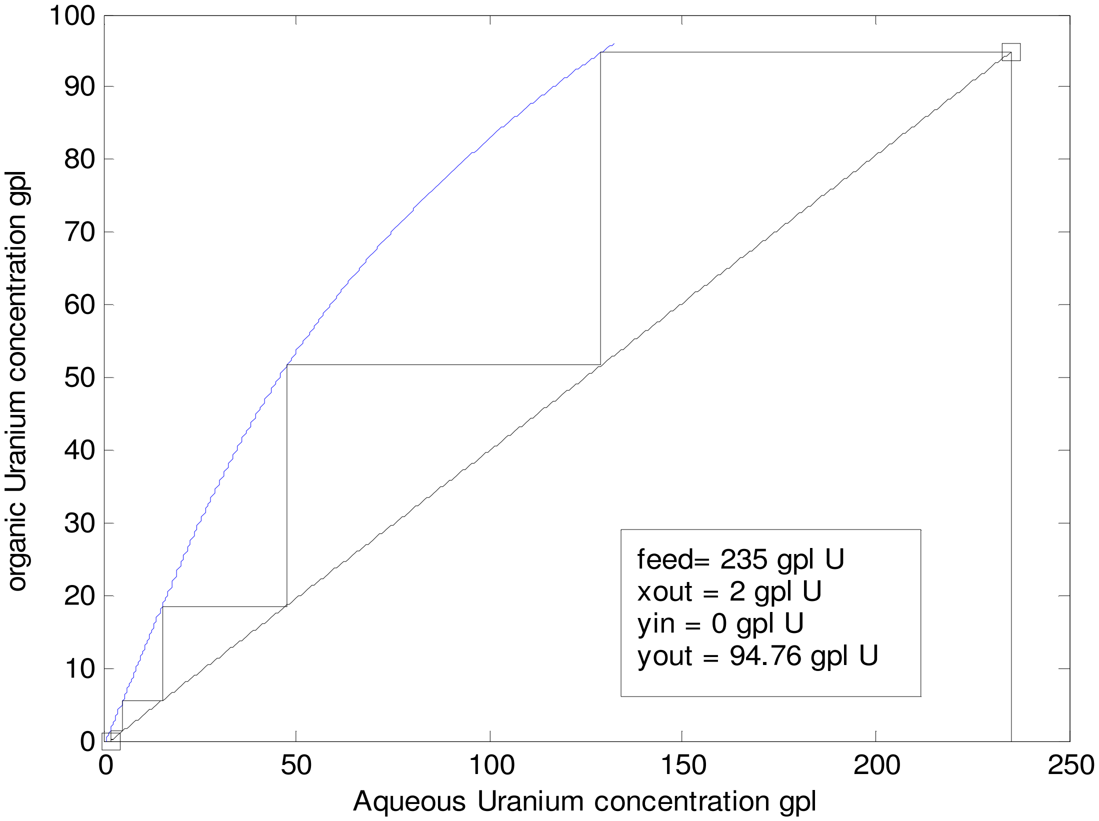


Fig. 6.5. McCabe-Thiele diagram for the solvent extraction study-1

[H^+]: 1.596 M; Feed: 235g/L U as UO_2^{2+}; 30 % TBP in NPH; No. of stages: 5; A/O: 0.406

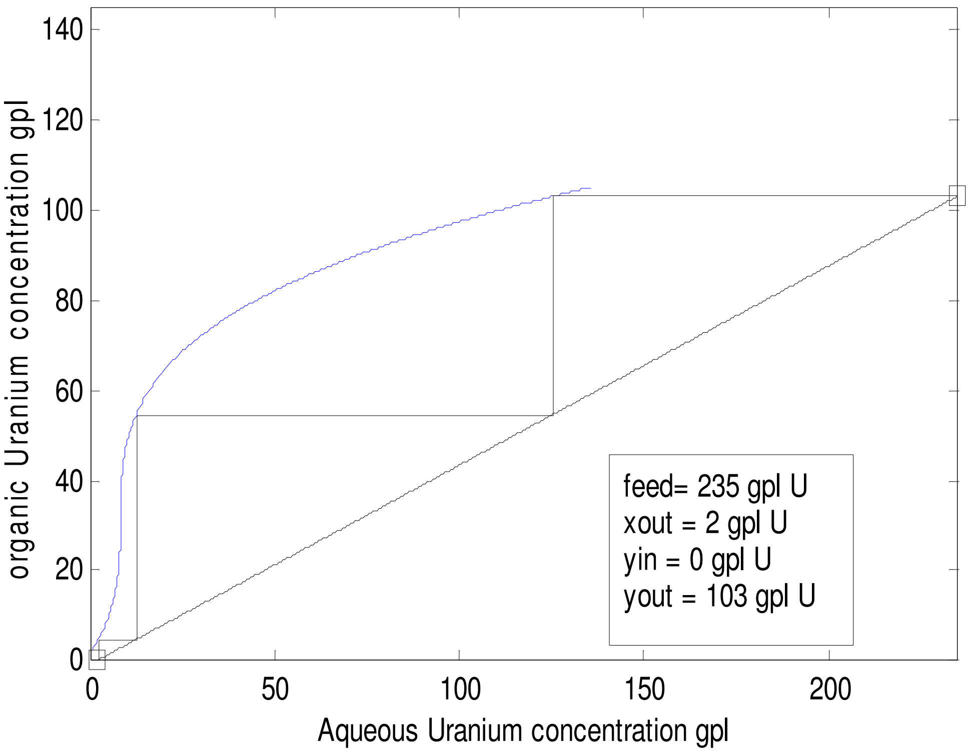


Fig. 6.6. McCabe-Thiele diagram for solvent extraction study-2

[H^+]: 3.3 M; Feed: 235 g/L U as UO_2^{2+}; 30 % TBP in NPH; No. of stages: 3,

A/O: 0.442

Figures 6.5 and 6.6 indicate the number of stages required for uranium extraction to be 5 and 3 in 1.5 and 3.0 M nitric acid concentrations respectively.

5.b. McCabe-Thiele DIAGRAM FOR URANIUM EXTRACTION IN THE PRESENCE OF AHA

Tables 6.4 and 6.5 present the data obtained from the solvent extraction study for uranium at 1.5 and 3.0 M acidity in the presence of 0.3 M AHA.

Table 6.4. Solvent extraction study-3 for uranium

Stage number	$[H^+]$/M		[U]/g/L		D_{H+}	D_U
	Loaded organic	Raffinate	Loaded organic	Raffinate		
Stage 1	0.54	1.06	94.78	132.46	0.51	0.71
Stage 2	0.35	0.63	68.75	63.71	0.55	1.08
Stage 3	0.19	0.43	37.64	27.58	0.44	1.36
Stage 4	0.10	0.30	13.94	14.26	0.33	0.98
Stage 5	0.07	0.24	5.29	7.18	0.29	0.74

Aqueous feed: [U]: 227.24 g/L; $[H^+]$: 1.6 M; [AHA]: 0.3 M; Organic feed: 30 % TBP in NPH; A/O: 1

Table 6.5. Solvent extraction study-4 for uranium

Stage number	$[H^+]$,M		[U],g/l		Kd(H^+)	Kd(U)
	Loaded organic	Raffinate	Loaded organic	Raffinate		
Stage 1	0.78	2.32	102.92	132.38	0.34	0.78
Stage 2	0.54	1.89	82.79	49.70	0.29	1.67
Stage 3	0.39	1.61	41.88	7.63	0.24	5.49
Stage 4	0.33	1.37	6.67	0.93	0.24	7.17
Stage 5	0.24	1.15	1.05	0.10	0.21	10.5

Aqueous feed: [U]: 235.3 g/L; $[H^+]$: 3.3 M; [AHA]: 0.3 M; Organic feed: 30 % TBP in NPH; A/O: 1

The McCabe-Thiele diagrams for the results tabulated in the Tables 6.4 and 6.5 for the study at 1.5 and 3.0 M acidity, in the presence of 0.3 M AHA are depicted in Figs. 6.7 and 6.8 respectively.

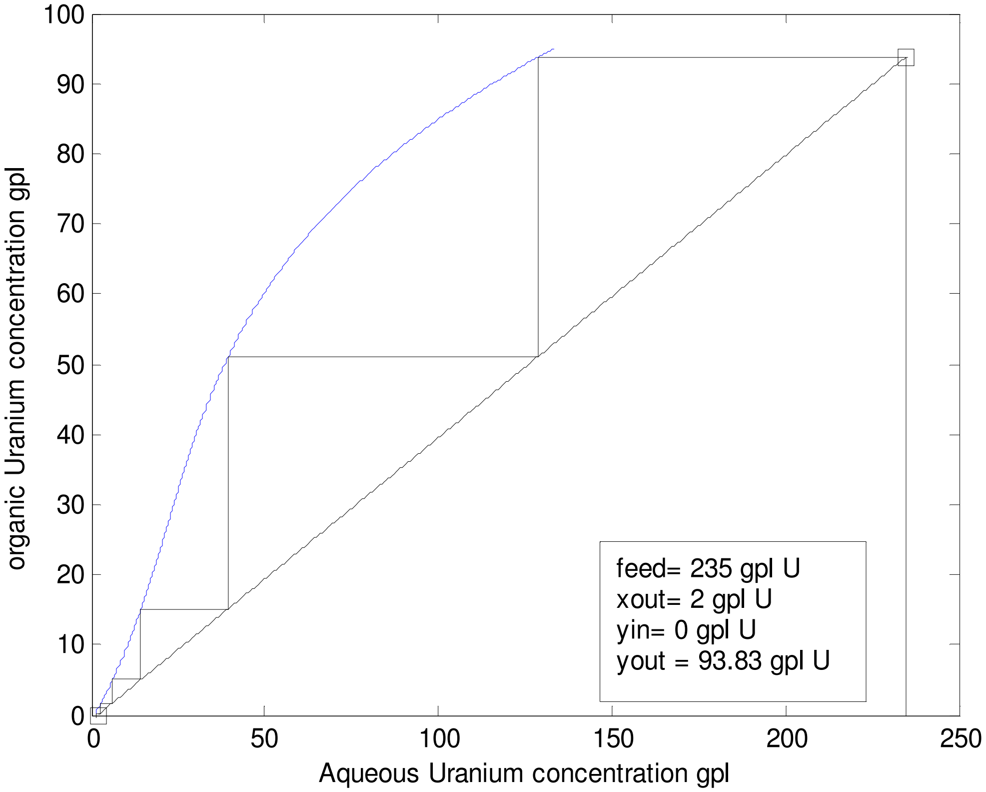


Fig. 6.7. McCabe-Thiele diagram for solvent extraction study-3

[H^+]: 1. 6 M; [AHA]: 0.3 M; Feed: 235 g/L U as UO_2^{2+}; 30 % TBP in NPH; No. of stages: 5; A/O: 0.4026

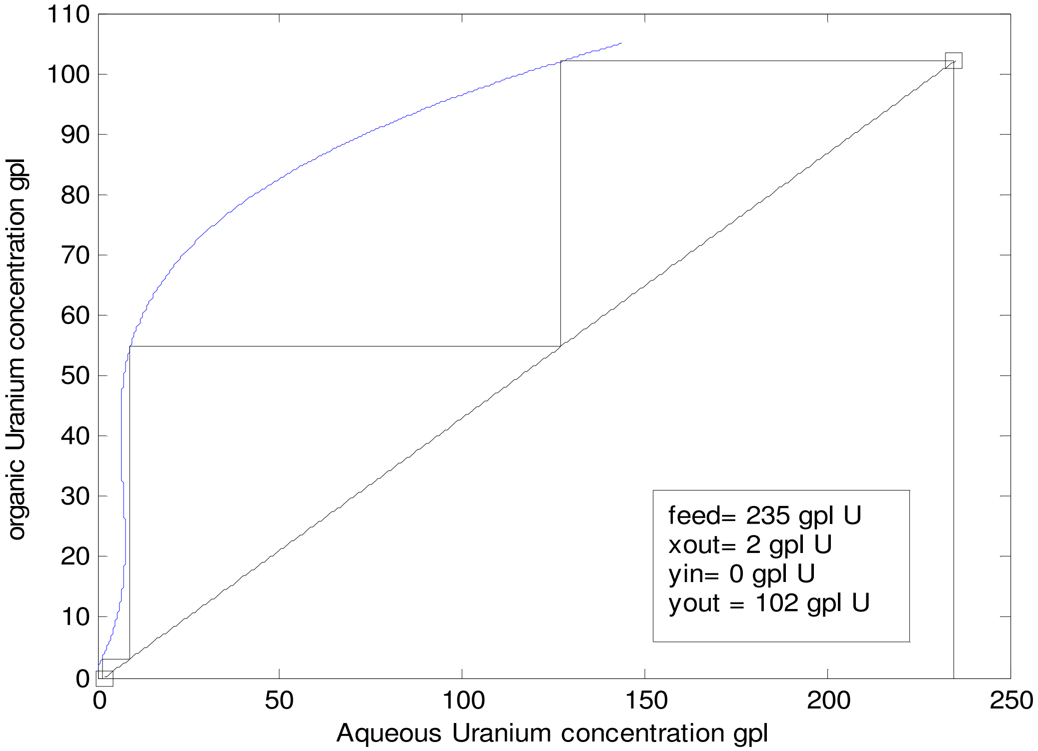


Fig. 6.8. McCabe-Thiele diagram for solvent extraction study-4: $[H^+]$: 3.3 M; [AHA]: 0.3 M; Feed: 235 g/L U as UO_2^{2+}; 30 % TBP in NPH; No. of stages: 3; A/O: 0.4378

The number of stages required for uranium extraction is 5 and 3 for the nitric acid concentration of 1.5 and 3.0 M respectively. These results did not vary from the results of uranium extraction in the absence of AHA. Thus, it is concluded from McCabe-Thiele diagram studies that AHA has no influence in U extraction.

6. EXTRACTION AND SCRUBBING OF URANIUM PRODUCT WITH PLUTONIUM CONTAMINATION

The data on extraction and scrubbing required for flow sheet optimization were generated by conducting studies with two different ratios of “U/Pu” (i.e. ≈ 25 and 125). Purification of uranium product was carried out by two options namely, (1) plutonium complexation in aqueous phase followed by extraction and scrubbing and (2) Extraction followed by scrubbing with AHA.

6.a. Complexation of plutonium by AHA, Followed by Extraction and Scrubbing (Option-1)

In the first option, uranium was extracted after the addition of AHA to the feed solution and subsequent scrubbing of organic phase was carried out with 0.3 M AHA in 1.5 or 3 M nitric acid depending on the concentration of uranium in the organic phase. A feed solution comprising about 26.5 g/L U and 1 g/L plutonium in 4 M HNO_3 and 0.3 M AHA was equilibrated with 30 % TBP. The aqueous phase was found to contain [U]: 0.9 g/L and [Pu]: 0.6 g/L, whereas the organic phase contained [U]: 25.6 g/L and [Pu]: 0.4 g/L. The aqueous phase obtained in this study could be treated for the recovery of plutonium in the plutonium reconversion laboratory. The organic phase obtained in this study had 15.6 mg of plutonium with respect to a gram of uranium, which does not meet the specification for table top handling of uranium. Hence, the organic phase was subjected to scrubbing with 0.3 M AHA in 1.5 M HNO_3. The data obtained in the first option for lower U/Pu ratio of the feed is given in Table 6.6.

Table 6.6. Pu complexation in aqueous phase followed by extraction and scrubbing

No. of Contacts	O/A	Feed I			
		Organic phase		Scrub product	
		[U] (g/L)	Pu in U (wt/wt) ppm	[U] (g/L)	[Pu] ppm
Feed	-	25.6	15625	-	-
1	1	23.90	4184	2.19	297
2	2	22.71	1453	2.44	135
3	2	21.37	421	2.68	47
4	2	20.81	96	2.74	10
DF		392			

Feed I: [U]: 26.5 g/L; [Pu]: 1.0 g/L; [H$^+$]: 4 M; [AHA]: 0.3 M; Volume: 50 mL

Loaded organic: [U]: 25.6 g/L; [Pu]: 0.4 g/L; Volume: 50 mL

Scrubbing reagent: 0.3 M AHA in 1.5 M HNO_3

No. of iterations: 2

The plutonium content was reduced from 15.6 mg in the organic feed to 96 µg. In the scrubbing steps, the concentration of uranium in the scrub product was around 2.5 g/L and for plutonium is 0.3 g/L. This plutonium can be treated for preconcentration, as followed in CORAL facility [106].

6.b. Extraction of uranium and plutonium from HNO_3 without AHA, Followed by Scrubbing with AHA (Option-2)

Table 6.7 gives the results of second option experiments with lower feed ratio of U/Pu. In option-2, uranium and plutonium were extracted into the organic phase followed by scrubbing Pu with 0.3 M AHA in 1.5 M nitric acid. In this option also, the decontamination factor was close to the method adopted in the first option.

Table 6.7. Extraction followed by scrubbing with AHA

No. of Contact	**O/A**	**Feed I**			
		Organic Phase		**Scrub Product**	
		[U] (g/L)	Pu in U (wt/wt) ppm	[U] (g/L)	[Pu] ppm
Feed	-	23.82	35894	-	-
1	1	21.30	5493	2.68	737
2	2	20.07	997	2.47	195
3	2	18.92	211	2.27	32
4	2	17.93	94.8	2.04	7
DF		424			

Feed I: [U]: 25.1 g/L; [Pu]: 1.01 g/L; [H^+]: 4 M; Volume: 50 mL
Loaded organic: [U]: 23.82 g/L; [Pu]: 0.855 g/L; Volume: 50 mL
Scrubbing reagent: 0.3 M AHA in 1.5 M HNO_3
No. of iterations: 2

Similar studies were carried out with higher U/Pu ratio containing feeds. The results of the first and second options with higher U/Pu ratio are given in Table 6.8 and 6.9 respectively. These data indicate that plutonium contamination is low, when uranium loading in the organic phase is high because of the higher percentage loading of uranium, thereby decreasing the extraction of plutonium. Plutonium contamination in the uranium product was found to be 2 ppm as compared to 91 ppm in the low uranium loading studies. Hence, loading of higher percentage of uranium in the organic phase had been selected for further studies.

Table 6.8. Pu complexation in aqueous phase followed by extraction and scrubbing

No. of contacts	O/A	Feed II			
		Organic phase		Scrub product	
		[U] (g/L)	Pu in U (wt/wt) ppm	[U] (g/L)	[Pu] ppm
Feed	-	77.5	206	-	-
1	1	69.88	57.2	7.62	13
2	2	60.16	8.3	19.44	7
3	2	52.47	3.8	15.38	1
4	2	45.10	2.2	14.74	0.3
DF		3438			

Feed II: [U]: 250 g/L; [Pu]: 1.9 g/L; [H$^+$]: 3.7 M; [AHA]: 0.3 M; Volume: 50 mL
Loaded organic: [U]: 77.5 g/L; [Pu]: 0.016 g/L; Volume: 50 mL
Scrubbing reagent: 0.3 M AHA in 3 M HNO_3
No. of iterations: 2

Table 6.9. Extraction followed by Scrubbing with AHA

No. of contacts	O/A	Feed I			
		Organic phase		Scrub product	
		[U] (g/L)	Pu in U (wt/wt) ppm	[U] (g/L)	[Pu] ppm
Feed	-	85.67	828	-	-
1	1	72.05	69.4	13.65	67
2	2	63.20	11	17.6	9
3	2	54.30	9.2	17.7	1
4	2	48.4	2.07	12.00	0.7
DF		3671			

Feed II: [U]: 250 g/L; [Pu]: 1.9 g/L; [H$^+$]: 3.7 M; [AHA]: 0.3 M; Volume: 50 mL
Loaded organic: [U]: 85.67 g/L; [Pu]: 0.071 g/L; Volume: 50 mL
Scrubbing reagent: 0.3 M AHA in 3 M HNO_3
No. of iterations: 2

The DF obtained with options I and II were nearly same; however, it is preferable to follow option I, i.e. complexing plutonium with AHA followed by uranium extraction to obtain Pu, devoid of bulk of uranium, so that the plutonium can be precipitated after a pre-concentration step if required [106]. Based on the results of the present study, a flow sheet has been proposed and is given in Fig. 6.9.

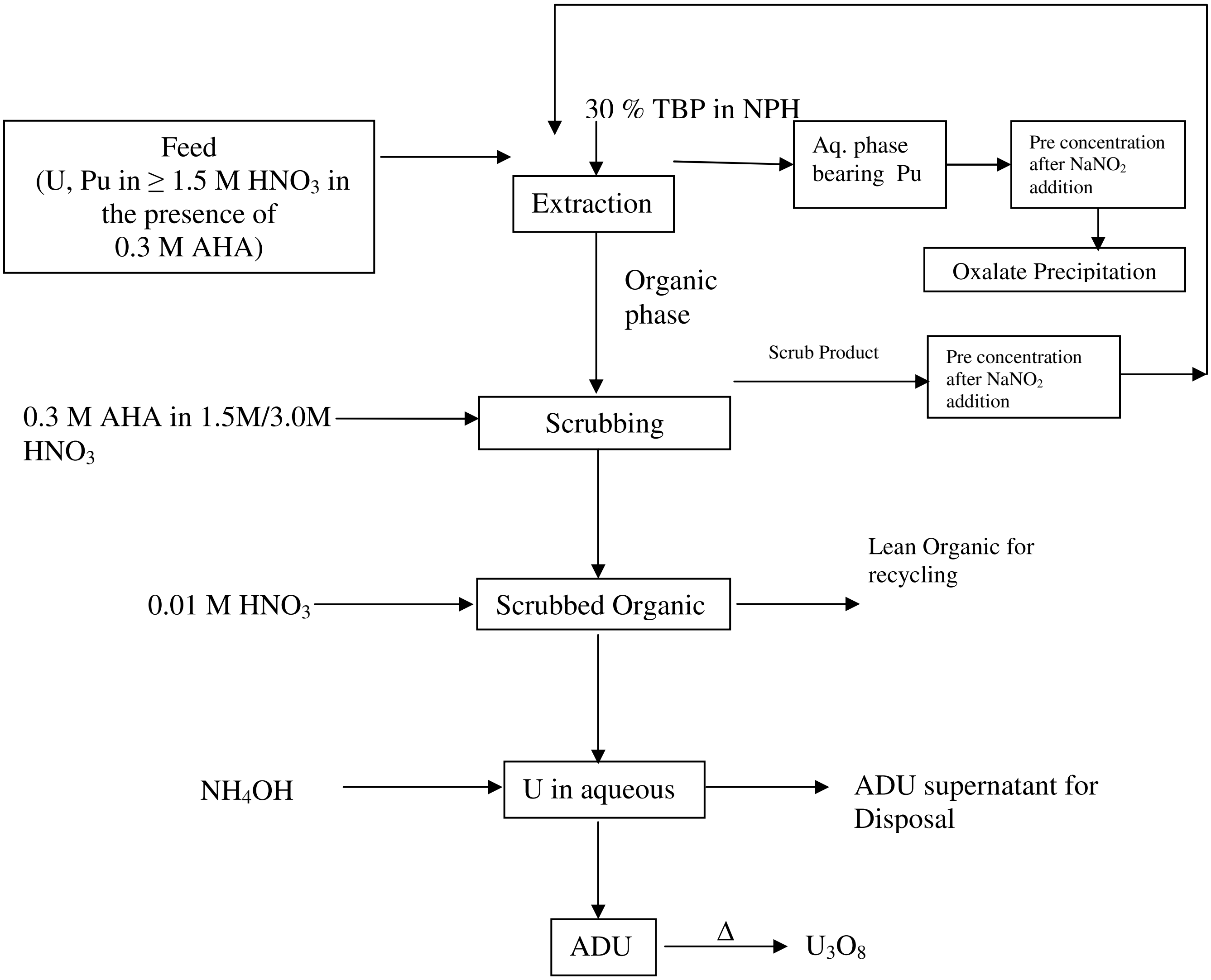


Fig. 6.9. Flow sheet for uranium purification process

The data in Tables 6.8 & 6.9 also indicate that the scrub product contains about 12 -14 g/L of uranium and the concentration of plutonium was 10 ppm. Scrub product solution was conditioned with $NaNO_2$ to destroy AHA and to adjust Pu valency, and was sent back to plant streams for the recovery of uranium.

Reconversion process of AHA stripped aqueous solutions containing higher Pu concentration into plutonium oxide was achieved by oxalate precipitation route.

7. CONCLUSION

Purification of uranium oxide product from plutonium was studied by two modes of approach. Initially, the acidity of scrubbing agent and concentration of AHA were standardized. Subsequently, uranium oxide product purification was carried out and a flow sheet had been arrived for the purification of uranium. Plutonium content of only 1.6 ppm (wt/wt) in the uranium product could be achieved by this method. This could be improved further to accomplish the table top specification of 0.4 ppm (wt/wt) by employing continuous mode multi stage contactors. The final recovery of plutonium from scrub product is also a simple oxalate precipitation process as in the PUREX process.

CHAPTER VII

SUMMARY, CONCLUSIONS AND SCOPE FOR FUTURE WORK

1. SUMMARY OF ALL THE EXPERIMENTS AND CONCLUSIONS

The present study was undertaken to investigate the mechanism of the reaction of AHA with metal ions in acidic medium and to evaluate its performance as a reducing agent in the separation of uranium and plutonium. As AHA is not readily available in the market, its preparation by a simple synthetic route was explored and the process parameters were optimized. For all the studies reported in the thesis, it was required to follow the concentration of AHA in each step. Hence, a spectrophotometric method was standardized for the estimation of AHA. The main findings of the present study are summarised as follows:

1.a. Spectrophotometric estimation of AHA

- The procedure for the estimation of AHA by spectrophotometric method was standardized.
- Intense red colour complex of AHA with Fe^{3+} ion was exploited for its estimation. Fe^{3+} ion forms a 1:1 complex with AHA which was verified by Job's variation procedure. Molar extinction coefficient of the complex was determined as 865 $mol^{-1}.lit.cm^{-1}$. λmax was found to be 498 nm. Range of measurement was 1.5 to 6.5 mg of AHA in 100 ml standard flask.

1.b. Synthesis of AHA

- AHA was prepared by a simple synthetic route at room temperature (≈ 30ºC).

- The precursors for the preparation of AHA were hydroxylamine hydrate and acetic anhydride.
- This method of preparation of AHA does not involve any salt intermediate, which resulted in obtaining AHA with high purity.
- The FTIR and NMR spectra recorded for the synthesized product were in conformity with the commercially available Sigma Aldrich compound.
- Purity of the product was ascertained from the absorbance of the AHA-Fe^{3+} complex in UV-Visible spectra.
- The purity of 98 % achieved for the synthesized AHA was comparable to the commercially available compound.

1.c. Mechanism of the Reaction of AHA with Metal Ions

- To understand the affinity of AHA towards metal ions, detailed investigations were undertaken with the following: (a) UV-Visible spectra of metal ion –AHA complexes (with iron, plutonium and cerium ions), (b) solubility of plutonium oxalate with and without AHA, (c) precipitation of AHA-Pu bearing solutions and (d) solvent extraction studies with Th^{4+} ion in 30 % TBP.
- AHA was observed to form complexes with Fe^{3+} and not with Fe^{2+} ion.
- AHA reacted with Pu^{4+} ion and not with Pu^{3+} ion, which was confirmed from spectral studies.
- Similarly, AHA showed some signature of complex formation with Ce^{4+} ion and did not form a complex with Ce^{3+} ion.
- Solubility measurements revealed the effect of AHA on the solubility of Pu(IV)oxalate; however, it has no effect on Pu(III) oxalate.

- AHA bearing solution of Pu^{4+} ion was precipitated by oxalate route. The supernatant loss was similar to that with Pu(III) oxalate supernatant.
- Solvent extraction studies of Th^{4+} ion with 30 % TBP, with and without AHA did not show any difference in the distribution ratio between the two cases.
- All these studies uphold the following mechanism proposed for the reaction of AHA with metal ions: In the reaction of AHA with metal ions, reduction of metal ions takes place initially. Subsequently, AHA complexes with the reduced **nacent** metal ions.

1.d. Comparison of the Performance of Uranous Reagent and AHA in the Partitioning of Uranium and Plutonium

- The efficiency of AHA and uranous ions as partitioning agents in the separation of uranium and plutonium had been compared using the actual loaded organic resulted from CORAL facility.
- Though U^{4+} is an efficient partitioning agent, the resulting strip product is contaminated with uranium and hence, uranium contaminated plutonium oxide product is obtained.
- AHA partitioning requires more number of stages due to the solvent degradation products. However, it produces plutonium product devoid of uranium contamination.
- U^{4+} partitioning brings ruthenium to the aqueous phase (plutonium product solution) and has no effect on the stripping of cesium.
- AHA partitioning strips some cesium into the aqueous phase, but has no role on ruthenium stripping.

1.e. Purification of Uranium Product from plutonium Contamination Using AHA

- For the purification of uranium product from plutonium contamination, 0.3 M AHA in 1.5 or 3.0 M HNO_3 was chosen as the extracting and scrubbing reagent, after optimizing the process conditions.
- Plutonium contamination in uranium product was brought down to 1.6 ppm in batch studies. It can be reduced further in counter current method, by adopting the parameters employed for the batch process.

2. SCOPE FOR FUTURE WORK

1. Scale up study is required for AHA preparation, which involves counter current extraction of AHA in the reaction medium with ethyl acetate and complete recovery of AHA from waste streams.
2. Performance of AHA as partitioning agent in counter current mode needs to be demonstrated for implementing the process in the plant.
3. AHA is a strong complexing agent and it degrades under moderate chemical conditions. This property can be exploited its application as a decontaminating agent for the removal of iron contamination in steam generators.
4. As AHA complexes plutonium strongly, its application as decontaminating reagent for Pu will be explored.
5. Separation of troublesome fission products from the high level waste solution will be investigated using AHA as the complexing agent.

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