SUPERCRITICAL FLUID EXTRACTION OF METAL IONS FROM VARIOUS MATRICES

By

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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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DEDICATIONS

I dedicate this dissertation to my doting parents,

Mrs. Dalia Pal

and

Mr. Jayanta Pal.

I take this opportunity to acknowledge their unwavering faith, persistence and instilling in me the essence of free thinking and quest for knowledge.

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Separation and purification of metal ions from various matrices forms the backbone of innumerable analytical and industrial operations. Though conventional separation techniques like solvent extraction, ion exchange, distillation and precipitation are extensively employed; there is strong impetus to search for alternative techniques. Supercritical fluid extraction (SFE) is an area of active research being pursued fervently owing to its simplicity, ease of operation and most importantly minimization of the generation of analytical waste. This aspect of waste minimization assumes considerable significance for metal ion separations relevant to the nuclear industry as this results in reduction of radioactive waste. CO_2 is a popular choice for the Supercritical Fluid (SCF) due to its attractive properties.

Present studies were focused on metal ions and matrices especially relevant to the nuclear industry and are expected to contribute towards application of this alternative separation technique for efficient extraction of metal ions. Efficiency of extraction is a function of multiple parameters (e.g. temperature, pressure, SCF flow rate, choice of complexing agent, amount of complexing agent etc.). Maximization of extraction efficiency by tuning parameters requires in depth understanding of effect of various parameters on extraction efficiency. Studies regarding the formation, solubility and stability of metal complex during extraction and dynamics of extraction will contribute to the basic understanding of SCF in general and the development of feasible technology for metal ion extraction in particular. The thesis centers around these objectives. It involves studies on the SFE of uranium and thorium employing different complexing agents from various matrices.

The thesis comprises of six chapters. Chapter 1 provides a brief introduction to separation science, its significance and the conventional techniques of separation. The importance of metal ion separation for nuclear industry, the emergence of SFE as alternative separation technique and its associated advantages are described. This is followed by the theoretical aspects of supercritical fluids in general, advantages of employing carbon dioxide in particular and the principles of SFE. The scope of the subsequent chapters is also described here. Chapter 2 provides a brief overview of the experimental set-up, general procedure of SFE and the method employed for uranium and thorium determination in the present work. This chapter also provides the experimental details of the work, which enable a better understanding of the investigations and implications of studies enumerated in subsequent chapters. Chapter 3 and 4 describe the SFE of metal ion from aqueous solution viz. uranium from nitric acid medium. Chapter 3 deals with SFE employing the organophosphorus reagent TBP. It provides an overview of the effect that various parameters have on the extraction efficiency and attempts to understand the reason for the observed behavior. Chapter 4 deals with crown ethers as complexing agent. In addition to examining the effect of various parameters, the study attempts to correlate the effect of substituents and ring size of the crown ethers on the efficiency of extraction. Chapter 5 deals with SFE of metal species loaded on solid matrix viz. thorium from tissue paper matrix employing organophosphorus reagents as well as β-diketones. The parametric effects are analyzed for the solid tissue paper matrix. Effect of the structure of organophosphorus reagents and extent of fluorination of β-diketones on the extraction efficiency is revealed. Chapter 6 describes the SFE of metal directly from solid matrices e.g. uranium oxides and oxides loaded on tissue paper matrix. Uranium oxides have been chosen from the various stages of nuclear fuel fabrication. The TBP-HNO_3 adduct has been used in the study in an attempt to avoid free acid usage.

CHAPTER 1

Introduction

Separation of component of interest from varied matrices has been carried out since the inception of human civilization. However, separation science was recognized as a branch of physical and analytical chemistry only in the 1960s. Separation of metal ions of interest from various matrices is of profound importance in chemical analysis, industrial chemistry and is practically indispensable in the various stages of nuclear fuel cycle. Separation methods may be based on the difference in solubility (extraction/ precipitation), difference in volatility (distillation), difference in interaction with ion exchange resin (ion exchange separation) and difference in rate of movement of a solute through stationary phase (chromatography).

Metal ion extraction involving Supercritical Fluid (SCF) is an area of current research. This holds tremendous potential for various industries especially the nuclear industry, in view of anticipated advantage of minimization in analytical waste generation. SCF can be used as extracting solvent for Supercritical Fluid Extraction (SFE). In 1879, Hannay and Hogarth were the first to report the solvating ability of supercritical fluids. Laintz et al. first reported metal ion extraction in 1990 when SFE of Cu^{2+} ion was carried out using fluorinated complexing agents. The supercritical fluids (SCF) possess hybrid properties of liquids and gases. Liquid like solvating characteristics enable extraction while gas like diffusivity, viscosity and surface tension facilitate rapid mass transfer, faster completion of extraction and deep penetration inside solid matrix. Also, SFE offers other attractive features such as favorable modification of solvent properties like density and viscosity by conveniently tuning the pressure/temperature of the system. Carbon dioxide is widely employed as supercritical fluid owing to its moderate and easily attainable critical constants (critical pressure = 72.9 atm, critical temperature = 304.3 K) and other attractive properties such as non-toxicity, chemical and radio-chemical stability, environment friendliness, being easily recyclable and less expensive.

Direct extraction of metal ions by supercritical CO_2 being inefficient, metal ion extraction is performed by the addition of a suitable organic complexing agent (may be referred to as co-solvent) to the supercritical fluid. Different classes of complexing agents have been explored for the current study and any correlation between their structural features and the efficiency of extraction has been sought for. The effect of various parameters viz. temperature, pressure, SCF flow rate etc. on extraction efficiency was closely examined. While carrying out the parametric study the aim was not only to arrive at the condition yielding maximum extraction but also to search for the fundamental cause of the nature of variation.

CHAPTER 2

Experimental Apparatus and General Procedure

This chapter describes the SFE apparatus used in the present study. Operation and functioning of each of the components viz. CO_2 cylinder, CO_2 delivery pump, co-solvent pump, thermostat, back-pressure regulator and collection vessel is briefly described. The general procedure of SFE that is to be followed throughout the present work is subsequently outlined which consists of loading of sample in the extraction vessel, attainment of requisite temperature and pressure conditions, subsequent extraction and collection of the extract. In order to quantify the efficiency of extraction, once SFE has been carried out determination of uranium/ thorium amount is required. In the present study, uranium/ thorium determination has been carried out on the respective metal-arsenazo III complex by measuring the absorbance at 655 nm. A brief theoretical description of the general spectrophotometric technique of metal ion determination is provided. Subsequently, procedure of color development and absorbance determination as followed throughout the present study is discussed.

CHAPTER 3

Supercritical Fluid Extraction of Uranium from Nitric Acid Medium employing TBP as Co-Solvent

Extraction of uranium from nitric acid medium with TBP as the complexing agent is very commonly encountered in various stages of nuclear fuel cycle and there exists extensive literature on the solvent extraction of this system. However, SFE differs significantly from solvent extraction. In the case of solvent extraction, chemical parameters such as pH, organic /aqueous phase volume ratio, nature of complexing agent play a significant role. The effect of physical parameters such as temperature is limited to shifting of equilibrium constant for the metal complex formation. On the other hand, density of supercritical fluid plays a vital role as solvent strength is directly related to density and density is markedly affected by pressure and temperature conditions. Few studies have been reported in literature where attempts have been made to decipher the extraction process employing supercritical fluids by studying the effects of pressure and temperature on distribution ratio of uranium under equilibrium conditions. However, equilibrium study provides only partial insight about the SFE process. This is because under equilibrium condition, when a substance gets distributed between aqueous phase and supercritical phase the supercritical fluid phase is not renewed. In the present study carried out under extraction conditions, the supercritical phase is continuously renewed by flowing SCF. The SFE process is, therefore, considered to be combined effect of equilibrium process and extraction kinetics.

For the study, various parameters affecting extraction efficiency were identified viz. extraction pressure, extraction temperature, CO_2 flow rate, percentage of TBP, molarity of acid medium, extraction time, mode of complexation (online/in-situ), mode of extraction (static/dynamic). Effect of variation of these parameters on extraction efficiency was studied and justification was sought for in order to obtain an insight into various aspects of the extraction process. The overall extraction process consists of many elementary processes resulting in the formation of $UO_2(NO_3)_2.2TBP$ which is carried into SC CO_2 phase. In the 150- 300 atm pressure range, variation in extraction efficiency resembled uranium distribution ratio variation under equilibrium conditions whereas below 150 atm extraction efficiency variation resembled SC CO_2 density variation with pressure. In this non-equilibrium region, supercritical CO_2 density increased with pressure that favored enhancement in solubility as well as extraction kinetics. Temperature increase affected the extraction efficiency in two ways: (i) increasing volatility of $UO_2(NO_3)_2.2TBP$ complex and (ii) decreasing SC CO_2 density. Upto 333 K temperature, extraction efficiency gradually increased due to high volatility enhancement followed by steep fall attributed to combined effect of saturation in volatility and the interesting phenomenon of formation of large clusters at densities near critical value but temperature and pressure conditions far off from criticality. Extraction efficiency was found to increase with nitric acid molarity upto 7 M and afterwards showed small decrease attributed to HNO_3 co-extraction. Upto CO_2 flow rate of 1 mL/min increase in extraction efficiency was observed which attained saturation afterwards. Linear increase in extraction efficiency was observed with TBP percentage. Extraction efficiency was found to increase linearly with logarithm of extraction time. Online complexation mode was more efficient than in-situ mode. Under optimized conditions, near complete uranium extraction could be achieved. Reproducibility and mass balance studies were carried out to further add credence to the extraction procedure.

CHAPTER 4

Supercritical Fluid Extraction of Uranium from Nitric Acid Medium employing Crown Ethers

Uranium being a valuable nuclear fuel it is desirable to expand the scope of uranium extraction and alternative sources like seawater need to be explored. Crown ethers are a versatile class of ion-specific extractants and literature for solvent extraction of actinides using crown ethers is available. There are only two reports of SFE where while evaluating various complexing agents for the SFE of uranium, only one crown ether appeared to have been used. Some reports on the solubility of few crown ethers in SC CO_2 have also been published.

The present work was taken up with the aim of carrying out a thorough and systematic study of SFE of uranium from nitric acid medium employing crown ethers. As a good strategy for enhancing extraction, CO_2-phillic fluorine containing pentadecafluoro-n-octanic acid (HPFOA), which dissociates to provide $PFOA^-$ as counter ion, was employed. Ring size and nature of substituents of the crown ethers were found to influence extraction efficiency. The effect of substituents was reflected while comparing efficiency for crown ethers of same ring size i.e. 18-crown-6 series. Electron donating cyclohexyl and/or ditertiary butyl substituents enhanced the extraction efficiency by increasing the basicity of ether oxygen atoms of the crown ether ring. While electron withdrawing benzo groups decreased the extraction efficiency by lowering the basicity of ether oxygen atoms of the crown ether ring. For crown ethers having same substituents (dibenzo) the enhancement in extraction efficiency with increasing ring size might be combined effect of enhanced cavity size as well as number of ether oxygen atoms.

Operating parameters such as pressure and temperature were found to influence extraction efficiency. For all isotherms, extraction efficiency decreased with increasing pressure, attained minima and subsequently increased afterwards. The increasing trend was similar to density versus pressure variation trend. Lower extraction efficiency initially could be assigned to large size cluster formation at low densities. Free energy of solvation of complex for large size clusters would be low, as a major portion of enthalpy of solvation would be utilized in overcoming entropy losses, resulting in lower solubility. Effect of molarity of nitric acid, uranium amount, uranium: crown mole ratio and crown: HPFOA mole ratio on extraction efficiency was studied. The extraction efficiency was found to increase with molarity of nitric acid upto 2M and decreased afterwards. The decrease was attributed to co-extraction of crown-nitric acid complex. Online and in-situ modes of complexation were studied and found to be comparable in terms of extraction efficiency. Effect of extraction time was studied. A combination of 20 minutes steady time and 20 minutes extraction time was found to be optimum. The variation of solvents for crown ether and HPFOA was found to have no significant effect.

CHAPTER 5

Supercritical Fluid Extraction of Thorium from Tissue Paper Matrix employing Organophosphorus Reagents and β-diketones

India has vast reserves of thorium in contrast to modest quantity of uranium. There is need to develop capabilities on all aspects of thorium fuel cycle, i.e. mining, fuel fabrication, reprocessing and waste management. In this context development of processes for separation and purification of thorium from various matrices, liquid as well as solid, is of utmost importance. Reports on SFE of thorium from cellulose based filter paper and sand employing fluorinated β-diketones and TBP have been published. SFE of uranium from tissue paper matrix has also been studied.

In view of limited study of SFE of thorium and its importance to nuclear industry, present study was taken up. Also, very few studies on the influence of operating parameters (pressure, temperature, flow rate, extraction time etc.) on the extraction of metal ions from solid matrix have been reported. In this work, the parametric study has been found to yield differences as against the SFE of uranium from nitric acid medium. In the present study it has been established that thorium can be extracted from tissue paper matrix by supercritical CO_2 employing various organophosphorus reagents as co-solvent. The extraction efficiency was found to be a function of density of SCF and volatility of metal complex from the pressure and temperature variation study. Various organophosphorus reagents (TBP, TOPO, TPP, TPPO, and TBPO) were evaluated.

Interesting correlations have been observed between extraction efficiency and structure of organophosphorus reagents:

(i) Among phosphates, if aliphatic group replaces aromatic group then extraction efficiency increases e.g. TBP and TPP.

(ii) Among phosphine oxides, higher the aliphatic chain length, higher is the extraction efficiency e.g. TOPO and TBPO.

(iii) Among phosphine oxides, if phenyl group is attached to P i.e. TPPO then extraction efficiency is intermediate to TOPO and TBPO.

(iv) On comparing phosphates with phosphine oxides, for aliphatic hydrocarbon, the extraction efficiencies are comparable e.g. TBP and TBPO. For aromatic ring, as in case of phosphine oxide extraction efficiency is higher than its phosphate analogue e.g. TPP and TPPO.

For study of combined effect, in case of TBPO and TPP (with TBP) enhancement in extraction efficiency was observed whereas for TOPO and TPPO there was no enhancement in extraction efficiency. Solvents have been found to affect the extraction efficiency. For alcohols extraction efficiency was found to decrease with increasing aliphatic chain length. Highest extraction efficiency was observed with TOPO (0.2 M) dissolved in methanol.

In order to improve efficiency, alternative complexing agents such as β-diketones were investigated. Various β-diketones viz. AA, TFA, HFA, TTA and FOD were evaluated as chelating agents for the supercritical fluid extraction of thorium from tissue paper matrix. Online and in-situ modes of complexation were studied. Thorium extraction efficiency was higher in in-situ chelation mode than online chelation mode. Combination of TBP and β-diketones was also studied and found to be more effective probably due to adduct formation.

The effect of fluorination of β-diketones on the thorium extraction efficiency has been discussed. Highly linear correlations were observed between extraction efficiency and degree of fluorination in the side arm of β-diketones in all the three modes of extraction. Fluorination influences the extraction firstly by enhancing the solubility of β-diketones and thorium-β-diketone chelates in SC CO_2 by the specific interactions between C-F bond and CO_2 molecules and secondly by enhancing the chelation ability with thorium. Higher fluorination results in higher percentage of enol content and greater dissociation into enolate ion of β-diketones leading to greater extent of chelation. Highest extraction efficiency with TTA was probably due to the presence of aromatic thenoyl group.

CHAPTER 6

Dissolution and Supercritical Fluid Extraction of Uranium from Solid Uranium Compounds

During the fabrication of uranium oxide based fuels, solid waste is being generated from which uranium needs to be recovered. The conventional process involves acid dissolution followed by solvent extraction, which results in generation of large volume of liquid waste. An alternative and attractive method is based on direct dissolution and extraction of uranium from solid uranium compounds. Recent reports show that the adduct of TBP and nitric acid (TBP-HNO_3 adduct) is capable of dissolving uranium oxides. $UO_2(NO_3)_2.2TBP$ thus formed could be extracted into SC CO_2.

Present study was carried out to thoroughly investigate the feasibility of extraction of uranium from solid UO_2 (powder, granule, green pellet and sintered pellet) generated during fuel fabrication process making use of supercritical fluid extraction. U_3O_8, the most stable uranium oxide that is widely used in nuclear industry as reference material for uranium analysis, was also included in the study. In fabrication process, uranium oxide loaded solid matrix is also generated. As a representative, tissue paper smeared with uranium oxides was taken for study. The solids could be dissolved in TBP-HNO_3 adduct thus avoiding the use of free acid. Dissolution time for various solids was not only dependent on temperature but also the nature of the solids. While UO_2 powder, granule and U_3O_8 powder could be easily dissolved at 323 K, UO_2 green and sintered pellets required a higher dissolution temperature of 353 K. Once dissolution is complete uranium exists as $UO_2(NO_3)_2$ irrespective of nature of solid oxide. Hence, extraction conditions should be same for all of them. This is due to fact that after dissolution efficiency would depend upon $UO_2(NO_3)_2.2TBP$ formation and solvation into SC CO_2.

Various parameters were found to influence the uranium extraction efficiency. Temperature was found to affect extraction efficiency. Efficiency increases upto 323 K which was assigned to volatility enhancement. Efficiency decreased in the range 323 K to 353 K, which was assigned to decrease in SC CO_2 density. Extraction efficiency was found to remain uninfluenced by pressure variation. Extraction efficiency enhanced sharply with TBP-HNO_3 amount due to higher formation of $UO_2(NO_3)_2.2TBP$. This was followed by gradual decrease afterwards, which was assigned to decrease in amount of SC CO_2 per mL of TBP-HNO_3. The acidity of the TBP-HNO_3 organic phase was found to increase with the acidity of nitric acid used for preparing TBP-HNO_3 complex from 1-8 M and saturation was observed afterwards. Higher acidity of TBP-HNO_3 adduct should lead to higher extraction efficiency as was indeed observed for UO_2 and U_3O_8 powder.

The extraction efficiency increased with the acidity of nitric acid used for TBP-HNO_3 preparation initially which was followed by saturation. Efficiency increased sharply with extraction time upto 20 minutes and got saturated afterwards. The effect of addition of TBP and TTA to the SC CO_2 stream was also investigated and was found to improve the extraction efficiency. Nearly complete extraction was achievable with addition of very small amount (2.5 %) TTA. Uranium was extracted from simulated tissue paper waste matrix smeared with uranium oxide solids. The study thus provides a basis for uranium recovery from solids generated during uranium oxide based fuel fabrication process.

Highlights of the Present Work

1) Investigations on the effect of various parameters on the SFE of uranium from nitric acid medium employing TBP aided in arriving at conditions for realizing near complete extraction of uranium. This study of interdependence of various parameters provided an insight for understanding the fundamental aspects of SFE process. One of the interesting observations was that even though the temperature and pressure conditions are far removed into the supercritical region, the combined effect of these parameters was such that the density of the fluid was very near the critical value. This had a significant influence on the extraction efficiency as the formation of large CO_2 clusters effectively diminishes the solvation and hence extraction.

2) Feasibility was established for the SFE of uranium from nitric acid medium employing various crown ethers as complexing agent. Key strategy was to employ CO_2-phillic fluorinated HPFOA for providing counter ion. Pressure, temperature, nitric acid molarity, uranium amount, extraction time were found to affect extraction efficiency. Efficiency was found to depend on the substituents and ring size of crown ethers.

3) For the SFE of thorium from tissue paper matrix investigations on effect of pressure, temperature, CO_2 flow rate and extraction time revealed quite different conditions for highest extraction from those of which metal ion extraction from nitric acid medium. Evaluation of various organophosphorus reagents revealed dependence of extraction efficiency on the structural feature of the reagent.

4) Assessment of various β-diketones for the SFE of thorium from tissue paper matrix revealed highly linear correlations between extent of fluorination and extraction efficiency. A combination of β-diketones and TBP yielded the highest extraction efficiency.

5) Direct dissolution and uranium extraction from solid uranium oxides obtained from various stages of fuel fabrication could be successfully carried out. The TBP-HNO_3 adduct was employed for dissolution thus avoiding free acid usage. Conditions for highest efficiency were arrived at.

6) The studies described not only establish the conditions for highest efficiency of SFE of uranium and thorium from different matrices, they also attempt to look into the basic reasons for the nature of parametric dependence. Various classes of complexing agents were assessed and any logical correlation with the structural feature was probed. The studies center around the objective of dealing with systems relevant to nuclear industry with an aim of minimizing the usage of complexing agents and avoiding acid treatment.

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CHAPTER 1

INTRODUCTION

While natural resources like plants and minerals have been the answer to varied needs of mankind since the onset of human civilization, development of innovative and strategic schemes for separation of components of interest from these various matrices and purification of the same forms the backbone of rapid industrial progress.

1.1 SEPARATION SCIENCE

Albeit separations have been practiced for millennia, the last hundred years or so have seen the elucidation of the fundamentals that lie behind many of these processes. Thus, although separations are most widely used for achieving some practical objective, a firm theoretical reasoning has been envisaged and put into place that allows the use of term **separation science**. Separation science was first recognized as a distinct subject area of physical and analytical chemistry in the 1960s and the term was first coined by J. Calvin Giddings, research professor at the University of Utah. Separation science may be defined as the science dealing with processes of any scale by which the components of a mixture are separated from one another without substantial chemical modification (1). Irrespective of the scale of separation the basic principles involved remain the same and the most important factor considered in all separations is the efficiency of the separation. Separations always require energy as the reverse process i.e. mixing at constant volume is spontaneous as it is accompanied by an increase in entropy.

Separation, in chemistry, deals with methods to purify substances or to isolate them from other substances, for either industrial or analytical purposes. Industrial applications involve separation procedures employed in large scale economic manufacturing of items with an ultimate goal to isolate a product of given purity. On the other hand, analytical separations occur on a much smaller scale.

Rarely any measurement technique for chemical analysis is specific for a single species. Sample is considered to be consisting of the substance to be analyzed, the analyte and the rest of the material, the **matrix** (2). Therefore, separation allows the isolation of the analyte leading to elimination or reduction of interferences so that quantitative analytical information can be obtained. Separations can be complete, involving isolation of each component of a complex mixture, or partial, involving isolation of a single component of interest from a mixture. Separations may involve the isolation of organic species, inorganic species or even elements in pure form. Metal ion separation and preconcentration constitute the pivotal step in numerous analytical, purification and waste treatment processes.

1.2 METHODS OF SEPARATION

Since its inception separation science has diversified into many branches, each of it having its own advantages, limitations and field of application. There are many types of separation methods based on a variety of properties of materials. Among the most commonly used properties are those involving solubility, volatility, adsorption and electrical and magnetic effects, although others have also been used to advantage. The most efficient separation will obviously be obtained under conditions for which the differences in properties between two substances undergoing separation are at a maximum. Some of the commonly employed separation methods are briefly touched upon in the following paragraphs (2, 3).

1.2.1 PRECIPITATION

Separation by precipitation requires large solubility differences between analyte and potential interferences.The theoretical feasibility of this type of separation can be determined by solubility calculations. This method is based on a solid as second phase.

Precipitation may be brought about by control of acidity, sulphide separations, by using other inorganic/ organic precipitants or by electrical potential as in electrolytic precipitation. For protein molecules, a specific mode of precipitation is induced by using salts.

1.2.2 DISTILLATION

Separation by distillation is based on difference in volatility of compounds and is widely used to separate volatile analytes from nonvolatile interferences. E.g. separation of nitrogen analytes from many other species by conversion of nitrogen to ammonia, which is then distilled from basic solution.

1.2.3 ION EXCHANGE

Ion exchange separation is based on difference in interaction of reactants (ions) with an appropriate ion-exchange material. This is a process by which ions held on a porous, essentially insoluble solid are exchanged for ions in a solution that is brought in contact with the solid. The ion-exchange properties of naturally occurring clays and zeolites are well known and have been recognized for a long time. Synthetic ion-exchange resins, first produced in 1935, are high molecular weight polymers containing large number of ionic functional groups per molecule. Cation-exchange resins have acidic groups (strong acids like $–SO_3^-H^+$ or weak acids like –COOH) and anion-exchange resins have basic groups (strong bases like quaternary amine, $–N(CH_3)_3^+OH^-$ or weak bases like secondary/tertiary amine).

Cation-exchange equilibrium may be represented as

$$\underset{\text{solid}}{xRSO_3^-H^+} + \underset{\text{soln}}{M^{x+}} \leftrightarrow \underset{\text{solid}}{(RSO_3^-)_xM^{x+}} + \underset{\text{soln}}{xH^+} \qquad (1.1)$$

Anion-exchange equilibrium may be represented as

$$xRN(CH_3)_3^+OH^- + A^{x-} \leftrightarrow [RN(CH_3)_3^+]_x A^{x-} + xOH^- \quad (1.2)$$

solid soln solid soln

Ion exchangers have widespread application in water softening, water deionisation, solution purification and ion separation.

1.2.4 CHROMATOGRAPHY

M. Tswett invented chromatography shortly after the turn of 20th century and employed it for the separation of various plant pigments, which appeared as colored bands on separation. This accounts for the name chromatography ("chroma" meaning "color" in Greek and "graphein" meaning "to write"). Chromatography is a technique in which the components of a mixture are separated based on differences in the rates at which they are carried through a fixed or stationary phase by a fluid mobile phase. The stationary phase in chromatography is fixed in place either in a column (column chromatography) or on a planar surface (planar chromatography). The mobile phase may be a gas (gas chromatography, GC) or a liquid (liquid chromatography, LC). An eluent is a solvent used to carry the components of a mixture through a stationary phase. Elution is a process in which solutes are washed through a stationary phase by the movement of a mobile phase. The mobile phase that exits the column is termed as the eluate.

All chromatographic separations are based on differences in the extent to which solutes are distributed between the mobile and stationary phases. The effectiveness of a chromatographic column in separating two solutes depends on the relative rates at which the two species are eluted. These rates in turn are determined by the relative affinities exhibited by the species towards the stationary column and how they get distributed between the moving liquid phase and the stationary solid phase. The distribution constant for a solute in chromatography is defined as the ratio of its molar concentration in the stationary phase to its molar concentration in the mobile phase. Retention time is the time between the injection of the sample and the appearance of a solute peak at the detector of a chromatographic column. Chromatography is a versatile tool for qualitative as well as quantitative separation and determination of closely related chemical species.

1.2.5 ELECTROPHORESIS

Electrophoresis separations are based on the different rates at which charged species migrate in an electric field. A. Tiselius developed this separation technique in the 1930s for the macro scale separation of inorganic cations and anions, amino acids, proteins etc. Though a remarkable method it was tedious, slow and required significant operator skill. In the early 1980s, capillary electrophoresis was developed which made high-speed micro scale separations possible. The electrophoretic mobility is the ratio of the migration rate of an ion to the applied electric field.

1.2.6 FIELD FLOW FRACTIONATION

Field flow fractionation techniques are based on a difference in interaction with a field or gradient applied perpendicular to transport direction. Different sub-techniques result from the application of different types of fields or gradients. The methods employed are sedimentation, electrical, thermal and flow field flow fractionation. This is a recent separation technique, which is highly complementary to chromatography.

1.2.7 EXTRACTION

Extraction may be defined as a method of separating the constituents of a mixture utilizing preferential solubility of one or more components in a second phase. Commonly, this added second phase is a liquid, while the mixture to be separated may be either solid or liquid.

Liquid-solid extraction may be considered as the dissolving of one or more components in a solid matrix by simple solution, or by the formation of a soluble form by chemical reaction. The field may be subdivided into the following categories: leaching, washing and diffusional extraction. Leaching involves the contacting of a liquid and a solid (usually an ore) and the imposing of a chemical reaction upon one or more substances in the solid matrix so as to render them soluble. In washing extraction the solid is crushed to break the cell walls, permitting the valuable soluble product to be washed from the matrix. In diffusional extraction the soluble product diffuses across the denatured cell walls (no crushing involved) and is washed out of the solid. The largest use of liquid/solid extraction is in the extractive metallurgy, vegetable oil and sugar industries. A recent development in liquid-solid extraction is the solid phase extraction (SPE) that uses membranes or small disposable syringe-barrel cartridges. A hydrophobic organic compound is coated on powdered silica to form solid extracting phase. The sample can be placed in the cartridge and by applying pressure the organic compounds from the sample may be concentrated on the solid phase, which can later be displaced using a solvent.

If the components to be separated are already present in a liquid (**liquid-liquid extraction or solvent extraction** (4)), then the added solvent must be immiscible or only partially miscible with the original and of such a nature that the components to be separated have different relative solubilities in the two liquid phases. As defined by IUPAC, the **solvent**, usually an organic compound or the solution of an extractant in an organic diluent is a liquid which is used to extract a substance from another liquid (usually aqueous). **Diluent** is an inert (organic) solvent used to improve physical properties (density, viscosity, etc) or the extractive properties (e.g. selectivity) of the extractant. The diluent itself has negligible extractive properties for the substance to be extracted. **Extractant** is the reagent that forms a complex or other adduct in the solvent with the substance extracted from the other phase. Extract is the separated phase (usually organic) containing the substance extracted from the other phase. **Stripping** is the process of the back-extraction of the distribuend from the extract (usually into the aqueous phase). **Distribuend** is the substance that is distributed between two immiscible liquids or liquid phases.

While extractions seem to have come into practical use without any great notice, it was Berthelot and Jungfleisch in 1870s who investigated the distribution of a large number of organic and inorganic compounds between ether or carbon disulfide and water. The extent to which the solute, both inorganic and organic, distributes between the two immiscible liquid phases differs enormously and this partition is an equilibrium phenomenon that is governed by the **Nernst distribution law.** Nernst derived the distribution law in 1898. If the solute species A is allowed to distribute itself between aqueous and organic phase, the resulting equilibrium may be written as

$$A(aq)\leftrightarrow A(org) \qquad (1.3)$$

The chemical potential, μ of the species in both the phases is given by

$$\mu_{aq}=\mu_{aq}^{\circ}+RT\ln(a)_{aq} \text{and} \mu_{org}=\mu_{org}^{\circ}+RT\ln(a)_{org} \qquad (1.4)$$

Where $(a)_{org}$, $(a)_{aq}$ are the activities, μ_{aq}° , μ_{org}° are the standard chemical potential and μ_{aq}, μ_{org} are the chemical potential of A in the two phases. R is the universal gas constant and T is the temperature in K.

Under equilibrium conditions, the chemical potential of the species is same in both the phases i.e.

$$\mu_{aq}=\mu_{org} \qquad (1.5)$$

$$\text{or,} \mu_{aq}^{\circ}+RT\ln(a)_{aq}=\mu_{org}^{\circ}+RT\ln(a)_{org} \qquad (1.6)$$

$$\text{or,} \mu_{aq}^{\circ}-\mu_{org}^{\circ}=RT\ln(a)_{org}-RT\ln(a)_{aq} \qquad (1.7)$$

$$\text{or,} \mu_{aq}^{\circ}-\mu_{org}^{\circ}=RT\ln(a)_{org}/(a)_{aq} \qquad (1.8)$$

At constant temperature, $\mu_{aq}^{\circ} = \mu_{org}^{\circ}$.

Thus, the ratio of the activities of A in the two phases will be constant and independent of the total quantity of A i.e.

$K=(a)_{org}/(a)_{aq}$ (1.9)

The equilibrium constant K is known as the **distribution constant**. For dilute solutions, activities may be replaced by concentration so that

$K=(a)_{org}/(a)_{aq}\approx[A]_{org}/[A]_{aq}$ (1.10)

Where $[A]_{org}$, $[A]_{aq}$ are the concentrations of A in each of the phases.

The distribution constant is valid for a single species in both the phases but the solute may undergo chemical reaction in one of the phases. E.g. metal ion (M^{n+}) extraction from aqueous to organic phase is preceded by complex formation (MLn) of the metal ion by reaction with complexing agent anions (L^-). This is because measures have to be taken to modify the species in order to enable efficient extraction into an organic phase. The most obvious way to do this is to neutralize the charge and produce a neutral species. This can be done mainly in two ways:

(a) Formation of chelated complexes using suitable organic complexing agents;
(b) Formation of ion-associated complexes.

If the ions dissolve only in the aqueous phase and the metal complex, undissociated acid HL dissolve only in organic phase, the overall extraction reaction may be represented as

$M^{n+}_{aq}+nHL_{org}\leftrightarrow ML_{n,org}+nH^{+}_{aq}$ (1.11)

and K_{ex} ,the overall extraction constant, is given by

$Kex=([ML_n]_{org*}[H^+]^n_{aq})/([M^{n+}]_{aq*}[HL]^n_{org})$ (1.12)

In such a case, the **distribution ratio, D** is defined as the ratio of total analytical concentration of metal in the organic phase to the total analytical concentration of metal in aqueous phase, measured at equilibrium.

$$D=[M]_{org}/[M]_{aq} \qquad (1.13)$$

Where metal is present in differently complexed forms in the aqueous and organic phase.

Liquid/liquid extraction separates the components of a homogeneous liquid mixture on the basis of differing solubility in another liquid phase. Because it depends on differences in chemical potential, liquid/liquid extraction is more sensitive to chemical type than to molecular size. This makes it complementary to distillation as a separation technique. One of the first large-scale uses was in the petroleum industry for the separation of aromatic from aliphatic compounds. Liquid/liquid extraction also has found application for many years in the coal tar industry. On a smaller scale, extraction is a key process in the pharmaceutical industry for recovery of antibiotics from fermentation broths, in the recovery and separation of vitamins and for the production of alkaloids from natural products.

1.3 ROLE OF SEPARATION SCIENCE IN NUCLEAR INDUSTRY

Due to the high degree of purity of materials needed for nuclear applications together with high value of these materials, separation science research (especially on solvent extraction) has been a major programme of various institutions involved in nuclear technology. At the very onset of the U.S. Manhattan project, in 1942, a diethyl ether based extraction process was developed to purify tons of uranium. Separation science plays a crucial role in all stages of Nuclear Fuel Cycle (NFC). Analytical separations are required in the mineral exploration step itself. Starting from the front end of the nuclear fuel cycle, industrial scale separations are needed during the processing of uranium and thorium ores and purification of uranium and thorium nitrate to obtain nuclear grade materials. The processing of ore and purification of important structural materials like zirconium as well as heavy water production also rely heavily on separation techniques. After the fuel utilization in the nuclear reactor, reprocessing of the fuel is almost entirely based upon efficient separation methodologies. The need for a continuous, multistage separation is unique to reprocessing of nuclear fuels because of the requirement for nearly quantitative recovery and separation of fissile uranium and plutonium from some 40 or more fission products belonging to all groups of the periodic table. A lot of research in current times has been solely directed towards exploring the novel and environmentally benign modes of nuclear fuel reprocessing and subsequent waste management. Remediation of radionuclides from moderator or primary heat transfer (PHT) streams in power reactors and from various NFC facilities are other examples of applications of separation science. Analytical separations are required during chemical quality control of fabricated fuel, nuclear material accounting and burn-up measurements.

The indispensability of separation science in nuclear technology has been aptly summarized recently in a report (5) “Advanced separation technology is key to the nuclear fuel cycle in order to relieve future generations from the burden of today's nuclear power industry; from reprocessing nuclear fuel (uranium, plutonium) for further power generation, to treating and minimizing radioactive waste for storage and disposal. Indeed, the future of the industry relies on the advancement of separations technology to ensure environmental protection, criticality-safety and non-proliferation (security) of radioactive materials by reducing their radiological content.”

Though distillation, solvent extraction, ion exchange and precipitation are the workhorse of separation in nuclear technology, metal ion separation involving membrane based techniques, ionic liquids and **Supercritical Fluid** (SCF) has gained impetus in recent times. Separations based on SCF scores over the conventional techniques owing to its simplicity, ease of operation and more importantly the reduction in the analytical waste generation. SCF can be used as extracting solvent for **Supercritical Fluid Extraction** (SFE) or as mobile phase for **Supercritical Fluid Chromatography** (SFC).

1.4 SUPERCRITICAL FLUID

1.4.1 HISTORICAL PERSPECTIVE

The critical point of a substance was discovered by Baron Cagniard de la Tour in 1822 (6). He heated substances, present as both liquid and vapor, in sealed cannon, which he rocked back and forth and discovered that at a temperature, the splashing ceased. Later he constructed a glass apparatus in which the phenomenon could be more directly observed. Andrews (7), during 1875-76, studied the critical properties of carbon dioxide and the critical parameter values reported by him are in close agreement to the presently accepted values. In 1879, Hannay and Hogarth (8) were the first to report the solvating ability of supercritical fluids. They studied the solubility of inorganic salts in supercritical ethanol. However, it was not until 1958 that Lovelock (9) suggested its use in chromatography and in 1962 Klesper, Corwin and Turner (10) demonstrated its use in chromatographic separation of nickel porphyrins. Metal ion extraction was first reported by Laintz et al. (11) only in 1990 when SFE of Cu^{2+} ion was carried out using fluorinated complexing agent. The SFE of actinides, uranium and thorium, was initiated by Y.Lin (12, 13) in 1994, 1995 employing organophosphorus compounds.

1.4.2 FUNDAMENTAL ASPECTS (14, 15, 16)

At any given temperature a gas may be converted to a liquid by compressing with sufficiently high pressure. But there exists a temperature above which however large pressure is applied the gas is not converted into liquid. This temperature is called the critical temperature (T_c) and the corresponding vapor pressure is called the critical pressure (P_c). The critical point is defined by the critical pressure and temperature, which are characteristic of a given substance. A substance is said to be in the supercritical fluid (SCF) state when its pressure and temperature exceed the critical point value. In the pressure-temperature phase diagram (Fig.1.1 a) the vapor pressure curve indicates the condition under which the vapor and liquid coexist. At the critical point the distinction between the coexisting liquid and vapor disappears. Andrews and Van der Waals called this the continuity of states.

Fig.1.1 b shows the pressure-volume phase diagram of the fluid. Coexistent vapor and liquid states have same pressure but different molar volume, so that the isothermal compressibility is infinite throughout the two-phase region. The critical point is the last point in the two-phase region and the only point in the one-phase region where the compressibility is infinite. As the molar volume and in turn density as well as the enthalpy change dramatically near critical point thermodynamics dictates that along with the isothermal compressibility, K_T, the isobaric heat capacity, C_P and expansion coefficient, α_P becomes infinite at critical point. These properties are unusually large in the critical regime.

Here, $K_T = -1/V\ (\partial V/\partial P)_T$,

$C_P = T/N(\partial S/\partial T)_P$ and

$\alpha_P = 1/V(\partial V/\partial T)_P$

Here, P, V, T are the pressure, volume, temperature and S is the entropy.

The conditions of criticality of a one-component fluid are

$$(\partial P/\partial V)_T=-(\partial^2 A/\partial^2 V)_T=0 \qquad (1.14)$$

$$(\partial^2 P/\partial V^2)_T=(\partial^3 A/\partial V^3)_T=0 \qquad (1.15)$$

Here A is the Helmholtz free energy. The first condition indicates that the limit of mechanical stability is reached and the second that Helmholtz free energy remains convex.

When a substance reaches the supercritical fluid state the physical properties of the fluid becomes intermediate between those of liquid and gas phases of the substance as can be seen from Table 1.1.

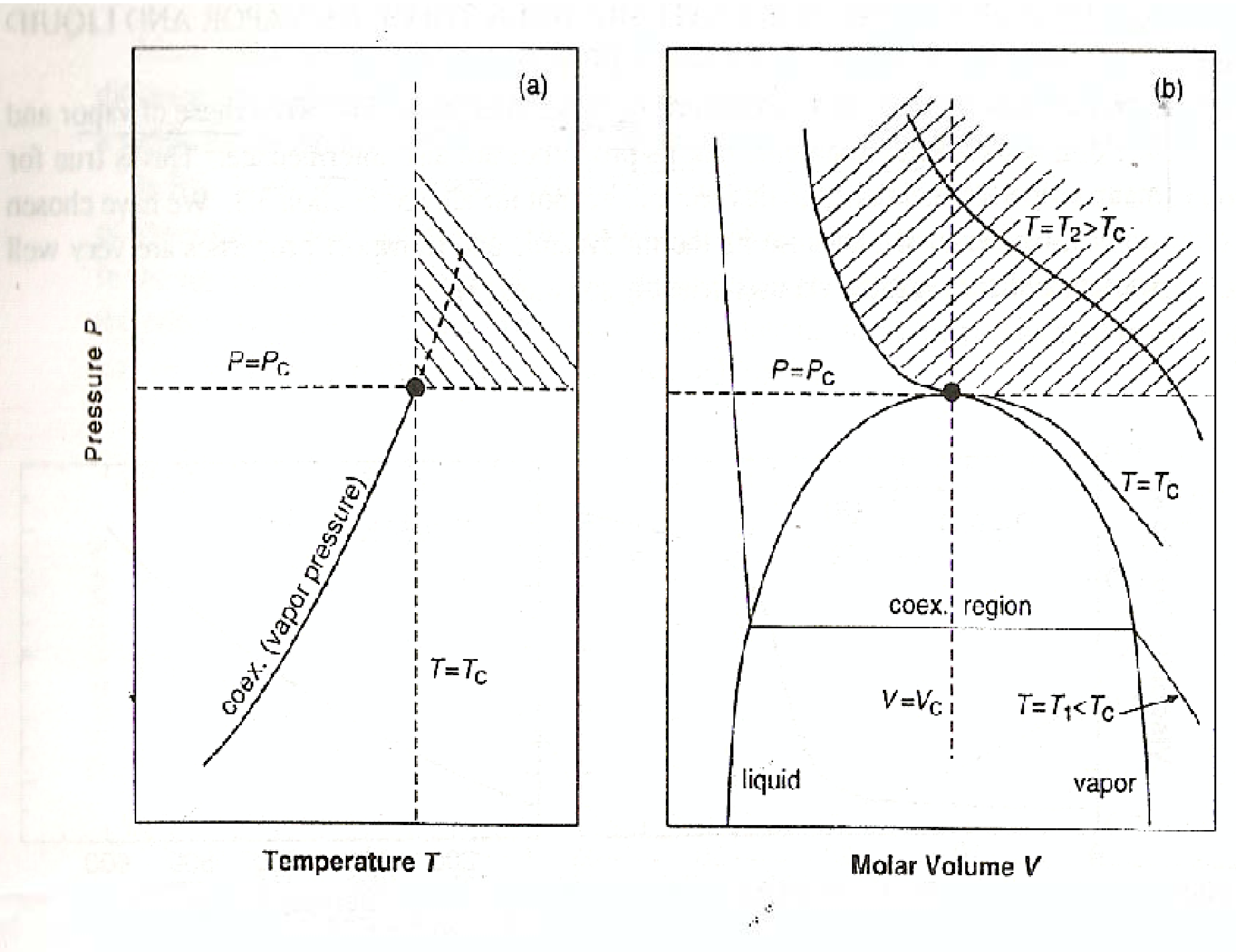
Table 1.1

Comparison of Physical Properties of Different States

State	**Density** **($g\ mL^{-1}$)**	**Viscosity** **(poise)**	**Diffusivity** **($cm^2\ s^{-1}$)**
Gas	10^{-3}	$(0.5\text{-}3.5)*10^{-4}$	0.01-1.0
Supercritical Fluid	0.2-0.9	$(0.2\text{-}1.0)*10^{-3}$	$(3.3\text{-}0.1)*10^{-4}$
Liquid	0.9-1.0	$(0.3\text{-}2.4)*10^{-2}$	$(0.5\text{-}2.0)*10^{-5}$

1.4.3 CHARACTERISTICS OF A SUPERCRITICAL FLUID (14, 15, 16)

Fig.1.2 shows how the density of a pure substance changes in the region of its critical point. For a reduced temperature (T_R=T/T_c) in the range 0.9-1.2 the reduced solvent density (ρ_R=ρ/ρ_c) can increase from gas-like values of 0.1 to liquid like values of 2.5 in the supercritical phase as the reduced pressure (P_R=P/Pc) is increased to values greater then ~ 1.0. Therefore, by operating in the critical region, the pressure and temperature may be tuned to manipulate the density, which in turn dictates the solvating power of the SCF. In essence, it is possible to avail a spectrum of solvent properties in a single SCF by merely changing the pressure and temperature conditions. This the most significant feature of a SCF as compared to liquid-liquid extraction.



(a) **(b)**

Fig.1.1 a (14) The P-T phase diagram of a one-component fluid, with the vapor pressure curve and the critical point

Fig.1.1 b (14) The same diagram in P-V space with the co-existence curve and several isotherms, including the critical

(The cross hatched region is considered supercritical)

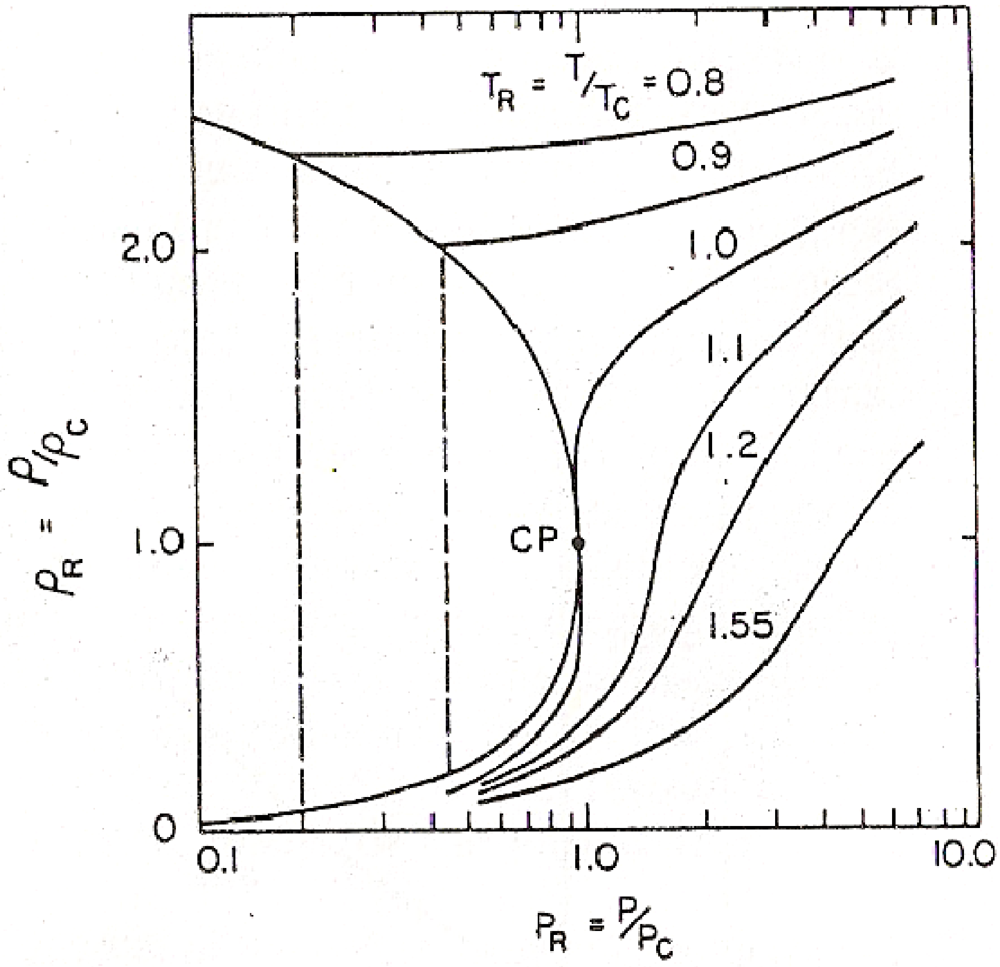


Fig.1.2 (15) Variation of the reduced density (ρ_R) of a pure component in the vicinity of the critical point

The behaviour of density, as well as other thermodynamic functions, as a function of pressure and temperature for any fluid can be predicted by an **equation of state (EOS)**. A large number of equations (17) have been used to predict EOS for CO_2. Prominent among them are:

A) Cubic equations of state (e.g. Peng-Robinson and Soave-Redlich-Kwang)

B) Three parameter corresponding states method (e.g. Lee-Kesler)

C) Multiparametric equation of state (Span-Wagner)

The EOS proposed by Span and Wagner accurately predicts the behavior of pure CO_2 over wide ranging pressures and temperatures but is very involved one consisting of a number of parameters. As only the gross behavior of CO_2, that too in a limited supercritical region (308 K-353 K and 80-300 atm) has been considered in the present investigations, the **Peng-Robinson Equation of State, PREOS** (1976), which is widely applied in the field of supercritical fluids (18, 19) was employed to interpret the experimental observations. The Peng-Robinson Equation is one of a family of cubic equations of state developed from **Van der Waals equation**. The Van der Waals equation, which for a one-component fluid is given by

$$P=RT/(V-b)+a/V^2 \qquad (1.16)$$

Where a and b are constants, known as Van der Waals parameters. The equation is an adaptation of the ideal-gas equation of state in which the ideal volume is obtained by correcting the measured volume by b, the excluded volume, to allow for the physical size of the molecules and the ideal pressure is obtained by correcting the measured pressure by a/V^2, the internal pressure, to allow for the effect of attraction between the molecules. Above the critical temperature and outside the liquid + gas region, the equation reproduces qualitatively the P-V-T behaviour of a fluid. It is described as a cubic equation of state because, when multiplied throughout by $V^2(V-b)$ to remove both denominators, the equation contains a V^3 term.

For the Peng-Robinson equation, the second term in the Van der Waals equation is modified by making the parameter a function of temperature and including b in the denominator, as shown below

$$P=RT/(V-b)-a(T)/(V^2+2Vb-b^2) \qquad (1.17)$$

By using the fact that, at critical point, the first and second derivatives of pressure with respect to volume are zero, the following relationships are obtained, when a and b are calculated from the critical temperature and pressure:

$a(T_c) = 0.45724R^2T_c2/P_c$ and $b = 0.07780RT_c/P_c$

Similarly, $V_c = 3.9514b$ and $Z_c = P_cV_c/RT_c = 0.3074$

Where V_c is the molar volume at critical point and Z_c is the compressibility factor. These values obtained from PREOS can be compared with the experimental values, which is closer to the theoretical values obtained from most other equations of state. It is for this reason that the Peng-Robinson equation is used in supercritical studies.

Other attractive features of SCF can be discussed by taking SC CO_2 as example. Fig.1.3 shows the **self-diffusivity** of carbon dioxide over a wide P-T range. Diffusion coefficients are approximately inversely proportional to fluid density. The self-diffusion coefficient for carbon dioxide is about one or two orders of magnitude higher than diffusivity of solutes in liquids. This has advantage of faster transport in extraction and band narrowing in chromatography.

Although the **viscosity** (η) changes rapidly in the critical region, even at higher pressure of 300-400 bar (Fig.1.4) it is an order of magnitude below typical viscosities of liquid organic solvents. The kinematic viscosity, $\kappa = \eta / \rho$, is proportional to the pressure drop through a non-turbulent system for a given mass flow rate. For a uniform capillary column of radius, a with gas flowing through at a given mass flow rate, m the pressure variation with length, l, along the column is given by

$$dp/dl=-(8m/\pi a^4)(\eta/\rho) \qquad (1.18)$$

Since the viscosity of a supercritical fluid is much closer to that of a gas than that of a liquid, the pressure across chromatographic columns and extraction vessels are less for the equivalent liquid process, which is advantageous.

Therefore, in addition to its tunable solvent characteristics, a SCF possesses certain other physicochemical properties that add to its attractiveness. Even though it possesses a liquid-like density over much of range of interest, it exhibits gas-like transport properties of diffusivity and viscosity. Additionally, the very low surface tension of SCF allows a facile penetration into porous materials to occur. The properties of gas-like diffusivity, viscosity and zero surface tension and liquid-like density combined with density dependent solvating power has provided the impetus for applying supercritical fluid technology to many extraction and separation requirements.

Another striking feature of supercritical fluids is the **critical opalescence** i.e. a near-critical fluid looks like a dense fog. This effect implies that there must be fluctuations in the refractive index and therefore in the density over ranges comparable to the wavelength of light, hundreds of times the molecular size. The number density around a given molecule in a fluid is not constant, but fluctuates in time and varies with distance from the molecule. The average, static structure of a fluid is known from X-ray and neutron scattering experiments and theoretically from integral-equation methods and computer simulations. The structure is described by means of the correlation function H(r). For spherical molecules, ΔH(r) measures the excess or deficit of the local density compared to the average density, as a function of the distance r from the center of a chosen molecule. The correlation function thus represents the average correlation in density between two points at a distance r in the fluid.

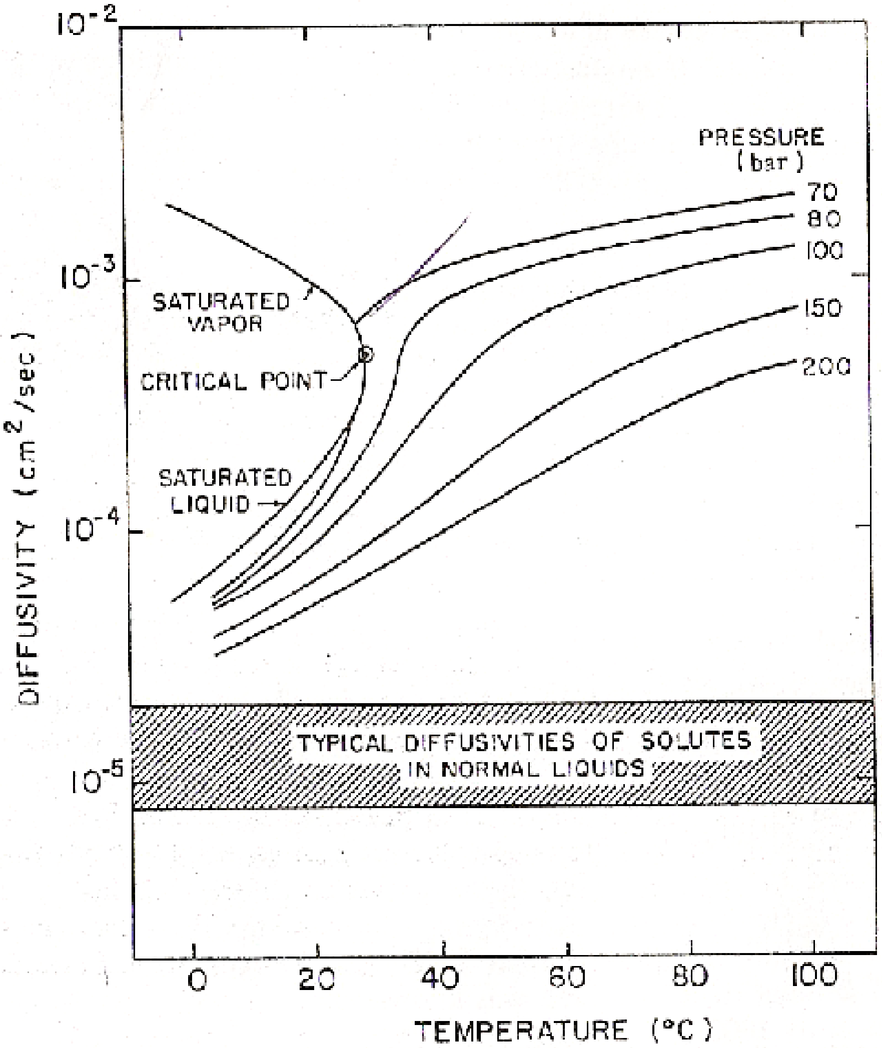


Fig.1.3 (16) Diffusivity behaviour of carbon dioxide

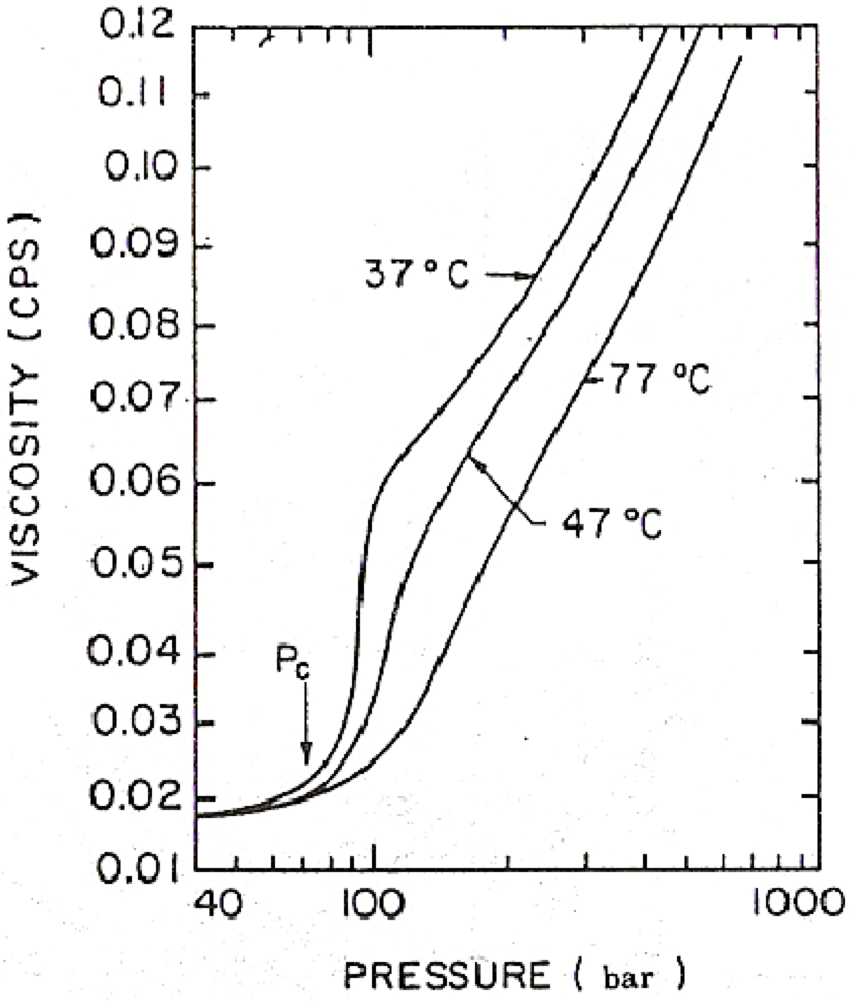
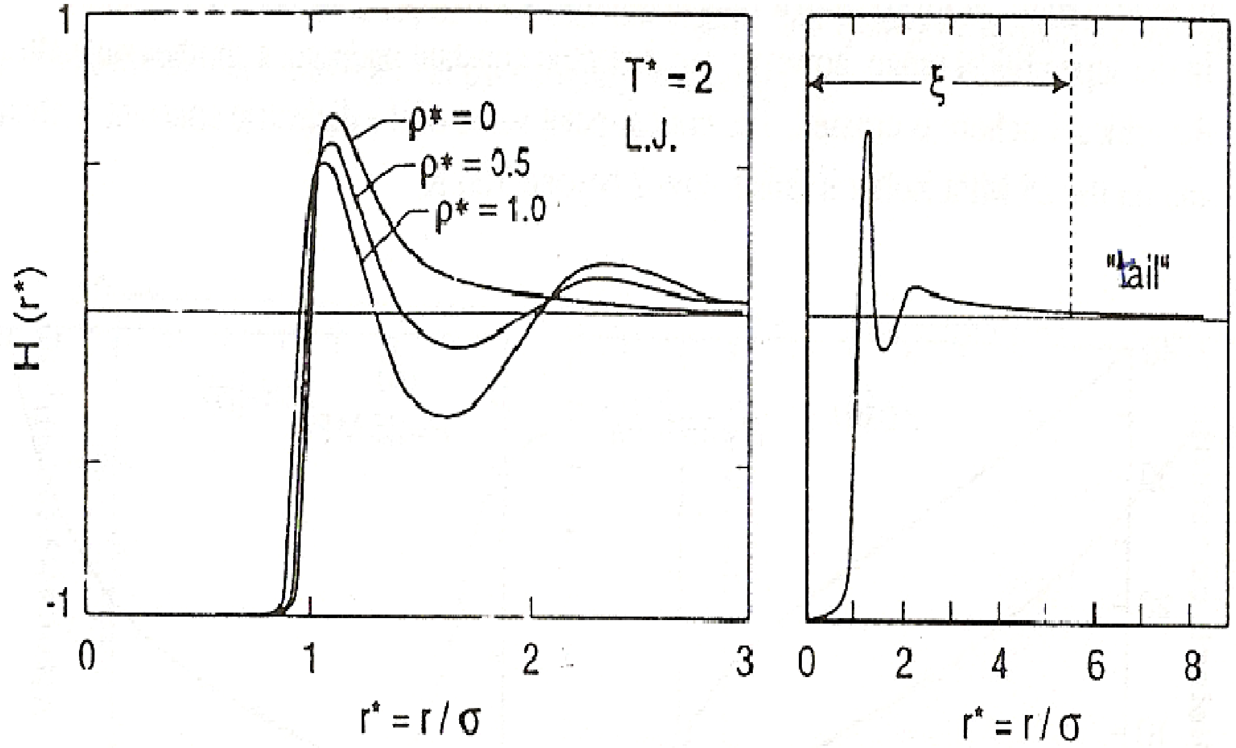


Fig.1.4 [16] **Viscosity behaviour of carbon dioxide**

The correlation function equals -1 as long as r is smaller than the diameter of the hard core or if it is well within the Lennard-Jones diameter σ. It falls off to 0 for large r (Fig.1.5 a). In the vapor phase, $\rho^* = 0$, where $\rho^* = \rho N\sigma^3$ (N= Avogadro's number and ρ = molar density). In the dense fluid, $\rho^* = 1$.molecular attraction induces an increase in local density near a chosen molecule and several shells of molecules pack around a central molecule, leading to oscillations in H(r) before it decays to 0. Near the critical point, the correlation function assumes a long tail, decaying very slowly to the average of zero (Fig.1.5.b). In fact, the integral of the correlation function diverges, because it is proportional to the isothermal compressibility. The range over which the tail extends is called the correlation length. The closer to the critical point, longer is the correlation length. The critical fluctuations are a consequence of the diverging compressibility, and thus a direct signature of criticality. These departures of local density from the bulk average have important effect on supercritical solubility. The environment around the central molecule is probed with spectroscopic techniques of light emission and absorption. Though mean-field (Van der Waals like) equations of state ignore any departure of local density from bulk average, much experimental evidence of local density enhancement has been published.



(a) **(b)**

Fig.1.5 a (16) About 30% above the critical temperature, the correlation function of one-component Lennard-Jonnes fluid, at low density ρ* = 0: one nearest neighbour peak, at a density about 30%higher than critical density ρ* =0.5: a second maximum, at a near close-packing ρ*=1: pronounced oscillations.

Fig.1.5 b (16) Schematically for a fluid near the critical point

1.4.4 CHOICE OF SUPERCRITICAL FLUID (14, 15, 20, 21)

There are many substances that have been studied for being used as a SCF. The choice of substance is guided by many considerations. The temperature and pressure required to push a substance into its critical region plays an important role. Table 1.2 enlists some of these substances used as SCF solvent along with their critical constants.

It is evident from the table, the critical temperature of a substance may differ by hundreds of degrees and this difference suggests the use of specific SCF for specific application. The critical pressure of the hydrocarbons are ~45 atm with enhancement of critical temperature with the molecular weight. Critical temperatures of carbon dioxide, nitrous oxide, ethane and ethylene are near ambient leading to its usage for processing heat sensitive natural products. But hydrocarbons are inflammable and nitrous oxide may explode at very high pressure. On the higher end of temperature spectrum, supercritical water has high T_c and is being used for the oxidation of toxic organic waste. However, usage of supercritical water is associated with corrosion problems. Ammonia has similar behavior, is often considered and discussed, but not often used. Many halocarbons have the disadvantage of cost or of being environmentally unfriendly. Xenon is expensive, but is useful for small-scale experiments involving spectroscopy because of its transparency in the infrared region.

For past 30 years, carbon dioxide has been the favorite candidate for separations using SCF chiefly because of its moderate critical temperature (31.1 °C) and critical pressure (72.8 atm). It is non-flammable, a significant safety advantage for its usage as solvent. It is environment-friendly and non-toxic. The TLV (threshold limit value for airborne concentration at 298 K for which nearly all workers may be daily exposed without any adverse effect) is quite high, 5000 ppm, rendering it less toxic than most of the organic solvents like acetone (TLV = 750 ppm) and chloroform (TLV= 10 ppm). It is benign and cross contamination of other phase or residual CO_2 in the material processed is not a matter of concern. CO_2 is chemically stable. It cannot be oxidized. It is an aprotic solvent and can be used in cases where labile protons may interfere with reaction. Also, it is immune to free radical reactions. Thus, CO_2 is inert towards reactive substances leading to environmental advantage of minimization of scope of byproducts.

Further, in the processing with SC CO_2 no residue is left in the extract as CO_2 escapes as gas at normal temperature and pressure. CO_2 is generally regarded as safe

(GRAS) solvent. Though it is a green house gas, it is naturally abundant. Therefore, it can be withdrawn from the environment, used in a process and returned to the environment without incurring any environmental detriment. It is inexpensive as it is obtained in large quantities as a byproduct of fermentation, combustion and ammonia synthesis. Also, in some nuclear applications such as uranium extraction, the solvents are degraded by hydrolysis and radiolysis and depending on the type of solvent such attacks produce nitrato esters, nitro compounds, carboxylic acids and diketones. Using CO_2 as SCF may be beneficial due to its radiochemical stability and may improve solvent quality.

1.5 APPLICATIONS OF SCF (14, 15)

SCF can be used as extracting solvent for Supercritical Fluid Extraction (SFE) as well as mobile phase for Supercritical Fluid Chromatography (SFC). SFE/SFC employing CO_2 has been a popular technology for rapid, contamination-free extraction in the food and pharmaceutical industries. Large commercial scale plants have in commercial operation since the late 1970s for decaffeination of coffee and tea, refining of cooking oils, recovering flavors from spices and other plant materials. A commercial plant was built in the 1980s for the separation of ethanol from water in combination with distillation. The processing of heavy hydrocarbons employing SCF has been commercialized already. Other applications of SFE include chemical separations and purification, polymer processing, regeneration of activated carbon and other adsorbents, deposition of materials in micro porous substrates etc. In addition to environmentally driven replacement of organic solvents, SCF have direct environmental application in the remediation of soil, water and waste remediation. The oxidation of organic contaminants in supercritical water has been studied extensively as an alternative to incineration. SCF has been investigated as solvent medium for several important chemical reactions.

Table 1.2

Substances used as SCF along with their critical parameters

SCF solvents	**Critical temperature (°C)**	**Critical pressure (atm)**
Carbon dioxide	31.3	72.9
Ethane	32.2	48.2
Ethylene	9.3	49.79
Propane	96.7	41.98
Propylene	91.9	45.64
Cyclohexane	280.3	40.20
Isopropanol	235.2	47.02
Benzene	289.0	48.30
Toluene	318.6	40.60
p-Xylene	343.1	34.77
Trifluoromethane	25.9	46.9
Chlorotrifluoromethane	28.9	38.72
Trichlorofluoremetnane	198.1	43.56
Dichlorodifluoromethane	111.8	40.7
Ammonia	132.5	112.5
Water	374.2	217.6
Xenon	16.6	58.4
Argon	150.9	48.0
Nitrous oxide	36.5	72.5

Despite such widespread applications and associated advantages, the SFE of metal ions was left unexplored for quite some time, as direct metal ion extraction is inefficient due charge neutralization requirement and weak solute-solvent interaction.

Metal ion extraction was reported only in 1990 when SFE of Cu^{2+} ion was carried out using fluorinated complexing agent. This opened up a whole new area of research into the usage of SCF in environmentally acceptable technology as extractive system of metal ions for analytical preconcentration as well as large-scale metallurgical purification. Since1994, the studies on SFE of actinides are also being reported.

1.5.1 PRINCIPLE OF SFE OF METAL IONS (21, 22, 23)

Supercritical fluid extraction (SFE) is a process akin to liquid-liquid or solvent extraction (section 1.2.7) where a Supercritical fluid (SCF) is contacted with a solid/ liquid matrix for the purpose of separating the component of interest from the original matrix. CO_2 is a popular choice of SCF for extraction for the many associated advantages (section 1.4.4). But it is apolar. It does have some limited affinity for polar solutes because of its large quadrupole moment. However, for highly polar solutes e.g. metal ions the use of CO_2 is restricted by its inadequate solvating power and charge neutralization requirement of metal ion. It is for this reason that initially SFE of metal ion was not considered to be feasible. However, when metal ions are complexed with suitable organic complexing agents they become quite soluble in supercritical CO_2 facilitating the extraction of the metal ion. The solvating ability of CO_2 may further be enhanced by the addition of small percentage of polar compounds like methanol to it. The SFE of metal ions can thus be considered to be comprising of at least two elementary steps:

1. Complexation of metal ions with suitable complexing agent

By the usage of a suitable organic complexing agent the charge on the metal ion may be neutralized and hydrophobic metal complex may be produced. The complexation of metal ions can be carried out in two ways, viz.

(i) Online complexation: Complexing agent is first dissolved in SCF, which is then directed through the matrix containing the metal ion.

(ii) In-situ complexation: Complexing agent is added directly to the matrix containing metal ion first and then SCF is allowed to pass through it.

2. Extraction of the soluble metal complex into SCF

The metal complex thus formed may become soluble in SCF. Solvating power of SC CO_2 is related to density. Several models have been put forward for quantitative prediction of solubility of a substance in supercritical fluids which either requires additional physical constants like critical constants for the equation of state approach or molar volumes and solid activities as in Hildebrand solubility parameter approach (24, 25). However, Chrastil (26) has arrived at a simple empirical correlation which relates the solubility (S, in g L^{-1}) of an organic compound to the density (ρ, in g cm^{-3}) of supercritical fluid.

$$\log S = k \log \rho + C \qquad (1.19)$$

Where 'k' corresponds to the number of CO_2 molecules solvating the solute molecule and 'C' is a constant term, which comprises of thermal properties such as the heat of solvation, heat of vaporization and/or the volatility of the solute. The solvation process was therefore closely related to the vapor pressure of the solute and the intermolecular interaction between the solute and the solvent. The equation predicts a linear correlation between lnS and lnD with a intercept of 'C' and slope of 'k'. This simple empirical correlation proposed by Chrastil was meant for organic compounds such as carboxylic acid, carboxylic esters etc. Smart et al. (23) found the above correlation to be valid for metal species as well by examining 15 free complexing agents and 49 metal complexes.

The extraction can be carried out essentially in two modes viz.

(i) Static mode: In the static mode the extraction system is allowed to withstand particular temperature and pressure condition for certain time period, followed by collection.

(ii) Dynamic mode: In case of dynamic mode, collection is carried out at particular temperature and pressure.

It is worth mentioning that any combination of complexation mode and extraction mode can be employed.

The overall efficiency of the process is measured by the extraction efficiency (E) which is defined as the percentage ratio of the metal complex in the SCF phase and the metal ion present initially in the aqueous phase. The important parameters influencing the SFE of metal species are as follows:

1. Choice of complexing agent

A suitable complexing agent should have a reasonable solubility in supercritical fluid and form stable and extractable complex with metal ions of interest. For large-scale applications, the complexing agent should be commercially available and inexpensive. Commonly employed complexing agents for metal extraction by SFE can be broadly categorized as:

i. Cation exchangers

The cation exchangers are either acidic (carboxylic acids, phosphoric and phosphinic acid) or chelating (β-diketones and dithiocarbamates). Chelating complexing agents have two functional groups that form bidentate complex with metal ions.

For a given metal ion (M^{n+}), reacting with complexing agent (HL) the following aqueous phase reactions and phase equilibrium reactions may be written:

Aqueous phase reactions

$CO_2(aq)+H_2O(l)\leftrightarrow H_2CO_3$ (1.20a)

$H_2CO_3\leftrightarrow HCO_3^-+H^+$ (1.20b)

$HL(aq)\leftrightarrow H^++L^-\quad K_L$ (1.20c)

$M^{n+}+nL\leftrightarrow ML_n(aq)\ \beta n$ (1.20d)

Phase equilibrium reactions

$CO_2(SCF)\leftrightarrow CO_2(aq)K_{CO2}$ (1.21a)

$HL(SCF)\leftrightarrow HL(aq)\quad K_{HL}$ (1.21b)

$ML_n(SCF)\leftrightarrow ML_n(aq)\ K_{MLn}$ (1.21c)

The primary reaction in the aqueous phase is dissociation of the complexing agent, characterized by the dissociation constant K_L and formation of the metal complex, characterized by the stability constant of the metal complex βn. Extraction with SC CO_2 can be more complicated than using organic solvents due to the formation of carbonic acid in contact with aqueous phase. The pH has been found to vary between 2.8 to 2.95 in the pressure range of 70-200 atm and temperature range of 298K -343K. While a high value of dissociation constant of complexing agent leads to higher availability of anion L^- and is beneficial for the high extraction efficiency, the dissociation reaction of cation exchanger is highly pH dependent and can be reversed by contacting with a strong acid.

To achieve the highest possible extraction efficiency, the concentration of the metal complex in the aqueous phase must be maximized. A large value o f βn favors this goal. For the SFE of metal ions using a cation exchanger the overall extraction reaction may be represented as:

$$M^{n+}_{aq}+nHL_{SCF}\leftrightarrow ML_{n,SCF}+nH^{+}_{aq} \qquad (1.22)$$

And the extraction efficiency is given by:

$$K_{ex}=([ML_n]_{SCF}*[H^+]^n_{aq})/([M^{n+}]_{aq}*[HL]^n_{SCF}) \qquad (1.23)$$

Naturally a higher value of extraction constant translates into higher extraction efficiency.One of the commonly employed chelating agents, the dithiocarbamates, have a general formula R_2NCS_2X (R =alkyl, X =alkali metal/alkylammonium cation). For example, NaDDC (solubility $1.5x10^{-4}$ at 150 atm, 60°C) extracts 40 metal ions from aqueous and organic solvent. Fluorination, enhancing alkyl chain length and using methanol as co-solvent enhances solubility of the dithiocarbamates. However, this class of complexing agent is unstable in aueous and acidic medium. Also, it is not suitable for lanthanides and alkali metals. β-diketones are another example of chelating agent. It is the enolate form which chelates with metal ion to give neutral complex e.g. AA, TFA. Fluorination, enhancing alkyl chain length increases solubility. Actinides, lanthanides and transition metals are widely extracted.

ii. Solvating extractants

Solvating extractants contain electron rich oxygen or sulphur atoms that can coordinate metal cations. Metal extraction is primarily dependent on the formation of an uncharged ion-pair or complex in the aqueous phase. The neutral and coordinatively saturated compounds, MX_nS_p, are adduct type complexes where X^- is an anionic complexing agent which can be inorganic and S is an uncharged organic lipophilic molecule which has donor properties strong enough to displace the water of hydration of MX_n. E.g. Alkyl phosphates, $(RO)_3$-P=O (TBP,TPP) and phosphine oxides, R_3-P=O (TBPO, TOPO). Fluorination, enhancing alkyl chain length increases solubility. They have been extensively used for extraction of actinides. One of the very important application of solvating extractant, TBP is in the reprocessing of irradiated fuel in the PUREX process where U(VI) is complexed by NO_3^- and extracted as an adduct complex $UO_2(NO_3)_2(TBP)_2$.

iii. Macrocyclic polyethers

This is a class of extractants that do not fit into the categories described above. They can form complexes with metal ion by fitting the ion in their cavity. Rather selective extraction may be possible due to the size dependent complexation. Eg. Crown ethers. Fluorination, long alkyl chain and MeOH as co-solvent increases solubility.

Anion exchangers used in solvent extraction are generally protonated forms of primary, secondary, tertiary amines and quaternary ammonium salts. However, SFE employing anion exchangers has not been studied till date.

2. Solubility of metal complexes

Once a suitable complexing agent has been chosen for the metal ion of interest another factor governing the extraction efficiency is the solubility of the metal complex formed in SC CO_2. Irrespective of the class of complexing agent as discussed in the previous section, the solubility of the metal complex is enhanced when fluorinated complexing agent is used as against non-fluorinated one. For example, a forty fold enhancement in solubility of $Cr(HFA)_3$ as against $Cr(AA)_3$ has been reported at 60º C and 200 atm (22). Enhancing the alkyl chain length of the complexing agent also enhances solubility of the corresponding metal complex. Another mode of enhancing solubility is the usage of MeOH as co-solvent. For crown ethers, the solubility of the metal complex may be enhanced by using a fluorinated counter ion like HPFOA.

3. Temperature and pressure

The temperature and pressure conditions play a decisive role in determining the extraction efficiency. The solubility of complexing agent as well as metal complex is enhanced by increasing the pressure and hence the density of SC CO_2. On the other hand, temperature affects efficiency by influencing the density of SC CO_2, volatility of solute and extraction kinetics. The effect of temperature can be complicated when taken into consideration the fact that while temperature enhancement leads to increase in solute volatility and generally a favorable impact on extraction kinetics, it also leads to a decrease in density and hence lessening of solvating ability of SC CO_2.

4. Chemical form of metal species

The extraction of metals is complicated as compared to organic molecules due to the possibility of existence of metals as organometallic species, ions, oxide, sulphide compound etc. the choice of complexing agent, mode of extraction and complexation and other extraction conditions will depend on the type of metal species present. SFE can be used for speciation study. E.g. for a sample containing mercury in organometallic as well as Hg^{2+} form, SFE can be first carried out with SC CO_2 alone with MeOH as co-solvent to remove the organometallic species. This may be followed by SFE using a dithiocarbamate to remove the Hg^{2+}.

5. Matrix

The matrix from which the metal species is to be extracted plays an important role in determining the extraction efficiency. Various situations may arise. The metal species may have to be extracted: (a) from an aqueous solution e.g. metal ion from nitric acid medium, (b) from a solid compound e.g. metal oxide, (c) from a solid matrix on which the solid metal compound is loaded e.g. metal nitrate/ oxide loaded on tissue paper/sand etc. The conditions of extraction, mode of complexation and extraction may be judicially chosen depending on the matrix. The accessibility of the metal species also depends on whether the matrix is spiked or a real environmental sample, conditions of spiking and the nature of interaction with the solid matrix.

6. Water and pH

Water and pH play an important role in determining the extraction efficiency in many cases. For example, the presence of water as moisture in a tissue paper matrix plays an important role in dislodging the metal ions from the active sites of the cellulose based matrix leading to an efficiency enhancement. Similarly, some complexing agents like dithiocarbamate are unstable in presence of water and acids. Also, the extraction efficiency with cation exchangers is largely influenced by the pH of the aqueous medium as pH regulates extent of dissociation of the complexing agent into the corresponding agent. Additionally, pH of the medium affects extraction efficiency with solvating extractants by the competitive co-extraction of acids and for macrocyclic crown ethers by competitive extraction of protons.

1.6.2 ADVANTAGES ASSOCIATED WITH SC CO_2 EXTRACTION

Since solvent extraction of heavy metals is utilized on a commercial scale, the replacement of organic solvents by SCF has been a major driving force behind the research efforts. As against liquid-liquid extraction employing organic solvents SC CO_2 extraction of metal ions is associated with several advantages like:

1. In conventional solvent extraction, since the target material must be accumulated in the organic phase during loading, the ratio of the aqueous phase to the organic volumes cannot usually be more than ~10. This leads to the use of large volumes of solvent, particularly when the feed is lean. This adverse effect can possibly be eliminated by the usage of non-toxic SC CO_2 for SFE.
2. Residual contamination of the aqueous solution by the organic solvent may be eliminated by employing SC CO_2.
3. In solvent extraction of metals, the chemical reactions occurring at the interface may be faster as compared to mass transfer processes making the mass transfer step the kinetically rate determining step. As the mass transfer characteristics of SCFs are excellent as compared to the liquid solvents due to low viscosity and high diffusivities, SFE should in principle, be a faster process.
4. SCFs have a lower surface tension than traditional organic solvents, resulting in an increased dispersed phase surface area, which may reduce the required equipment size for a particular solvent-to-feed ratio.
5. The tunability of density of SC CO_2 by varying temperature and pressure conditions lead to the accessibility towards a spectrum of solvent properties for a single SCF facilitating processing of multiple products in a single plant.
6. SFE is generally thought to be energy intensive. However, the energy needed to attain the SCF state for CO_2 is compensated by the negligible energy required for solvent recovery from extract by simple depressurization as well as low cost of CO_2, higher concentration of desirable component in extract and no effluent pollution related cost.
7. Solid matrices loaded with metal compounds may be directly subjected to SFE due to high penetration ability of SCFs leading to extraction of component of interest. Thus, SFE may lead to minimization in the usage of acid required for pre-treatment of matrices before conventional solvent extraction.

8. Minimization of acid usage and organic volume is a very important advantage with respect to the nuclear industry where management of secondary nuclear waste poses a great problem.

9. In certain nuclear applications like the reprocessing of irradiated fuel, the problems associated with radiolytic degradation of organic solvent are a mater of concern. This may be solved by usage of radiochemically stable SC CO_2.

Therefore, SCF provide faster, cleaner and efficient extractions, as they generally become gas after the extraction and escape leaving the dissolved solute.

1.7 THESIS OBJECTIVE

Currently metal ion extraction employing SC CO_2 is an area of active research. 1.11 Many aspects of this alternative separation technique remain unexplored and deserve investigation in terms of different complexing agents as well as modes of operation and experimental parameters. Extraction efficiency is a function of multiple parameters (e.g. temperature, pressure, SCF flow rate, choice of complexing agent, amount of complexing agent etc.). Maximization of extraction efficiency by tuning parameters requires in depth understanding of effect of various parameters on extraction efficiency. Studies regarding the formation, solubility and stability of metal complex during extraction and dynamics of extraction will contribute to the basic understanding of SCF in general and the development of feasible technology for metal ion extraction in particular.

Present study was focused on metal ions and matrices especially relevant to the nuclear industry and is expected to contribute towards search for alternative separation technique, particularly in terms of minimization of radioactive liquid waste generation. The thesis comprises of studies on the SFE of uranium and thorium employing different complexing agents from various matrices. Chapter 2 provides a brief overview of the experimental set-up, general procedure of SFE and the method employed for uranium, thorium determination in the present work. Chapter 3 and 4 describe the SFE of metal ion present in aqueous solution viz. uranium from nitric acid medium. While Chapter 3 deals with the SFE employing organophosphorus reagent TBP, Chapter 4 deals with crown ethers as complexing agent. Chapter 5 delves with SFE of metal species loaded on solid matrix viz. thorium from tissue paper matrix employing organophosphorus reagents as well as β-diketones. Chapter 6 describes the SFE of metal from solid compound itself as well as compound loaded on solid matrix viz. uranium oxides themselves and oxides loaded on tissue paper matrix.

1.7.1 EXPERIMENTAL APPARATUS AND GENERAL PROCEDURE

The chapter describes the SFE apparatus used in the present study. The set-up consists of CO_2 delivery pump, co-solvent pump, thermostat, detector, back-pressure regulator and collection vessel. In addition to microprocessor, each unit can be controlled through computer. The sample for SFE is loaded in the extraction vessel. Once the operation and functioning of the apparatus has been described, the general procedure to be followed in subsequent chapters for carrying out SFE is described. This consists of loading of sample in the extraction vessel, attainment of requisite temperature and pressure conditions, subsequent extraction and collection of the extract. After SFE, in order to quantify the extraction efficiency, determination of uranium/ thorium amount becomes inevitable. In the present study, uranium/ thorium determination has been carried out spectrophotometrically by developing colored complex with arsenazo III metal indicator and measuring the absorbance at 655 nm wavelength. A brief theoretical description of the spectrophotometric technique of metal ion determination provided. Subsequently, procedure of color development and absorbance determination as followed throughout the present study is discussed.

1.7.2 SUPERCRITICAL FLUID EXTRACTION OF URANIUM FROM NITRIC ACID MEDIUM EMPLOYING TBP AS CO-SOLVENT

Uranium dissolved in nitric acid medium with TBP as the complexing agent is very commonly encountered system in various stages of nuclear fuel cycle. Solvent extraction is carried out under atmospheric pressure and the density of the solvent does not change significantly with temperature. Hence, in solvent extraction, the effect of temperature has been found to be through shifting of equilibrium constant for the metal complex formation. On the other hand, SCF density plays a vital role as solvent strength is directly related to density and density is markedly affected by pressure and temperature conditions. Chrastil's empirical correlation relates the solubility of a solute to the density of supercritical fluid. Few studies on effect of parameters have been reported in literature where attempts have been made to decipher the extraction process by studying the effects of pressure and temperature on distribution ratio of uranium under equilibrium condition. However, under equilibrium condition, a substance gets distributed between aqueous phase and supercritical phase. Supercritical fluid phase is not renewed under equilibrium condition. Hence, equilibrium study provides only partial insight about the SFE process.

In the present study carried out under extraction conditions, the supercritical phase is continuously renewed by flowing SCF. The SFE process is, therefore, considered to be combined effect of equilibrium process and extraction kinetics. For the study, various parameters affecting extraction efficiency were identified to be extraction pressure, extraction temperature, CO_2 flow rate, percentage of TBP, molarity of acid medium, extraction time, mode of complexation (online/in-situ), and mode of extraction (static/dynamic). Effect of variation of these parameters on extraction efficiency was studied and justification was sought for in order to obtain an insight into various aspects of the extraction process. Under optimized conditions, reproducibility and mass balance studies were carried out to further add credence to the extraction procedure.

1.7.3 SUPERCRITICAL FLUID EXTRACTION OF URANIUM FROM NITRIC ACID MEDIUM EMPLOYING CROWN ETHERS

Uranium being a valuable nuclear fuel it is desirable to expand the scope of uranium extraction and alternative sources like seawater need to be explored. Crown ethers are a versatile class of ion-specific extractants and literature for solvent extraction of actinides using crown ethers is available. However, there are only two reports of SFE where while evaluating various complexing agents for the SFE of uranium, only one crown ether appeared to have been used. Some reports on the solubility of few crown ethers in SC CO_2 have also been published.

The present work was taken up with the aim of a thorough and systematic study of uranium SFE employing crown ethers. As a good strategy for enhancing extraction, CO_2-phillic fluorine containing pentadecafluoro-n-octanic acid (HPFOA), which dissociates to provide $PFOA^-$as counter ion, was employed could be the use of counter ions consisting of several C-F bonds. Feasibility of supercritical carbon dioxide (SC CO_2) extraction of uranium from nitric acid medium employing various crown ethers was studied. The ring size and nature of substituents of crown ethers was found to influence the extraction efficiency. Operating parameters such as pressure (100-300 atm) and temperature (323-353 K) were found to influence extraction efficiency by affecting SC CO_2 density. Extraction efficiency is influenced by many factors. Effect of molarity of nitric acid, uranium amount, uranium: crown mole ratio and crown: HPFOA mole ratio was studied. Online and in-situ modes of complexation were studied. Effect of extraction time was studied. Effect of various solvents for crown ether and HPFOA was also investigated.

1.7.4 SUPERCRITICAL FLUID EXTRACTION OF THORIUM FROM TISSUE PAPER MATRIX EMPLOYING ORGANOPHOSPHORUS REAGENTS AND β-DIKETONES

India has vast reserves of thorium in contrast to modest quantity of uranium. There is need to develop capabilities on all aspects of thorium fuel cycle, i.e. mining, fuel fabrication, reprocessing and waste management. In this context development of processes for separation and purification of thorium from various matrices, liquid as well as solid, is of utmost importance. Reports on SFE of thorium from cellulose based filter paper and sand employing fluorinated β-diketones and TBP has been published. SFE of uranium from tissue paper matrix has also been studied.

In view of limited study of SFE of thorium and its importance to nuclear industry, present study was taken up. Also, very few studies on the influence of operating parameters (pressure, temperature, flow rate, extraction time etc.) on the extraction of metal ions from solid matrix have been reported. In this study, the parametric study has been found to yield differences as against the SFE of uranium from a nitric acid medium. Various organophosphorus reagents (TBP, TOPO, TPP, TPPO and TBPO) were evaluated. Effect of various parameters like pressure, temperature, flow rate, extraction time have been studied. By taking a combination of TBP and a organophosphorus reagent, synergistic improvement in extraction efficiency have been examined. Additionally, various solvents have been tried out for the organophosphorus reagents to investigate solvent influence on the extraction efficiency.

In order to improve efficiency, alternative complexing agents such as β-diketones were investigated. Online and in-situ modes of complexation were studied. The effect of fluorination of β-diketones on the thorium extraction efficiency has been discussed. Combination of TBP and β-diketones was also studied.

1.7.5 DISSOLUTION AND SUPERCRITICAL FLUID EXTRACTION OF URANIUM FROM SOLID URANIUM COMPOUNDS

Uranium dioxide is employed as fuel in boiling water reactors (BWR), pressurized water reactors (PWR) and pressurized heavy water reactors (PHWR) all over the world. Solid waste is being generated at various stages of fuel fabrication. Uranium needs to be recovered from the solid waste. The conventional process involves acid dissolution followed by solvent extraction. Extraction process results in generation of large volume of liquid waste, which is highly undesirable in nuclear industry. An alternative and attractive method is based on direct dissolution and extraction of uranium from solid uranium compounds. Recent reports show that the organic complex of TBP and nitric acid (TBP-HNO_3 complex) is capable of dissolving uranium oxides. $UO_2(NO_3)_2$.2TBP thus formed could be extracted into SC CO_2.

Present study was carried out to thoroughly investigate the feasibility of extraction of uranium from solid UO_2 (powder, granule, green pellet and sintered pellet) generated during fuel fabrication process making use of supercritical fluid extraction. U_3O_8, the most stable uranium oxide which is widely used in nuclear industry as reference material for uranium analysis, was also included in the study. In fabrication process, uranium oxide loaded solid matrix is also generated. As a representative, tissue paper smeared with uranium oxides was taken for study. These solid oxides were dissolvable in TBP-HNO_3 complex. Various parameters i.e. temperature, pressure, extraction time, dissolution time, TBP-HNO_3 amount and molarity of nitric acid for preparing TBP-HNO_3 complex were found to influence the uranium extraction efficiency. Effect of addition of TBP and TTA to the SC CO_2 stream was also investigated.

CHAPTER 2

EXPERIMENTAL APPARATUS AND GENERAL PROCEDURE

2.1 DESCRIPTION OF EQUIPMENT (27)

A schematic of the setup used in the present work is shown in Fig.2.1. The supercritical fluid extraction setup consists of the following units as briefly described below:

(i) CO_2 Gas Cylinder

This supplies CO_2, which is converted to supercritical fluid. The cylinder is connected to CO_2 delivery pump. The pressure of new cylinder is 57 – 59 atm and can be used up to 40 atm. The purity of CO_2 is 99.9%.

(ii) CO_2 Delivery Pump

The gas from CO_2 cylinder is fed to CO_2 delivery pump. The pump is provided with a cooling system (electronic cooling by Peltier element), which cools CO_2 to –10 °C resulting in liquefaction. The cooling process is monitored by indicator light. When the temperature of the cooling unit reaches or falls below –4 °C green light glows. Stable delivery of liquid CO_2 is maintained below –4 °C. The liquefied gas is pumped at desired flow rate to the extraction vessel/chromatography column. The pump provides extremely consistent solvent delivery via slow suction quick delivery (SSQD). The pump can be operated in either constant pressure or flow rate mode. In the present study, constant flow rate has been employed. However, if required, pump can be operated in programme mode, via a user-defined time programme to adjust composition, flow rate, event relay etc. The flow rate can be varied from 0.001 to 10 mL min^{-1} in steps of 0.001 mL min^{-1}. The pump can operate upto a maximum pressure of 500 atm. In the LCD, mode of operation (flow/pressure), flow rate, operating pressure, maximum and minimum pressure and timer status are displayed. In self-diagnostic functions the items checked are memory (ROM, RAM), pressure sensor, DC power, memory backup. The pressure sensor is flow through type strain gauge transducer. Maintenance program includes flow rate correction function and pressure sensor test function.

(iii) Co-solvent Pump

The pump is used to add desired percentage of co-solvent to the CO_2 stream via a T-joint. The stream is then fed to a six-port valve, which has provision for selecting or bypassing the extraction vessel. The co-solvent pump is a high performance, high functionality pump having features of HPLC pump. The pump is similar to CO_2 pump except the absence of cooling unit. It has SSQD, safety and maintenance features similar to the CO_2 delivery pump. Like CO_2 delivery pump, co-solvent flow rate can be varied from 0.001 to 10 mL min^{-1} in steps of 0.001 mL min^{-1}. In addition to this, pump is provided with purge valve for replacing solvent and degassing air from the pump head.

(iv) Thermostat

The thermostat maintains the desired temperature by air circulation. Temperature control is achieved using Peltier elements. The temperature can be varied from room temperature -15 °C to 80 °C in steps of ± 0.1 °C. Time programming functions are also included. The thermostat has inbuilt safety features such as heating/cooling power shut off when unusually high temperatures or flammable solvent leaks are detected. The system has provision for detecting the leak in the extraction vessel and giving audio/video alarm. In the LCD screen, current and set temperatures are displayed. In self-diagnostics, the items included are abnormal temperature, flammable solvent leaks, memory (ROM, RAM) and DC power voltage.

The stream from T-joint passes through a 5-meter long spiral coil for thorough mixing. Further, the stream is passed through a 10 mL capacity vessel containing spherical pebbles of teflon for complete homogeneity. Spiral coil and mixing vessel are contained in the thermostat. The extraction vessel can be loaded/unloaded inside the thermostat as per experimental requirement. The vessel is cylindrical in shape, has capacity of 10 mL and is made up of stainless steel. Extraction vessel has both inlet and outlet at the top. The inlet stainless steel tube (0.5 mm ID) passing through center from top is extended upto bottom for purging $SCCO_2$ through the solution.

(v) Back-pressure Regulator

It controls the pressure of the extraction vessel. The pressure is controlled by opening/closing of variable stroke needle valve. Pressure can be varied from 0 to 500 atm in steps of ± 1 atm. A flow-through type strain gauge pressure transducer is used to measure the pressure and the unit is designed to minimize the dead volume. The LCD screen displays current/set pressure and current/set temperature. Error messages are also displayed when problem occurs. This unit has no computer interface and is solely microprocessor controlled. In self-diagnostics, items checked are memory (ROM, RAM), DC power, valve control, pressure sensor and temperature sensor.

(vi) Collection Vessel

The extract is collected in a tube at atmospheric pressure. CO_2 escapes as gas. The arrangement can be heated to avoid condensation.

The units (CO_2 delivery pump, co-solvent pump, thermostat, back-pressure regulator) are independently controlled by in-built microprocessor. All units together (except back-pressure regulator) can also be controlled through computer. The front panel of each unit has LCD screen for displaying operation status, parameter settings and various messages operated by inbuilt microprocessor. The panel has control/edit keys to set various operations like start/stop, parameter selection, inputting parameter values and creation of time programme etc. The units have in-built maintenance function such as self-diagnostics. Each unit has a power switch used to turn power on/off and inbuilt safety features such as automatic shutoff. In addition to microprocessor, each unit can be controlled through computer.

(vii) Computer Interface (LC-NET II/ ADC) and System Control Program

The HSS-2000 system control programme is a management system for extraction. The programme operates under Microsoft Windows 2000 and provides various functions, including pump control. Operating status monitoring, spectrum processing, instrument diagnostics, validation and history management can be used in chromatography. It can control CO_2 delivery pump rate, co-solvent pump rate, temperature of the thermostat and detector operation. The system is interfaced to computer by LC-NET II/ADC interface box. The interface box can accept four analog signal inputs. It has two external trigger input and event relay output. The LC-NET II/ADC interface box is connected to the PC's ethernet port directly via ethernet cables and to the units via analog signal cables.

2.2 OPERATING PROCEDURE (27)

A known amount of sample was taken in the extraction vessel. The extraction vessel was then loaded into the thermostat. Inlet and outlet tubes were tightened to avoid leakage due to high pressure. In the instrument, there is provision for bypassing /selecting the extraction vessel by means of a six port valve. While loading and unloading, the extraction vessel was bypassed. Then the required temperature was set in the thermostat. The liquid CO_2 and co-solvent were pumped at required flow rates which after getting thoroughly mixed, in the spiral coil and mixing vessel, entered the extraction vessel. The desired pressure was set by back-pressure regulator. Then extraction was performed for required time and the extract was collected in collection tubes at atmospheric pressure. CO_2 flow rate and co-solvent flow rate were increased gradually, in steps of <0.5 mL min^{-1} as sudden pressurization/depressurization might damage the system. It is worth mentioning here that after every extraction system was depressurized gradually to atmospheric pressure.

As mentioned in section 1.6.1, the extraction can be carried out in two modes, viz. **static** and **dynamic.** In the static mode of extraction the extraction vessel is maintained under given temperature and pressure condition without further flowing of SCF so that no collection takes place. In case of dynamic mode, the SCF is constantly pumped at a given flow rate leading to collection under a given pressure and temperature. The time for which static or dynamic extraction is carried out may be referred to as static and dynamic time period respectively.

Similarly, complexation can be carried out in two modes, viz. **online** and **in-situ**. In the online complexation mode the solution of the complexing agent is pumped by the co-solvent pump, which then gets mixed with CO_2 stream and the resulting mixture is introduced in the extraction vessel containing the metal ion sample. On the other hand, in in-situ mode the complexing agent is added along with sample in the extraction vessel and only SC CO_2 is introduced in it.

The extraction efficiency of metal ion can be determined by two ways. Firstly, by determining the amount of metal ion left in the extraction vessel. Secondly, by etermining the amount of metal ion in collection vessel.

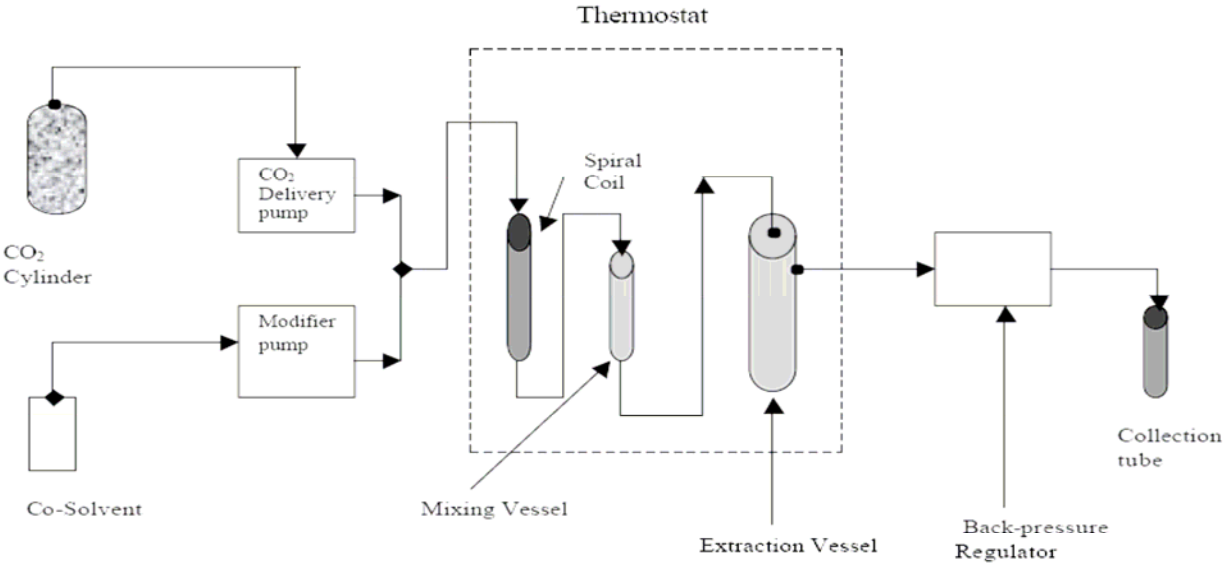


Fig.2.1. Schematic diagram of SFE set up

Fig.2.2. SFE set-up

2.3 DETERMINATION OF METAL IONS

Different experimental approaches have been suggested to determine metal ions in various matrices. The variation of the color of a system with change in concentration of some component forms the basis of **colorimetric analysis**. The color is usually due to the formation of a colored compound by the addition of an appropriate reagent, or it may be inherent in the desired component itself. In **spectrophotometric analysis** a source of radiation is used that extends into the ultraviolet region of the spectrum. From this, definite wavelengths of radiation are chosen possessing a bandwidth of less than 1 nm.

The chief advantage of spectrophotometric method is that it provides a simple means of determining the minute quantities of substance.

2.3.1 THEORY OF SPECTROPHOTOMETRY (3, 28)

Spectrophotometry deals with the following regions of the electromagnetic spectra: ultraviolet 185-400 nm; visible 400-760 nm; infrared 0.76-15 μm while colorimetry is concerned with the visible region of the spectrum. When electromagnetic radiation, either monochromatic or heterogeneous, falls upon a homogeneous medium, a portion of the incident radiation is reflected, a portion absorbed within the medium and the rest is transmitted. The light intensities are expressed as follows: I_o for incident, I_a for absorbed, I_t for transmitted and I_r for reflected radiation. Then

$I_o = I_a + I_t + I_r$

Eliminating I_r for given air-quartz interface,

$I_o = I_a + I_t$

The two laws governing absorption are known as **Beer-Lambert law**.

Lambert's law states that when a monochromatic radiation passes through a transparent medium, the rate of decrease in intensity with the thickness of the medium is proportional to the intensity of the radiation. In other words, the intensity of the emitted light decreases exponentially as the thickness of the absorbing medium increases arithmetically. The law may be expressed by the differential equation

$-dI/dl = kI$

where I is the intensity of the incident light of wavelength λ, l is the thickness of the medium and k is a proportionality factor for the wavelength and the absorbing medium used. Integrating and putting I = Io when l = 0, we obtain

$\ln(I_o/I_t) = kl$

or, $I_t = I_o e^{-kl}$

Beer's law states that the intensity of a beam of monochromatic radiation decreases exponentially as the concentration of the absorbing substance increases arithmetically. This may be written as

$I_t = I_o e^{-k'c}$

Where c is the concentration.

Combining the two equations and changing from natural to common logarithmic scale, we have

$\log(I_o/I_t) = \varepsilon cl$

This is the fundamental equation of spectrophotometry and is known as the **Beer-Lambert law.** Here, if c is expressed in mol L^{-1} and l in cm, ε is known as the **molar absorption coefficient or molar absorptivity**. For a given species, it depends on the wavelength of the incident radiation, the temperature and the solvent employed. I_o/I_t is the **absorbance**, A of the medium. I_t/I_o is the fraction of the radiation transmitted by a thickness l of the medium and is called the **transmittance**, T.

2.3.2 BASIC INSTRUMENTATION (3, 28)

An optical spectrometer is an instrument possessing an optical system, which can produce dispersion of incident electromagnetic radiation, with which measurements can be made of the quantity of transmitted radiation at selected wavelengths of spectral range. A photometer is a device for measuring the intensity of transmitted radiation or a function of this quantity. When combined in the spectrophotometer, the spectrometer and the photometer produce a signal that corresponds to the difference between the transmitted radiation of a reference material and the transmitted radiation of the sample, at selected wavelengths. In the present study, CARY 500 Scan UV-Vis-NIR spectrophotometer has been employed.

Fig.2.3. [28] Block diagram of spectrophotometer

2.3.3 ARSENAZO III AS SPECTROPHOTOMETRIC REAGENT [28, 29]

Reagents, which give the color reaction, upon which spectrophotometric methods are based, are called **spectrophotometric reagents**. Arsenazo III is a very useful bis-azo dye based on chromotropic acid and o-aminophenylarsonic acid. It is moderately soluble in acid solutions. The absorbance of free arsenazo III (λ_{max} 520-530 nm) at the absorption maxima of metal complexes (λ_{max} 655-665 nm) is rather negligible. The large difference between the wavelengths of the absorption maximas of the complexes and the free reagents is important. Only one side of the symmetrical molecule arsenazo III participates in the formation of complexes with metal ions. The metal ion bonds to the nitrogen atom of the azo group, the oxygen atom of the arsonic acid group and the oxygen atom of the hydroxyl group. The distortion of the symmetry of the reagent molecule gives rise to two neighboring absorption maxima in the visible spectra of arsenazo III metal complexes.

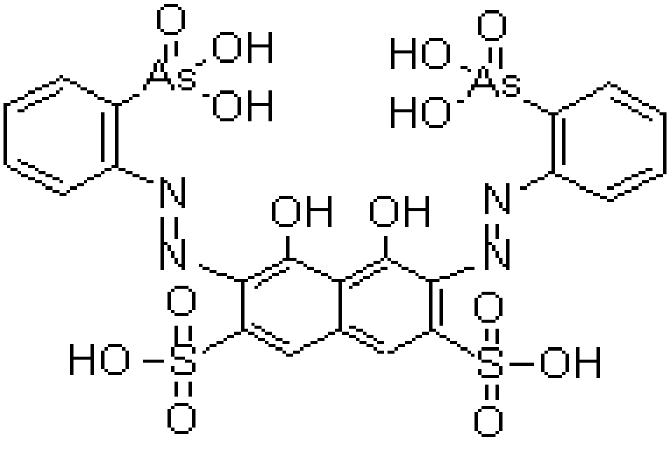


Fig.2.4. Structure of arsenazo III

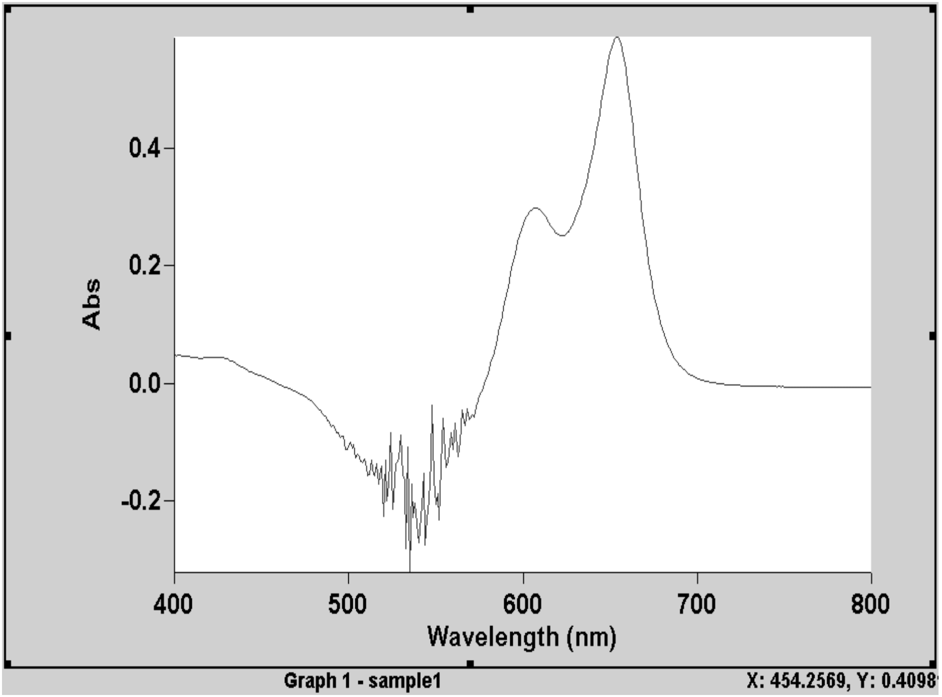


Fig.2.5. Spectra of UO_2^{2+}-arsenazo III

2.3.4 GENERAL PROCEDURE FOR SPECTROPHOTOMETRIC DETERMINATION OF URANIUM AND THORIUM

Uranium (as UO_2^{2+}) /thorium (as Th^{4+}) amount extracted was determined spectrophotometrically. Colored complex was developed employing arsenazo III metal indicator. The method was based on plotting of the calibration curves. Calibration graph was plotted for U/Th amount for the standard solutions (in μg mL^{-1}) versus absorbance at 655 nm and straight line was obtained. In case of uranium standards U concentration was varied from 1-10 μg mL^{-1}. Th concentration was varied from 0.1-1.5 μg mL^{-1} for thorium standards. The calibration standards were prepared by aliquoting required volumes of U/Th stock solution by micropipette followed by the addition of 1 mL of 1 M sulphamic acid and 1 mL of arsenazo III (1mg mL^{-1}). The volume was then made upto 10 mL using HNO_3. Similarly, a known volume of the U/Th samples was taken for color development and absorbance at 655 nm was recorded. From the slope and intercept of the graph the U/Th concentration in sample was calculated.

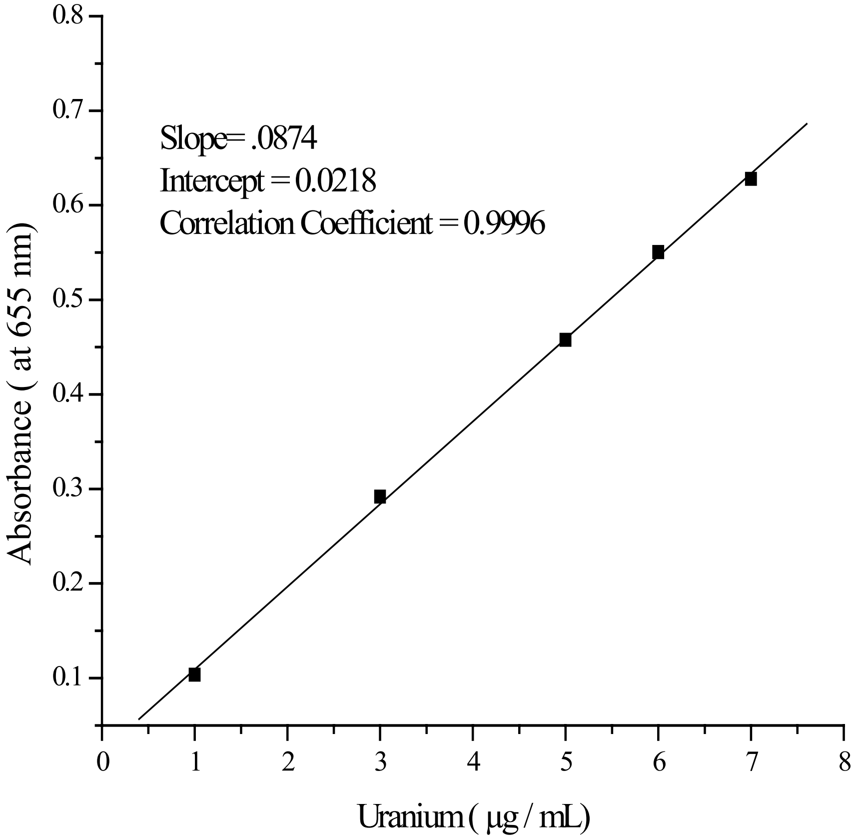


Fig.2.6. A typical calibration curve

CHAPTER 3

SUPERCRITICAL FLUID EXTRACTION OF URANIUM FROM NITRIC ACID MEDIUM EMPLOYING TBP AS CO-SOLVENT

3.1 INTRODUCTION

Extraction of uranium from nitric acid medium with TBP as the complexing agent is very commonly encountered in various stages of nuclear fuel cycle and there exists significant amount of literature on the solvent extraction of this system. In 1993, Lin *et al.* (12, 13) were successful in performing SFE of lanthanides and uranyl ion from solid materials by supercritical CO_2 containing a fluorinated β-diketone. The very next year they reported the SFE of thorium and uranium from solid and liquid materials with fluorinated β-diketones and tributyl phosphate. In 1995, Lin *et al.* (30) carried out SFE of uranium and thorium from nitric acid solution with various organophosphorus reagents. The SFE behavior with variation of nitric acid concentration of medium was found to be similar to that of solvent extraction.

Supercritical fluid extraction can be compared to solvent extraction process. In solvent extraction metal-complex gets distributed between organic and aqueous phases. Extraction of solute is achieved by equilibrating the two immiscible phases, (organic and aqueous) and separating the organic phase. In SFE also metal-complex gets distributed between two phases viz. aqueous and supercritical CO_2 phase. However, extraction process in SFE is quite different from solvent extraction as extraction is achieved by flowing of supercritical CO_2 through the extraction vessel for certain time period and collecting the extract in a collection vessel at atmospheric pressure allowing the CO_2 to escape as gas. However, one major difference between solvent extraction and supercritical fluid extraction is the density of supercritical fluid. In solvent extraction, fluid density does not vary much within operational temperature and pressure range, and apparently has insignificant effect on extraction efficiency. Whereas in SFE, SCF density plays a vital role as solvent strength is directly related to density. Moreover, SCF density is markedly affected by pressure and temperature conditions. Since extraction efficiency is governed by distribution ratio, factors enhancing distribution ratio would lead to higher extraction efficiency.

Meguro *et al.* (31, 32, 33) have made attempts to decipher the extraction process by studying the effects of pressure and temperature on distribution ratio of uranium under equilibrium condition. Under equilibrium condition, a substance gets distributed between aqueous phase and supercritical phase. Supercritical fluid phase is not renewed under equilibrium condition. Hence, equilibrium study provides only partial insight about the SFE process. Under extraction conditions, the supercritical phase is continuously renewed by flowing SCF. Overtly in SFE, extraction efficiency depends on two basic factors: (i) distribution ratio of metal-complex and (ii) kinetics of transport of metal-complex into supercritical CO_2. The distribution ratio of metal-complex is determined under equilibrium conditions. Here at a certain pressure and temperature liquid phase and supercritical phase are thoroughly mixed by stirring (for ~ 60 minute) and aqueous phase is sampled at operational pressure and temperature so that equilibrium condition is not disturbed. In equilibrium study neither extract collection is performed nor is SCF purged through the solution. Whereas in SFE, SCF is continuously flown (purged) through solution and hence extraction efficiency is also influenced by the kinetics of transport of metal-complex into supercritical CO_2.

The present study was taken up to understand of the effects of various parameters on extraction efficiency and optimization of the parameters. Extraction efficiency is a complicated function of various parameters viz. extraction pressure, extraction temperature, CO_2 flow rate, percentage of co-solvent, molarity of acid medium, extraction time, mode of chelation (online/in-situ), mode of extraction (static/dynamic).

3.2 METHODS AND MATERIALS

3.2.1 CHEMICAL REAGENTS

CO_2 gas employed for preparing supercritical fluid was of 99.9% purity. Uranium standard solution was prepared by dissolving high purity U_3O_8 powder in 4 M nitric acid. TBP used as co-solvent was of Merck grade (for extraction analysis). Aldrich grade Arsenazo III was used for color development in the spectrophotometric uranium determination. Sulphamic acid was of Merck grade (99%), A.R. grade nitric acid and ammonium sulphate were employed.

3.2.2 SUPERCRITICAL FLUID EXTRACTION PROCEDURE

Uranium solution in acidic medium, of known concentration was taken in the extraction vessel and SFE was performed as described in section 2.2.

3.2.3 BACK-EXTRACTION OF URANIUM INTO AQUEOUS PHASE

Uranium-TBP complex emerging from extraction vessel was collected in collection tube containing chloroform. For carrying out spectrophotometric determination (section 2.3), uranium was back-extracted into aqueous phase by employing 10% ammonium sulphate solution. Back-extraction efficiency was obtained by determining the uranium amount left unextracted in extraction vessel and uranium amount present in aqueous phase. Back-extraction efficiency was defined by eq.3.1.

$$\text{Back - extraction efficiency} = \frac{U_{aq}}{(U_{init} - U_{unext})} \times 100 \qquad (3.1)$$

Where 'U_{init}' .and 'U_{unext}' are the uranium amounts taken for extraction and left unextracted in the extraction vessel respectively. Whereas 'U_{aq}' is the uranium amount back-extracted into the aqueous phase. Back-extraction was performed with ~1:1

volume ratio of organic and aqueous phase. In Table 3.1, back- extraction efficiency for three extractions is shown. While calculating uranium extraction efficiency, the back-extraction efficiency was taken into consideration.

Table 3.1 Uranium back-extraction efficiency with no. of extractions

Total no. of extractions	Uranium back-extraction efficiency
1	(62 ± 3) %
2	(72 ± 3) %
3	(85± 3) %

3.3 RESULTS AND DISCUSSION

3.3.1 THEORETICAL ASPECTS OF SFE OF URANIUM

A probable extraction scheme for uranium extraction from nitric acid medium into supercritical CO_2 is depicted in Fig.3.1. Uranium extraction process into supercritical CO_2 involves many equilibria processes.

$$H^{+}+NO^{-}_{3}+TBP \rightleftharpoons H(NO_3).TBP \qquad (3.2.a)$$

$$UO_2^{2+}+2NO^{-}_{3}+2TBP \rightleftharpoons UO_2(NO_3)_2.2TBP \qquad (3.2.b)$$

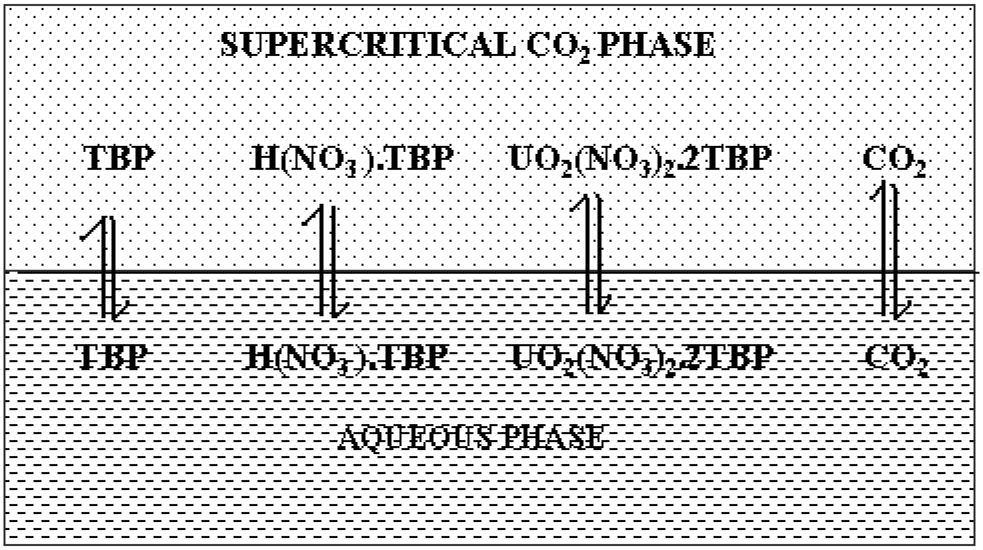


Fig.3.1. Extraction scheme of UO_2^{2+} from nitric acid into supercritical CO_2 employing TBP

Meguro *et al.* (31) from equilibrium study found that uranium is extracted as $UO_2(NO_3)_2.2(TBP)$ into supercritical CO_2 phase. They proposed uranium extraction mechanism for overall extraction reaction, which is very similar to the conventional mechanism for uranium extraction from acidic medium by solvent extraction employing TBP as extractant. According to the proposed mechanism the extraction reaction involves at least three elemental processes: (i) Distribution of TBP between aqueous and supercritical CO_2 phases (ii) Formation of complex $UO_2(NO_3)_2.2(TBP)$ in the aqueous phase and (iii) Distribution of the complex between aqueous and supercritical CO_2 phases. The overall extraction reaction could be expressed by the following formula:

$$UO_2^{2+}{}_{aq} + 2TBP_{SF} + 2NO^-_{3aq} \underset{}{\overset{K_{ex}}{\rightleftharpoons}} \{UO_2(NO_3)_2.2(TBP)\}_{SF} \tag{3.3}$$

Where, K_{ex} is extraction constant defined by following equation:

$$K_{ex} = \frac{[UO_2(NO_3)_2.2(TBP)]_{SF}}{[UO_2^{2+}]_{aq}\,[TBP]^2_{SF}\,[NO^-_3]^2{}_{aq}} \tag{3.4}$$

The phase distribution constants of TBP, $K_{D,TBP}$ and U-TBP complex, $K_{D,U\text{-}TBP}$ are defined as:

$$K_{D,TBP} = \frac{[TBP]_{SF}}{[TBP]_{aq}} \tag{3.5}$$

$$K_{D,U\text{-}TBP} = \frac{[UO_2(NO_3)_2.2TBP]_{SF}}{[UO_2(NO_3)_2.2TBP]_{aq}} \tag{3.6}$$

and formation constant of U-TBP complex in the acid solution, $K_{f,U\text{-}TBP}$ is defined as

$$K_{f,U\text{-}TBP} = \frac{[UO_2(NO_3)_2.2TBP]_{aq}}{[UO_2^{2+}]_{aq}[NO_3]_{aq}^2[TBP]_{aq}^2} \tag{3.7}$$

The eq.3.4 could also be written as :

$$K_{ex} = \frac{[UO_2(NO_3)_2.2TBP]_{SF}[UO_2(NO_3)_2.2TBP]_{aq}\left[TBP\right]_{aq}^2}{[UO_2(NO_3)_2.2TBP]_{aq}\left[TBP\right]_{SF}^2\left[TBP\right]_{aq}^2[UO_2^{2+}]_{aq}[NO_3^-]_{aq}^2} \tag{3. 8}$$

From eq. 3.5, 3.6, 3.7 and 3.8, K_{ex} can be expressed as :

$$K_{ex} = \frac{K_{D,U\text{-}TBP}.K_{f,U\text{-}TBP}}{K_{D,TBP}^2} \tag{3.9}$$

By taking log on both sides, K_{ex} could be expressed by following equation:

$$\log K_{ex} = \log K_{D,U\text{-}TBP} - 2\log K_{D,TBP} + \log K_{f,U\text{-}TBP} \tag{3.10}$$

The distribution ratio D_U of uranium between aqueous and supercritical CO_2 phase is given by:

$$D_U = \frac{\left[UO_2(NO_3)_2.2(TBP)\right]_{SF}}{\left[UO_2^{2+}\right]_{aq}} \tag{3.11}$$

Eq.3.8 and eq.3.11 could be combined so that D_u can be related to $K_{ex.}$

$$D_U = K_{ex}.[NO_3]_{aq}^2[TBP]_{SF}^2 \tag{3.12}$$

By taking log on both sides and substituting the values of K_{ex} from eq.3.10, we get

$$\log D_U = \log K_{D,U-TBP} + \log K_{f,U\text{-}TBP} - 2\log K_{D,TBP} + 2\log[NO_3]_{aq} + 2\log[TBP]_{SF} \tag{3.13}$$

Extraction efficiency depends upon solvating power of supercritical CO_2. Chrastil $^{(26)}$ has arrived at a simple empirical correlation (eq.1.19), which relates the solubility of a solute to the density of supercritical fluid.

The phase distribution constant, 'K_D' of a substance (extractant, extracted complex) can be correlated to solvent property of supercritical CO_2. 'K_D' of a substance can be expressed in terms of its solubilities by eq.3.14

$$K_D = \frac{S_I}{S_{II}} \qquad (3.14)$$

Where 'S_I' and 'S_{II}' are the solubilities of a substance in solvent I and solvent II.

The eq.3.5 and eq.3.6 can be generalized on the basis of eq.3.14 in the eq.3.15.

$$\log K_{Dj} = \log\left({}^{S_{j,SF}}\!\big/_{S_{j,aq}} \right) \qquad (3.15)$$

which on expansion gives

$$\log K_{Dj} = \log S_{j,SF} - \log S_{j,aq} \qquad (3.16)$$

where 'j' denote a particular substance.

On substituting the value of 'log S' from eq.1.19 into eq.3.16, we get

$$\log K_{Dj} = k_j \log \rho + C_j - \log S_{j,aq} \qquad (3.17)$$

Thus, the phase distribution constant of a substance could be related to the density of supercritical fluid and the constant C_j, which comprises of thermal properties such as the heat of solvation, heat of vaporization and/or the volatility of the substance.

3.3.2 EFFECT OF VARIOUS PARAMETERS

The extraction efficiency is expected to be influenced by operating parameters viz. pressure, temperature, TBP %, nitric acid molarity, extraction time. In order to investigate the effect of an operating parameter on extraction efficiency, particular parameter was varied while keeping all other parameters fixed. During the study, online complexation mode and dynamic extraction mode were adopted. The experimental conditions under which the effect of various parameters was investigated are shown in Table 3.2a.

Table 3.2 Experimental conditions for parameter study of SFE of uranium

Uranium concentration	500.8 μg mL^{-1}
Uranium solution in extraction vessel	5 mL
Molarity of uranium solution	4 M
Extraction time	30 minute
Extraction mode	Dynamic
Complexation mode	Online
Collection liquid ($CHCl_3$)	3 mL
CO_2 flow rate	1 mL min^{-1}
TBP flow rate	0.1mL min^{-1}

3.3.2.1 Effect of Pressure

Effect of pressure on extraction efficiency was studied at 333 K by varying the pressure of the extraction vessel from 80-300 atm. The variation in uranium extraction efficiency with pressure is depicted graphically in Fig.3.2. In the figure, the variation in SC CO_2 density with pressure at 333 K, as obtained from Peng-Robinson equation of state (15), is also shown. As is evident from the graph, the variation in uranium extraction efficiency with pressure is not a straightforward affair; pressure affects extraction efficiency in a very complicated manner. The graph displays initial steep rise in extraction efficiency with increasing pressure followed by a gradual decline. Density versus pressure graph also shows initial steep rise in SC CO_2 density and gradual increase afterwards with increasing pressure. Thus, it is seen that the effect of pressure on the extraction efficiency has two distinct components; one in the range of 80 to 150 atm and another in the range of 150 to 300 atm. It is interesting to note that density of SCF, which is an important parameter in deciding the extent of extraction, has a direct relation to the pressure of the SCF. Enhancement in density of SCF (consequent to increase in pressure) also increases the solubility of solute in SCF resulting in enhanced extraction. The experimental observations indicate that beyond 150 atm this does not hold good and in fact the extraction efficiency decreases as the density (or pressure) increases. It seems different mechanisms are simultaneously getting manifested and are responsible for the observed extraction behavior. An attempt has been made to rationalize this interesting observation.

Meguro *et al.* (32) from equilibrium study observed a continuous decrease in uranium distribution ratio in the 100-400 atm pressure range. Whereas in the present SFE study the decreasing trend is observed in 150-300 atm range only and in the range of 100-150 atm steep rise in extraction efficiency was observed. Clifford *et al.* (34) put forward a mode of visualization of extraction process by assuming spheres of uniform size of aqueous solution immersed in flowing supercritical fluid. It could be assumed that the SCF is continuously purged through aqueous phase dispersing it into very small droplets. Hence, SFE can be considered as non-equilibrium process and is not expected to resemble uranium distribution ratio variation trend as observed by Meguro *et al.* However, eventually any non-equilibrium process progresses towards attaining equilibrium. In the present SFE study, equilibrium behavior is reflected only in 150-300 atm pressure range. In this range, the theory corresponding to equilibrium process can be adopted to explain the SFE behavior.

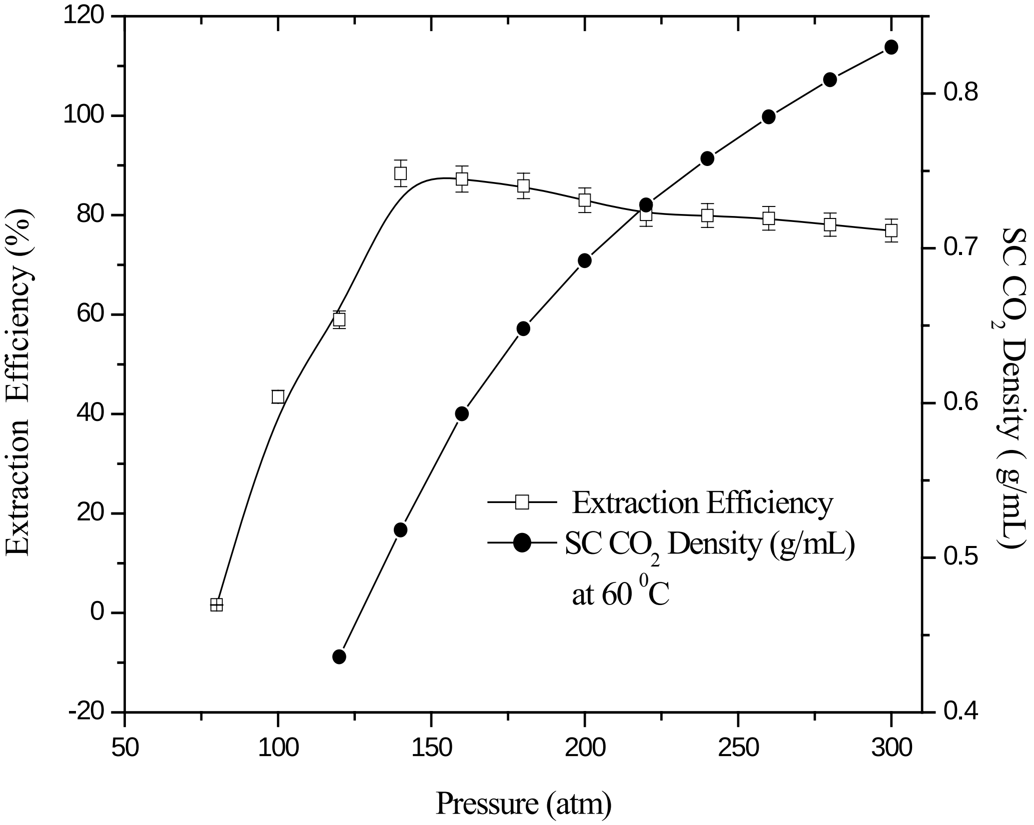


Fig.3.2. Variation of uranium extraction efficiency/ SC CO$_2$ density with pressure (CO$_2$ flow rate = 1 mL min^{-1}, TBP flow rate = 0.1 mL min^{-1}, Temperature = 333 K, Uranium amount = 2504 µg)

(Error bar is ± 3% of the value)

Substituting the values of phase distribution constants of TBP and U-TBP complex according to eq.3.17 into eq.3.12, the expression for uranium distribution ratio 'D_U' becomes:

$$\log D_U = k_{U\text{-}TBP} \log \rho + C_{U\text{-}TBP} - \log S_{U\text{-}TBP,\,aq} - 2\,k_{TBP} \log \rho - 2C_{TBP} + 2\log S_{TBP,\,aq} + \log K_{f,U\text{-}TBP} + 2\log[NO_3^-]_{aq} + 2\log[TBP]_{SF} \quad (3.18)$$

The eq.3.18 can be rearranged to eq.3.19 so that 'D_U' can be related to supercritical CO_2 density by eq.3.19:

$$\log D_U = (k_{U\text{-}TBP} - 2\,k_{TBP})\log\rho + A + B \tag{3.19}$$

Where $A = \log K_{f,U\text{-}TBP} + (C_{U\text{-}TBP} - 2C_{TBP}) - \log\left({S_{U\text{-}TBP,aq}} \Big/ {S^2_{TBP.aq}} \right)$ (3.20)

and $B = 2\ \log[NO_3^-]_{aq} + 2\log[TBP]_{SF}$ (3.21)

'A' is a pressure-independent constant and 'B' is a variable determined by the distribution equilibrium of HNO_3. Eq.3.19 can be further simplified in the following form.

$$\log D_U = \alpha\ \log\rho + \beta \tag{3.22}$$

Where $\alpha = k_{U\text{-}TBP} - 2\,k_{TBP}$ and $\beta = A + B$.

Thus, a linear correlation is expected between logD and logρ with β as the intercept and α as the slope. Iso *et al.* (35) indeed studied the pressure dependence on uranium distribution ratio under equilibrium condition and observed linear plots between 'log D_U' and 'log ρ'. The plots had negative slopes (corresponding to $k_{U\text{-}TBP} - 2\,k_{TBP}$) implying decrease in '$D_U$' with increasing SC CO_2 density. Meguro *et al.* (32) determined the value of k_{TBP} to be 21.8 and that of $k_{U\text{-}TBP}$ to be 40.6 at 333 K. From these values of 'k_{TBP}' and '$k_{U\text{-}TBP}$', the α was calculated to be -3. Hence, the decrease in extraction efficiency with increasing pressure at constant temperature is due to negative value of slope. In the present work, for SFE in the pressure range (150-300 atm), the dependence of extraction efficiency on pressure could be fitted into a linear equation: E = 98.785 – 0.075 P, having correlation coefficient -0.9912. Where 'E' and 'P' represent extraction efficiency and pressure respectively.

Extraction behavior in the pressure range 80-150 atm resembles SC CO_2 density versus pressure graph. The SFE process can be visualized as two step process. First step involves formation of U-TBP complex at the aqueous–supercritical CO_2 interface. Second step consists of dissolution of the U-TBP complex in the SC CO_2 phase. The dissolved U-TBP complex is immediately carried away by flowing SC CO_2. Thus, a non-equilibrium steady state is established. Uranium is brought to the aqueous–supercritical CO_2 interface at certain rate by a diffusion controlled process. As shown in Fig.3.2 higher the pressure higher will be SC CO_2 density. Pressure in extraction vessel was achieved by feeding SCF mixture by pumping liquid CO_2 and TBP while keeping fixed ratio of flow rates. After achieving the desired pressure, extraction was carried out by flowing SCF mixture for fixed time. Hence, during extraction same amount of CO_2 and TBP were flown through the extraction vessel independent of pressure. However, to achieve higher pressure, SCF mixture needs to be fed for larger time period resulting in higher amount of SC CO_2 as well as TBP in the supercritical phase.

As per eq.3.3, according to Le Chatelier principle higher TBP amount in SC CO_2 phase will result in higher U-TBP complex formation. Similarly, Le Chatelier principle can be applied for predicting dissolution of U-TBP complex in the SC CO_2, more is the CO_2 (i.e. higher SC CO_2 density) higher will be the dissolution of U-TBP in supercritical phase, consequently higher will the extraction efficiency. In addition, solubility data for TBP and U-TBP complex indicate enhanced solvent strength with increasing pressure. Solubility is an indication of solvent strength. Meguro *et al.* (33) observed increase in TBP solubility with rising pressure. At a temperature of 333 K, TBP solubilities were 0.00064, 0.42, 0.71, 1.1 mol/ L at pressures of 85, 100, 120,150 atm respectively. Similarly, increase in the solubility of $UO_2(NO_3)$.2TBP was observed by Addleman *et al.* (36) at 323 K in the pressure range of 85-160 atm determined by on-line laser induced fluorescence. These studies indicate that solvent strength abates at lower SC CO_2 density. Obviously, dissolution process will be favored by enhanced solvent strength.

Hence in range of 80-150 atm, extraction efficiency resembles the SC CO_2 density versus pressure graph. The extraction efficiency (E) dependence on pressure (P) could be fitted into linear relationship $E = -103.618 + 1.379 P$ having correlation coefficient 0.9846.

Moreover, extraction kinetics model (as described later in section 3.2.6) proposed by Clifford *et al.* (34) found that diffusion is slow in case of high partition (high

'D_U'), whereas poor partition (low 'D_U') is associated with rapid diffusion. As per study by Meguro *et al.* (32) at lower pressure 'D_U' is high, implying slower diffusion i.e. U-TBP complex is transported to the surface of aqueous phase at slow rate resulting in lower extraction efficiency. As the pressure increases, 'D_U' decreases causing higher diffusion rate leading to further increase in extraction efficiency. Upto 150 atm, pressure as well as extraction efficiency increases indicating the dynamics of the process. Beyond 150 atm, observation in present investigation is similar to that of Meguro *et al.* (32). It may be noted that Meguro *et al.* carried their studies under equilibrium condition. Similarity of current observation to that of Meguro *et al.* leads to the conclusion that equilibrium may be setting in. Present study shows that SFE process is combination of many factors, which affect the extraction process in a very complicated manner. One has to carefully select and optimize these factors while designing the extraction process. The pressure was optimized at 150 atm.

3.3.2.2 Effect of Temperature

The effect of extraction temperature was evaluated by performing SFE at 150 atm pressure and varying the extraction temperature from 308 to 353 K. The variation in extraction efficiency with temperature is depicted graphically in Fig.3.3 along with SC CO_2 density versus temperature plot. The graph displays linear decrease in SC CO_2 density with rising temperature. Decrease in density should cause lowering in extraction efficiency. However, observed trend is not in accordance with the expected trend. The extraction efficiency increases in the temperature range of 308-333 K followed by steep fall in the region of 333-353 K. According to eq.3.23 the uranium distribution ratio is influenced by two terms i.e. density of SC CO_2 ('ρ')and term 'β'. The temperature can affect uranium distribution ratio in eq.3.23 in two ways: (i) influencing SC CO_2 density; the increase in temperature lowers SC CO_2 density (ii) influencing term 'β' by affecting volatility of the U-TBP complex. The volatility of U-TBP complex increases with temperature. Thus, temperature affects the density and volatility factors in opposite manner. On one hand, rising temperature tends to lower the extraction efficiency by decreasing SC CO_2 density. On the other hand, rising temperature tends to enhance the extraction efficiency by increasing volatility. Similar behavior is also discussed in literature (15). The observed trend in the 308-333 K region indicates that volatility of U-TBP complex increases so sharply that it compensates the effect of decrease in density. While considering the temperature dependence of extraction efficiency, interestingly it is worth considering the increase in 'k' value (no. of CO_2 molecules solvating U-TBP complex) with temperature reported by Meguro *et al.* (32). They determined the value of 'k' to be 10.4 and 40.6 at 323 and 333 K respectively. The higher 'k' values implies higher heat of solvation and consequently enhanced solubility of U-TBP complex.

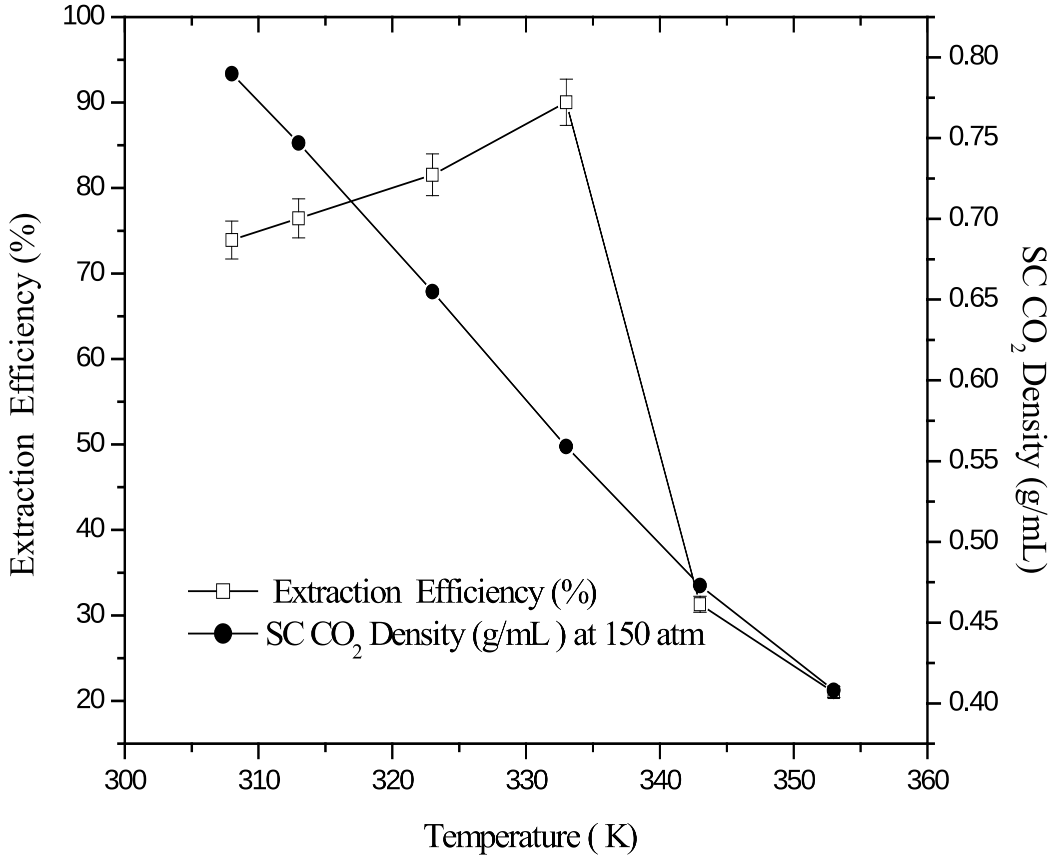


Fig.3.3. Variation of uranium extraction efficiency/ SC CO_2 density with temperature

(CO_2 flow rate = 1 mL min^{-1}, TBP flow rate = 0.1 mL min^{-1},

Pressure = 150 atm, U amount = 2504 μg)

(Error bar is ± 3% of the value)

Even though volatility is a monotonic function of temperature, decrease in extraction efficiency indicates that the influence of volatility of the U-TBP complex on extraction efficiency has reached its maximum value around 333 K and afterwards the effect of decrease in density on extraction efficiency is the dominating factor. The decrease in extraction efficiency is very steep and the density decrease factor alone does not suffice. This steep decrease could probably be attributed to the peculiar behavior of supercritical fluids near the critical point. Solubility behavior is related to thermodynamic properties such as partial molar volume and partial molar enthalpy. These properties diverge near critical point. The divergence is related to isothermal compressibility $K_T = (1/\rho)(\partial\rho/\partial P)_T$. The isothermal compressibility diverges near critical point. As 'K_T' is proportional to the mean squared density fluctuations $^{(37)}$. 'K_T' is proportional to $\int r^2|g(r)-1|dr$. The pair correlation function '$g(r)$' is the ratio of local to bulk density at a distance 'r' away from a molecule. Therefore divergence of 'K_T' is consequence of '$g(r)$', a finite quantity becoming long ranged. The quantity 'ξ' called correlation length is a measure of the range of density fluctuations. Near critical point, 'ξ' is abnormally large. For CO_2, ξ = 55 Å at 1 K above T_c and ξ = 13 Å it 10 K above T_c. The average intermolecular distance at critical density is 5.4 Å. Large size cluster formation is peculiar feature of density near critical point. The densities at 343 K and 353 K are 0.47 g mL^{-1} and 0.41 g mL^{-1} respectively, which are very close to critical density of CO_2 i.e. 0.47 g mL^{-1}. It is expected that at elevated temperature and pressure conditions whenever density approaches that of density near critical point, similar large size cluster formation should occur. Free energy of solvation is given by $\Delta G = \Delta H - T\Delta S$. In solvation process, solute molecule is surrounded by cluster of solvent molecules. In large cluster, the solvation process provides enthalpy gain for solubility enhancement whereas entropy loss due to gathering of solvent molecules disfavor solubility. For large clusters, the entropy loss is very high and net effect is decrease in solubility. The temperature was optimized at 333 K.

Pressure and temperature influence the extraction efficiency by affecting the SC CO_2 density. Hence it is more appropriate to view the variation in extraction efficiency with change in SC CO_2 density. Graph of extraction efficiency versus SC CO_2 density under pressure/ temperature variation conditions is shown in Fig.3.4. The plots exhibit almost similar behavior. It is interesting to note that there is an optimum density (~0.58 g mL^{-1}) at which maximum extraction efficiency is obtained in both the cases.

Beyond this both the plots show a gradual decrease. However, at densities below 0.58 g mL^{-1} the extraction efficiencies are significantly different. The temperature has a more profound effect than the pressure. The entropy effects and the larger cluster formation at higher temperatures when the density of the super critical fluid is very near that of critical density are more pronounced than when pressure is varied. Thus different physical parameters may be responsible for this difference in the extraction behavior.-

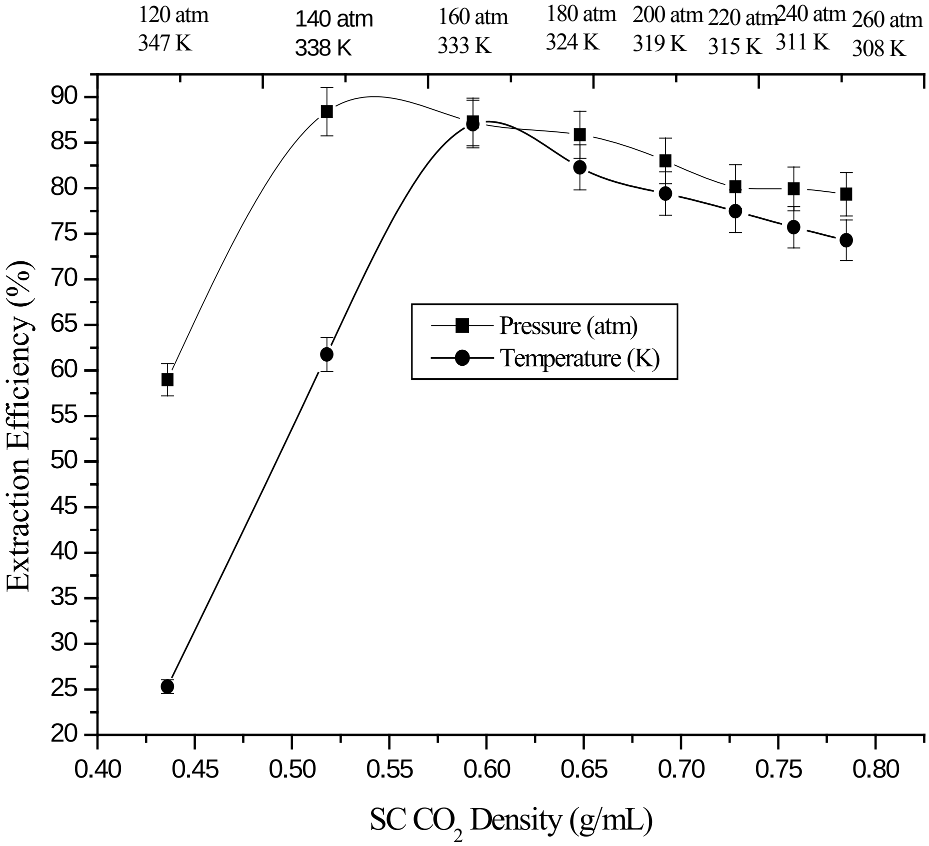


Fig.3.4.Variation of extraction efficiency with SC CO_2 density at various pressure and temperature

(Error bar is ± 3% of the value)

3.3.2.3. Effect of CO_2 Flow Rate

Effect of CO_2 flow rate on extraction efficiency was studied for 30 min. dynamic extraction by keeping pressure fixed at 150 atm, temperature at 333 K and varying the flow rate from 0.5 to 3 mL min^{-1}. The graph (Fig.3.5 a) of CO_2 flow rate versus extraction efficiency indicates that extraction efficiency increases upto flow rate of 1 mL min^{-1} and nearly attains saturation afterwards. As per the model proposed by Clifford *et al.* (34) the over all extraction process consists of partitioning of uranium between aqueous and supercritical CO_2 phase and uranium is brought to the aqueous surface by diffusion process. The model assumes that equilibrium between aqueous and supercritical CO_2 phase is rapidly established whereas diffusion in aqueous phase is a slow process. The extraction process can be visualized as spheres of aqueous phase immersed in flowing supercritical CO_2 phase.

The U-TBP complex from the aqueous phase is carried by flowing supercritical CO_2 into collection vessel. Initial part of the graph (Fig. 3.5 a) indicates that lower flow rates are insufficient in carrying the U-TBP complex into collection vessel. Flow rate of 1 mL min^{-1} and above could successfully transport U-TBP complex into the collection vessel, and enhanced flow rates have no significant gain on extraction efficiency. This is due to the fact that at flow rates higher than 1 mL min^{-1} extraction process is limited by diffusion rate. Supercritical CO_2 flow rate was optimized at 1 mL min^{-1} for 10 mL extraction vessel containing 5 mL solution.

Extraction efficiencies were also compared for various CO_2 flow rates while constant volume of SC CO_2 and TBP was passed through the extraction vessel (Fig.3.5 b). For flow rate higher than 1 mL min^{-1}, the extraction efficiency is nearly constant. At flow rate lesser than 1 mL min^{-1} efficiency was low, again indicating lower flow rates are insufficient in carrying the U-TBP complex into collection vessel.

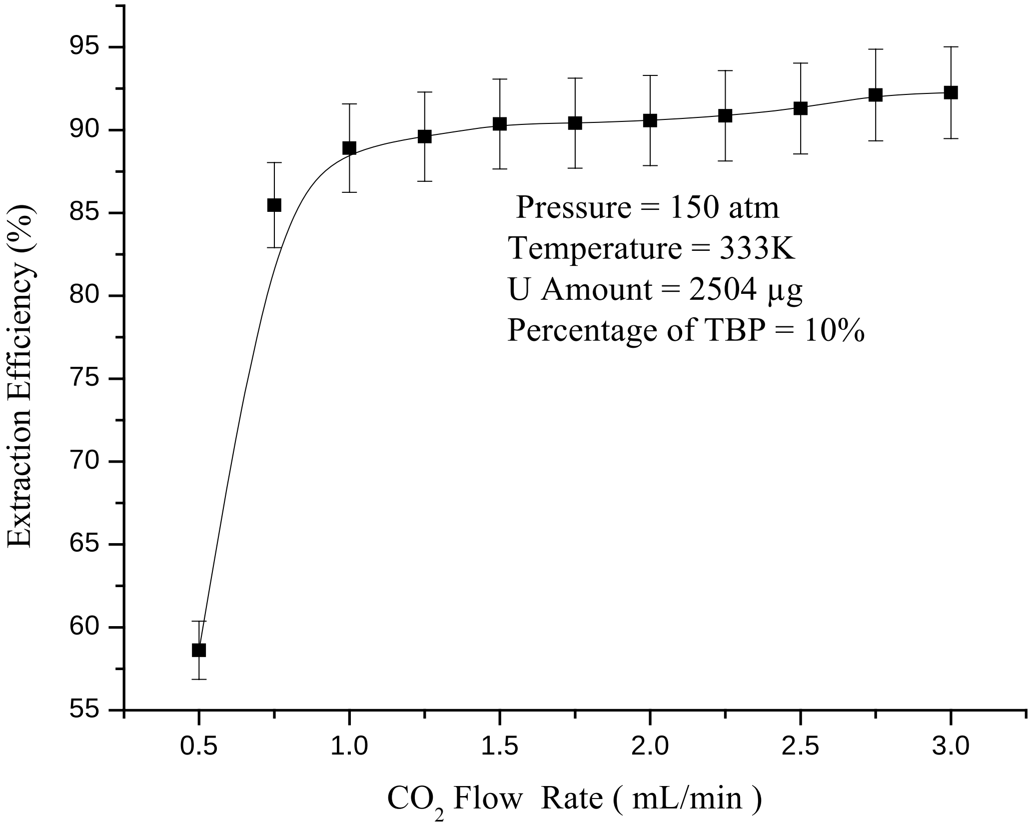


Fig.3.5 a. Variation of uranium extraction efficiency with CO_2 flow rate

(Error bar is ± 3% of the value)

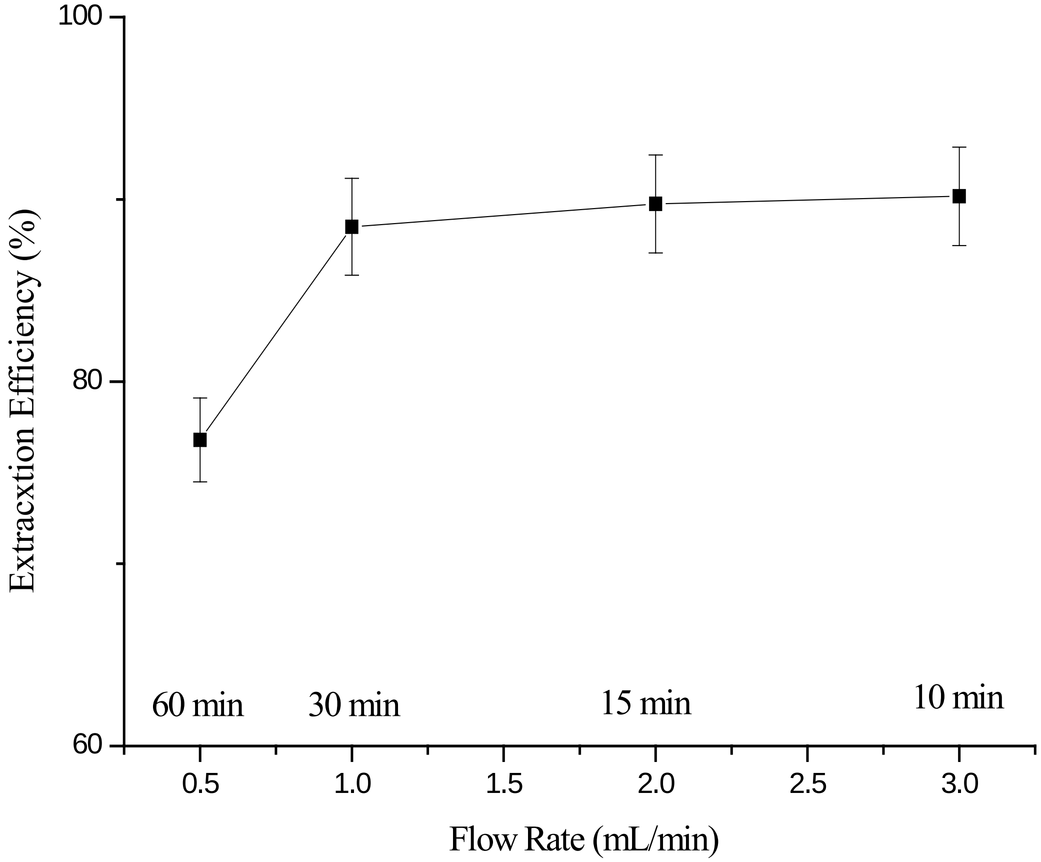


Fig.3.5 b. Variation of uranium extraction efficiency with CO_2 flow rate for constant total volume of CO_2 and TBP

(CO_2 = 30 mL and TBP = 3 mL)

(Error bar is ± 3% of the value)

3.3.2.4 Effect of TBP

Effect of TBP percentage on extraction efficiency was studied for 30 min. dynamic extraction by keeping pressure fixed at 150 atm, temperature at 333 K and CO_2 flow rate at 1 mL min^{-1}. The TBP percentage was varied upto 10%. Uranium extraction proceeds according to eq.3.3. Therefore, as per Le Chatelier rule higher amount of TBP in SC CO_2 should result in increase in U-TBP complex in SC CO_2 phase leading to higher extraction efficiency. As shown in Fig.3.6, the observed trend is in accordance with the predicted trend. The graph between uranium extraction efficiency versus TBP percentage is a straight line having correlation coefficient 0.9829. TBP has a P_c = 20.08 atm and T_c = 817 K. Further enhancement in TBP percentage was avoided in view of the resultant large deviation from the critical parameters of CO_2, which was not desirable. Therefore, the percentage of TBP was fixed at 10% for further studies.

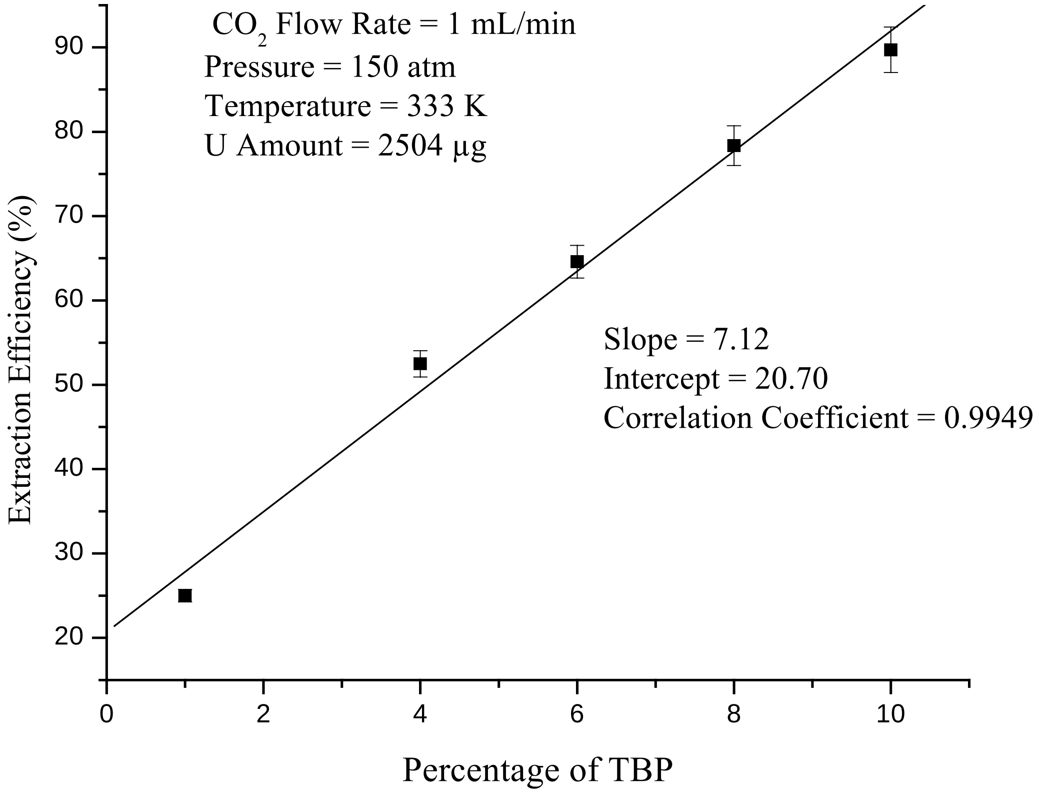


Fig.3.6. Variation of uranium extraction efficiency with TBP percentage

(Error bar is ± 3% of the value)

3.3.2.5 Effect of Molarity of Nitric Acid

The effect of molarity of nitric acid on extraction was investigated under optimized conditions of pressure, temperature, CO_2 flow rate and % of co-solvent. The observed trend is depicted in Fig.3.7. Extraction efficiency increases with molarity of nitric acid upto 7 M and slight decrease is observed afterwards. For solvent extraction, the uranium partition coefficient values for 19% v/v TBP in kerosene (38) were converted into extraction efficiency and plotted w.r.t. molarity of nitric acid for comparison. The effect of molarity of nitric acid on extraction is similar to that observed in solvent extraction. Both the graphs merge at ~6.3 M and afterwards almost same trend of slight decrease was observed.

From eq.3.3 and eq.3.19, as per Le Chatelier rule increase in NO_3^- concentration in aqueous phase should increase the concentration of $UO_2(NO_3)_2 \cdot 2(TBP)$ complex in the supercritical fluid phase, resulting in higher uranium distribution ratio and subsequently higher extraction efficiency. The observed trend is as per predicted trend upto 7 M nitric acid. Under equilibrium condition Meguro *et al.* (32) found that $\log D_U$ linearly increases with $\log [HNO_3]_{aq}$ having slope of 2 which is in complete agreement with eq.3.14. However, their study was carried out in the 0.5-3 M HNO_3 range.

The probable explanation for decrease in extraction efficiency after 7 M nitric acid can be attributed to co-extraction of HNO_3 into supercritical CO_2 phase similar to solvent extraction process. In fact, molecular dynamics study on dissolution of nitric acid in supercritical CO_2 by TBP by Schurhammer *et al.* (39) revealed the presence of strong hydrogen bonding interactions of TBP with HNO_3 . These interactions were found to be stronger than TBP.....H_2O, H_2O……H_2O, HNO_3…..HNO_3 interactions. They found that in absence of TBP no acid was dissolved in supercritical CO_2. According to study the species dissolved in supercritical CO_2 phase were $TBP(HNO_3)x$, $TBP(H_2O)$, $TBP(HNO_3)(H_2O)x$; where x = 1 or 2.

Under equilibrium conditions Meguro *et al.* (31) found that nitric acid gets extracted into supercritical CO_2 phase. They proposed that the extraction proceeds via eq. 3.23

$$H^{+} + NO_3^{-} + TBP_{SF} \rightleftharpoons (HNO_3).(TBP)_{SF} \qquad (3.23)$$

On the basis of above equation they arrived at eq.3.24 relating NO_3^{-} concentration to distribution ratio D_H of HNO_3 and initial concentration of HNO_3 (C_{HNO_3})

$$[NO_3^{-}] = \frac{1}{D_H + 1} C_{HNO_3} \qquad (3.24)$$

$$[TBP]_{SF} = C_{TBP} - \frac{D_H}{D_H + 1} C_{HNO_3} \qquad (3.25)$$

They determined D_H to be 0.044 ± 0.005. The D_H was found to be independent of pressure and temperature. Hence, eq.3.18 can be written as:

$$[NO_3^{-}] = 0.958\ C_{HNO_3} \qquad (3.26)$$

$$[TBP]_{SF} = C_{TBP} - 0.042\ C_{HNO_3} \qquad (3.27)$$

Extraction of nitric acid is a competing reaction for SFE of uranium. As per eq. 3.25 higher the molarity of nitric acid, higher the nitric acid extracted into supercritical CO_2 phase decreasing TBP concentration in supercritical CO_2 phase. As per eq.3.25 uranium distribution ratio will be lowered.

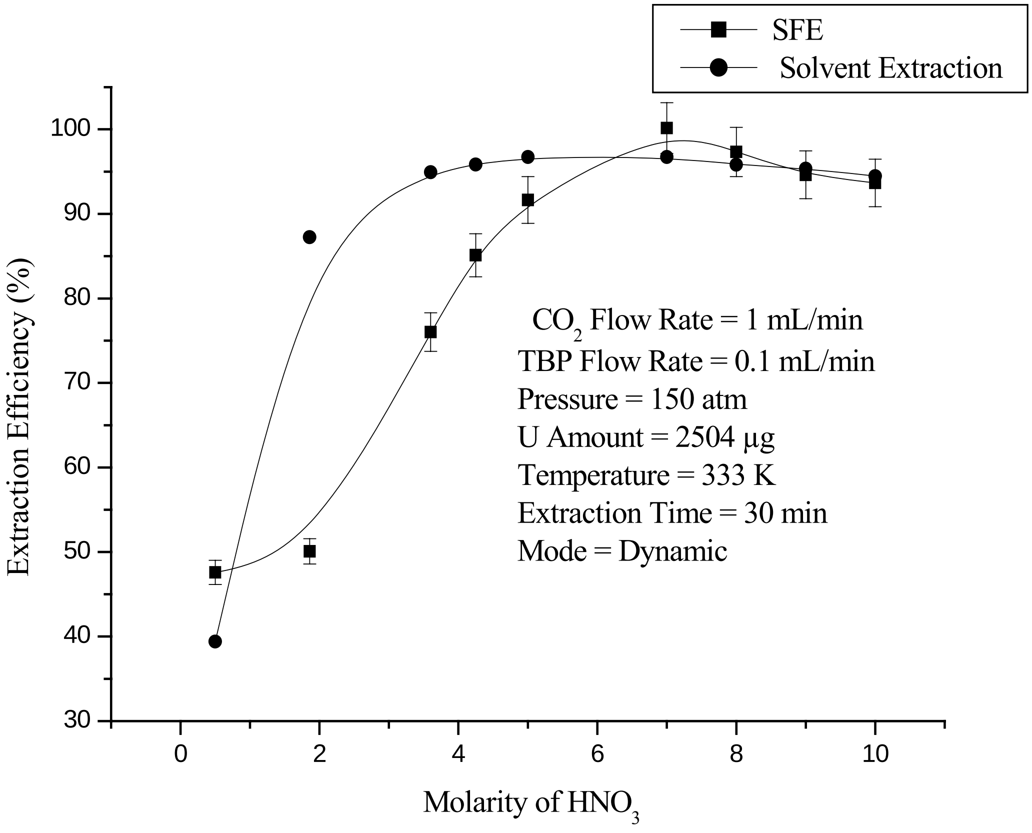


Fig.3.7. Variation of uranium extraction efficiency with molarity of nitric acid

(Error bar is ± 3% of the value)

3.3.2.6 Effect of Extraction Time

The effect of extraction time on extraction efficiency was investigated by carrying SFE of uranium from the acid solution and collecting the extract after every 5 minutes upto 60 minutes. The observed trend is depicted graphically in Fig.3.8, which is similar to the trend observed by Clifford et *al.* (34). Equation, y = 32.235 ln x- 41.582 (y = extraction efficiency, x = extraction time) has been found to fit into the graph having correlation coefficient 0.9943. As is evident from Fig.3.9, upto 40 minutes the amount of uranium extracted in 5 minutes decreases sharply with time. Afterwards the decrease is sluggish indicating that initially the extraction is fast and slows down subsequently. This also indicates that uranium extraction is a diffusion controlled phenomenon. Diffusion rate is controlled by concentration gradient, which decreases with the progress of extraction.

The graph between logarithm of uranium fraction unextracted and initial uranium amount shows linear decrease with extraction time having correlation coefficient of – 0.9948 (Fig.3.10). During the SFE, geometry of the liquid system changes in complex and chaotic way. For sake of simplicity in Clifford's extraction model, an approximation has been assumed that aqueous solution is present in the system as spheres of uniform size immersed in flowing $SC\ CO_2$. The uranium is transported to aqueous-supercritical fluid interface by diffusion process. The uranium amount in the solution at particular time was obtained by solving the diffusion equation (Fick's Second Law) within sphere, subject to boundary condition at its surface determined by partition, obtained from Fick's first law. Concentration gradient is initially high, but abates with time. The observed trend in present study is in accordance with the model's prediction.

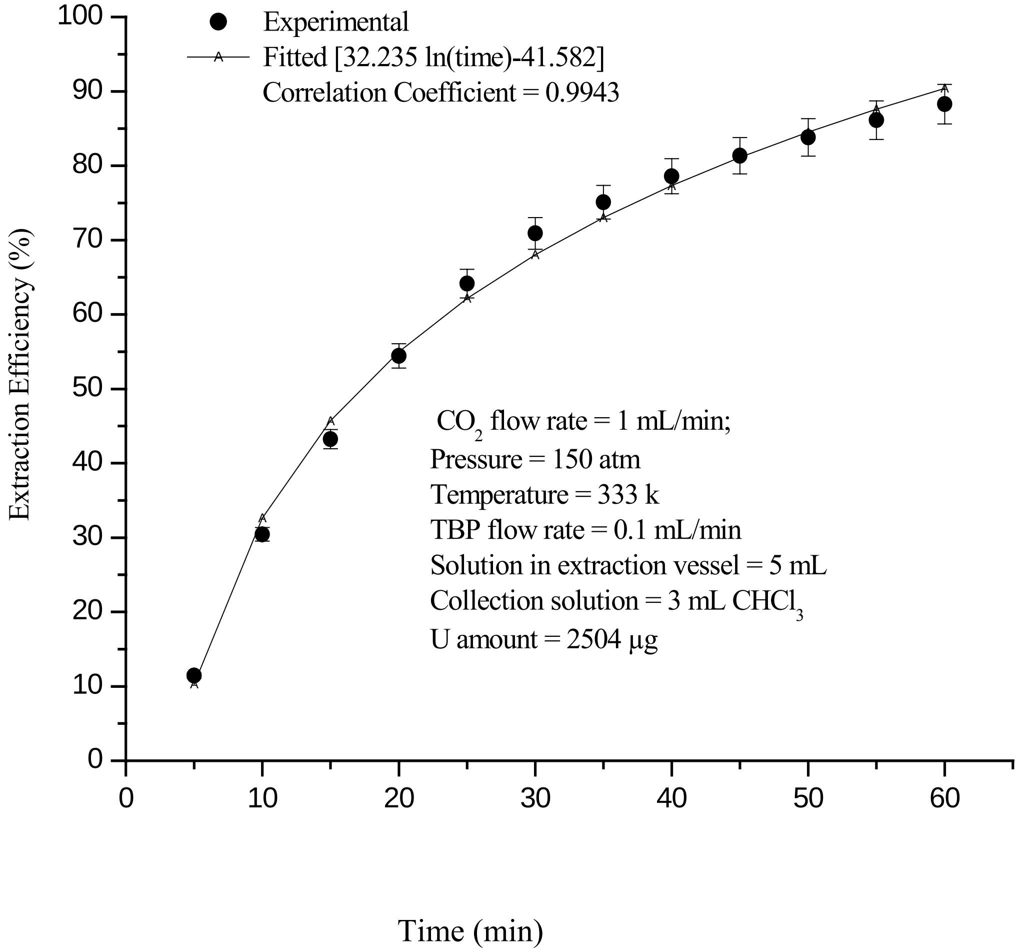


Fig.3.8. Variation of extraction efficiency with time

(Error bar is ± 3% of the value)

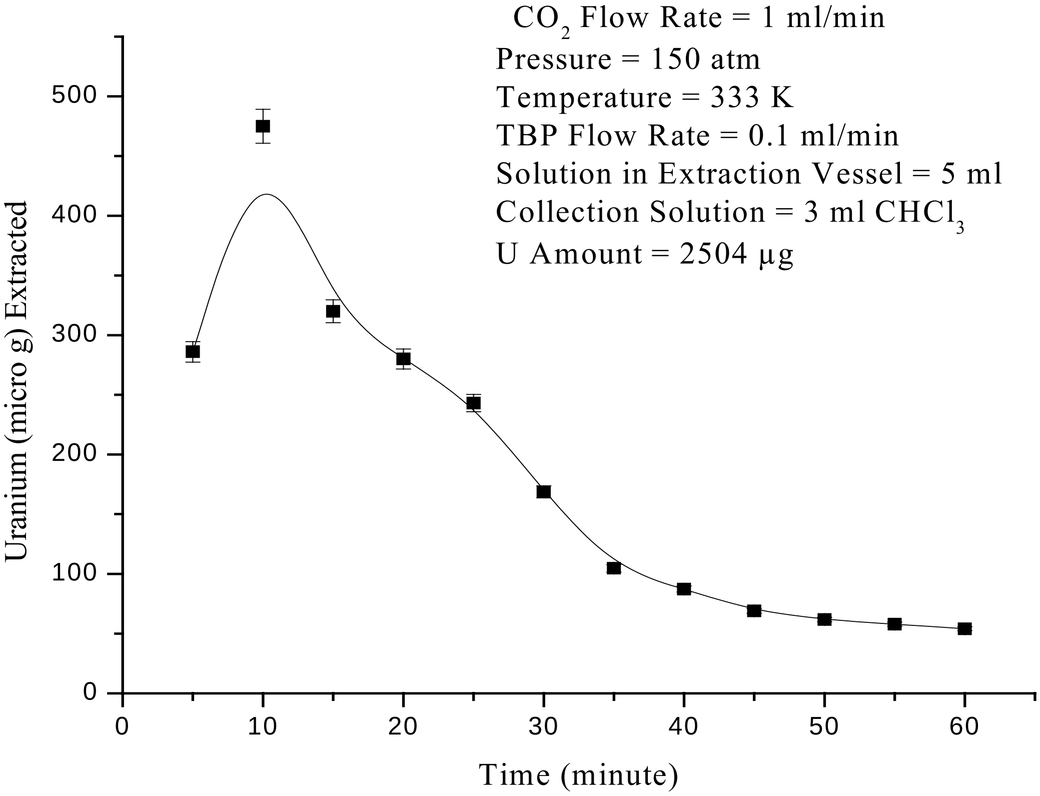


Fig.3.9. Uranium (μg) extracted in 5 minute interval at different time

(Error bar is ± 3% of the value)

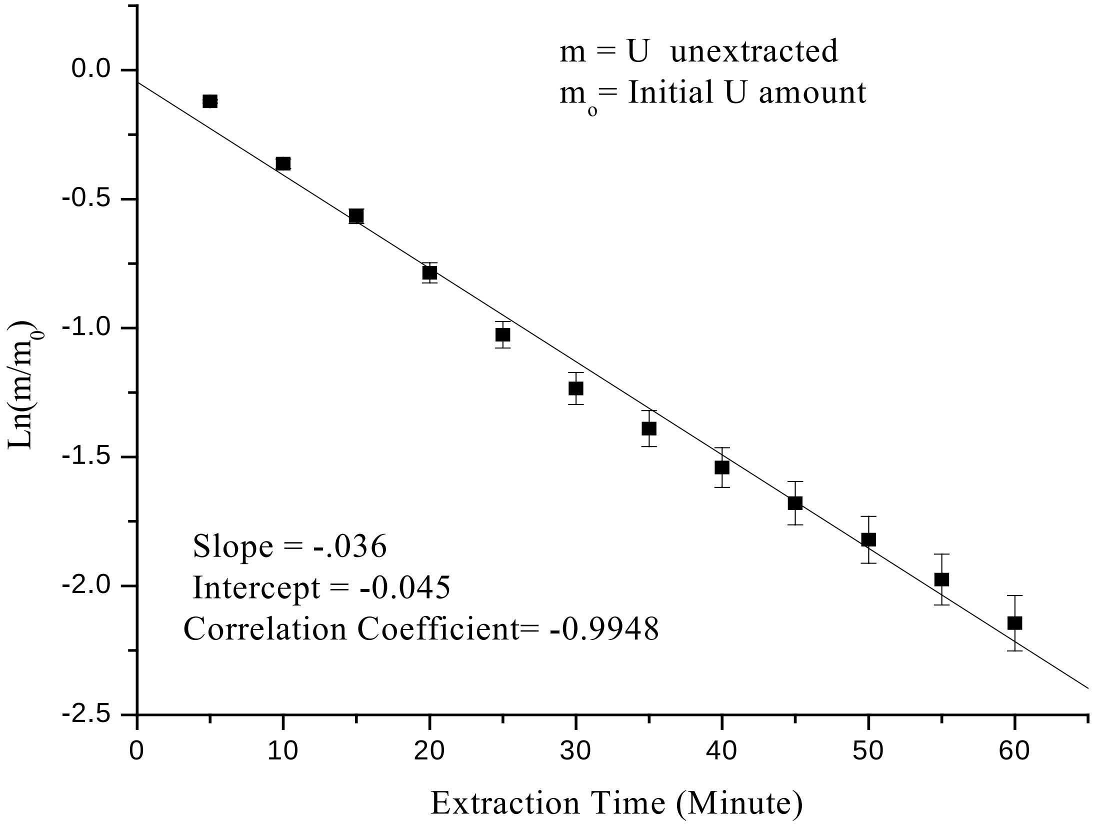


Fig.3.10. Variation of fraction of uranium unextracted with logarithm of extraction time

(Error bar is ± 3% of the value)

3.3.3 COMPARISON STUDY OF MODES OF EXTRACTION

SFE could be carried out in two modes viz. static and dynamic. In static mode, pressure and temperature of the extraction vessel was kept constant for 20 minutes followed by 20 minutes of extraction under same conditions of pressure and temperature. In dynamic mode, extraction was carried out at a particular pressure and temperature for

30 minutes. The uranium amount extracted as well as uranium amount unextracted was determined. To know the mass balance, extracted and unextracted amounts were added up. The results are shown in Table 3.3. In both modes, mass balance of ~100% could be obtained. It is evident from Table 3.3 that 30 minutes dynamic extraction equivalent to 40 minutes in static mode.

Table 3.3

Comparison of static and dynamic mode

Mode	**Uranium extracted (μg)**	**Extraction efficiency**	**Uranium unextracted (μg)**	**Extracted +unextracted (μg)**	**% Mass balance**
Dynamic	2385	95	95	2480	99
Static	2289	92	214	2503	100

(U amount taken = 2504 μg; Molarity of nitric acid = 7 M;
CO_2 flow rate = 1 mL min^{-1}; TBP flow rate = 0.1 mL min^{-1}; Temperature
= 333 K; Pressure = 150 atm; Solution in extraction vessel = 5 mL)

3.3.4 COMPARISION STUDY OF MODES OF COMPLEXATION

For SFE of uranium from nitric acid solution, the metal complexation could be performed via two modes viz. online and in-situ complexation mode. In online complexation mode, CO_2 and TBP were pumped at desired flow rates into extraction vessel containing uranium solution. In the in-situ complexation mode, the TBP was directly added to the extraction vessel containing uranium solution. The system was allowed to withstand the pressure and temperature conditions for 20 minutes followed by

20 minutes collection. With 1 mL of TBP, 63 % uranium extraction efficiency was obtained which further got lowered with 2 mL and 3 mL of TBP (Table 3.4). Hence, for uranium extraction from acidic solution with TBP as co-solvent, the online complexation mode is preferable.

Table 3.4

In-situ SFE of uranium

TBP taken (ml)	**Uranium extracted (µg)**	**Extraction efficiency (%)**
1	312	62
2	285	57
3	277	55

(U amount taken = 500.8 µg; CO_2 flow rate = 1 mL min^{-1}; Pressure = 150atm; Temperature = 333 K; Volume of uranium solution = 5 mL; Molarity = 4 M)

3.3.5 REPRODUCIBILITY AND MASS BALANCE STUDY

Reproducibility study of uranium SFE was performed on a set of 5 samples under identical conditions. SFE was carried out under optimized conditions (Table 3. 2b) in the online complexation mode for 30 minutes of dynamic extraction. The amount of uranium left in the extraction vessel was also determined to study the mass balance. The mass balance calculations yielded results acceptable in the range of experimental error (100 ± 1)% giving full credence to the extraction process. From the reproducibility study (Table 3.5) the uranium extraction efficiency was found to be (98 ± 2)%. Also extraction efficiency could determined from the knowledge of uranium amount left unextracted in the extraction vessel, defined as:

$$\text{Extraction efficiency}=(1-\frac{\text{U amount unextracted}}{\text{U amount taken}})\text{X}100 \qquad (3.28)$$

The extraction efficiency calculated from unextracted uranium was found to be (97 ± 1)%. The extraction efficiencies obtained by both modes i.e. by determining uranium back extracted into aqueous phase and uranium left unextracted in extraction vessel are in excellent agreement.

Table 3.5

Reproducibility and mass balance study

S. No.	U extd.	U unextd.	U extd. + unextd.	%Mass Balance	Extraction Efficiency	
	(μg)	(μg)	(μg)		Direct	Back Ext.
1	2435	79	2513	101	97	98
2	2385	95	2480	99	96	96
3	2519	21	2540	101	99	101
4	2428	73	2501	100	97	97
5	2507	38	2545	102	98	100

(Extraction efficiency: Direct= (97 ±1)%;
Back extraction (98 ± 2)%; Mass balance = (100±1)%)
(U amount taken = 2504 μg; Molarity of nitric acid = 7 M;
CO_2 flow rate = 1 mL min^{-1}; TBP flow rate = 0.1 mL min^{-1};
Pressure = 150 atm; Temperature = 333 K;
Solution in Extraction Vessel = 5 mL; Mode = Dynamic)

3.4 CONCLUSIONS

In the present study effects of various parameters on SFE of uranium from nitric acid employing TBP as co-solvent have been examined. The parameters influencing SFE were identified as pressure, temperature, molarity of acid, CO_2 flow rate, percentage of TBP, mode of complexation (online/in-situ), mode of extraction (dynamic/static) and extraction time. This study of interdependence of various parameters provides us an insight for understanding the SFE process which indeed is very helpful in selecting pressure, temperature and other conditions for higher extraction efficiency. The study has enabled us to understand the extraction mechanism in SFE. The overall extraction process consists of many elementary processes resulting in the formation of $UO_2(NO_3)_2.2TBP$ which is carried into SC CO_2 phase. Extraction efficiency is affected by distribution ratio of uranium ('D_U'), density of SC CO_2, diffusion rate and number of CO_2 molecules solvating TBP/U-TBP complex.

In the 150-300 atm pressure range, variation in extraction efficiency resembled to that of uranium distribution ratio variation under equilibrium conditions. Extraction efficiency was found to decrease gradually. The decrease in extraction efficiency was attributed to the term $(k_{U\text{-}TBP} - 2\,k_{TBP})$ which has a negative value. $(k_{U\text{-}TBP} - 2\,k_{TBP})$ is the slope of plot of '$\log D_U$' versus '$\log \rho$'. Below 150 atm mismatch between uranium distribution ratio under equilibrium conditions and extraction efficiency was observed. Extraction efficiency variation resembled with SC CO_2 density variation with pressure. The behavior in this region could be attributed to non-equilibrium nature persisting in the extraction system. In the non-equilibrium region, SC CO_2 density increased with pressure which favored enhancement in solubility as well as extraction kinetics. The non-equilibrium process eventually progressed towards attaining equilibrium at 150 atm.

Temperature increase was found to affect the efficiency in two ways: (i) enhancement in volatility of solute (ii) decreasing SC CO_2 density. Upto 333 K, extraction efficiency increased linearly indicating the volatility increases to higher extent so that it not only compensates the solubility decrease due to SC CO_2 density decrease but results in overall increase in extraction efficiency. Steep fall in 333 K-353 K range most probably indicate a saturation in volatility, so that SC CO_2 density decrease governs the extraction process. Steep fall was attributed to the formation of large size cluster formation at densities approaching near critical point densities. Molarity of nitric acid has been found to influence efficiency almost in similar fashion as in case of solvent extraction. The extraction efficiency increased upto 7 M nitric acid followed by slight decrease. This behavior was assigned to the fact that increase in molarity leads to the higher formation of U-TBP complex as well as higher co-extraction of HNO_3 via formation of HNO_3.TBP complex. CO_2 flow rate of 1 mL min^{-1} was found to be sufficient, no significant gain in extraction efficiency was observed at higher flow rates. Extraction efficiency was found to linearly increase with percentage of TBP.

The optimum parameters were 150 atm pressure, 333 K temperature, 1mL min^{-1} CO_2 flow rate, 0.1 mL min^{-1} TBP flow rate (10 % TBP), 7 M nitric acid and 30 minute dynamic extraction time. Under optimized conditions in online complexation mode, nearly complete, (98 ± 2)% uranium extraction efficiency was achievable. A mass balance of (100 ±1)% was observed giving full credence to the extraction process. 30 minutes dynamic extraction mode was found equivalent to 40 minutes static mode. Online complexation mode was more efficient than in-situ mode.

CHAPTER 4

SUPERCRITICAL FLUID EXTRACTION OF URANIUM FROM NITRIC ACID MEDIUM EMPLOYING CROWN ETHERS

4.1 INTRODUCTION

Natural or slightly enriched uranium in different forms is employed as fuel in nuclear reactors. Uranium extraction is of interest to the chemists studying hydrometallurgy. Also, alternative sources like seawater need to be explored for selective extraction of uranium. In nuclear industry, uranium extraction is of utmost importance.
Crown ethers are a versatile class of ion-specific extractants. These cyclic polyethers have gained importance as cation binding agents due to their size selective nature (40-43). Solvent extraction of actinides employing crown ethers has been studied (44-54) In many cases, the structure of uranium-crown ether complexes has also been enunciated (55-57). There are few reports in literature on solubility of some crown ethers in SC CO_2 (58, 59), whereas study on SFE of actinides with crown ethers is very limited. While evaluating various complexing agents for the SFE of uranium, only one crown ether appeared to have been used (60, 61). Thorough and systematic study of relevant parameters for uranium SFE employing crown ethers has not been carried out so far to the best of our knowledge. Hence, present study was taken up. As nitric acid is employed for dissolution of nuclear fuel, we have also selected nitric acid medium in the present study.

Uranium extraction employing crown ethers involves ion-pair formation. In nitric acid medium nitrate ion serves as counter ion. However, solubility of fluorinated compounds in SC CO_2 is known to be very high due to special interaction between electron rich C-F bonds with relatively electron poor CO_2 molecules (62). Hence, one good strategy for supercritical fluid extraction could be the use of counter ion consisting of several C-F bonds. In literature, use of pentadecafluoro-n-octanic acid (HPFOA) for counter ion has been reported for SFE of strontium (63). In view of this, we have selected HPFOA for counter ion. Extraction efficiency is influenced by many factors. Effect of pressure, temperature, molarity of nitric acid, uranium amount, uranium: crown mole ratio and crown: HPFOA mole ratio was studied. Online and in-situ modes of complexation were studied. Effect of extraction time was studied. Effect of various solvents for crown ether and HPFOA was also investigated.

4.2 METHODS AND MATERIALS

4.2.1 CHEMICAL REAGENTS

The crown ethers used in the study were procured from Aldrich (Germany) having purity >98% and were used without further purification. CO_2 gas employed for preparing supercritical fluid was of 99.9% purity. Uranium standard solution was prepared by dissolving nuclear grade U_3O_8 powder in 4 M nitric acid. Aldrich make (Germany) HPFOA (purity 96%) was used for the generation of counter ion. Merck make (Germany) Arsenazo III was used for color development in the spectrophotometric determination of uranium. Merck grade (Germany) sulphamic acid of 99% purity was used. A.R. grade (Sisco Research Laboratories, Mumbai, India) nitric acid was employed for uranium dissolution. A.R. grade (Sisco Research Laboratories, Mumbai, India) methanol was used for the dissolution of crown ethers and HPFOA.

4.2.2 SUPERCRITICAL FLUID EXTRACTION PROCEDURE

Uranium solution in acidic medium, of known concentration was taken in the extraction vessel and SFE was performed as described in section 2.2. The crown ether and HPFOA solutions were prepared in methanol. The uranium amount left unextracted was determined spectrophotometrically (section 2.4). The extraction efficiency was calculated from the difference in uranium amount taken in the extraction vessel and uranium amount left unextracted after extraction.

4.3 RESULTS AND DISCUSSION

4.3.1 GENERAL ASPECTS OF SFE OF URANIUM EMPLOYING CROWN ETHERS

Basic extraction process: Distribution equations similar to those of Meguro *et al.* (33) could be derived for uranium extraction into SC CO_2 employing crown ethers. The single liquid phase of methanol containing crown ether and HPFOA in the extraction vessel contained UO_2^{2+}, NO_3^-, $PFOA^-$ whereas crown ether, metal-crown ether complex were distributed between the two phases, liquid and SC CO_2. The probable extraction scheme is depicted in Fig.4.1. As is evident from Fig.2 the process of uranium extraction into supercritical CO_2 involves many elementary equilibria processes. Overall uranium extraction process could be expressed by following equations.

$$UO_2{}^{2+}{}_{aq} + 2\,NO_3^-{}_{aq} + xCE_{SF} \rightleftarrows \{UO_2(CE)x(NO_3)_2\}_{SF} \qquad (4.1\ a)$$

$$UO_2{}^{2+}{}_{aq} + 2PFOA^-{}_{aq} + xCE_{SF} \rightleftarrows \{UO_2(CE)x(PFOA)_2\}_{SF} \qquad (4.1\ b)$$

Where x is the number of crown ether (CE) units present in the uranium-crown ether complex (U-CE). The extraction constants for eq.(1.a) and eq.(1.b) are given as follows:

$$K_{ex(NO_3)} = \frac{[UO_2(CE)_x(NO_3)_2]_{SF}}{[UO_2^{2+}]_{aq}[NO_3^-]^2_{aq}[CE]^x_{SF}} \qquad (4.2\ a)$$

$$K_{ex(PFOA)} = \frac{[UO_2(CE)_x(PFOA)_2]_{SF}}{[UO_2^{2+}]_{aq}[PFOA^-]^2_{aq}[CE]^x_{SF}} \qquad (4.2\ b)$$

The phase distribution constants of crown ether $K_{D,CE}$, U-CE complex with nitrate as counter ion $K_{D,U\text{-}CE\text{-}NO3}$ and $PFOA^-$ as counter ion $K_{D,U\text{-}CE\text{-}PFOA}$ are defined as:

$$K_{D,CE} = \frac{[CE]_{SF}}{[CE]_{aq}} \tag{4.3 a}$$

$$K_{D,U\text{-}CE\text{-}NO_3} = \frac{[UO_2(CE)_x\ (NO_3)_2]_{SF}}{[UO_2(CE)_x\ (NO_3)_2]_{aq}} \tag{4.3 b}$$

$$K_{D,U\text{-}CE\text{-}PFOA} = \frac{[UO_2(CE)_x\ (PFOA)_2]_{SF}}{[UO_2(CE)_x\ (PFOA)_2]_{aq}} \tag{4.3 c}$$

Formation constant for U-CE-NO$_3$ and U-CE-PFOA complexes are defined as

$$K_{f,U\text{-}CE\text{-}NO_3} = \frac{[UO_2(CE)_x(NO_3)_2]_{aq}}{[UO_2^{2+}]_{aq}\,[NO_3^-]^2_{aq}\,[CE]^x_{aq}} \tag{4.4 a}$$

$$K_{f,U\text{-}CE\text{-}PFOA} = \frac{[UO_2(CE)_x(PFOA)_2]_{aq}}{[UO_2^{2+}]_{aq}\,[PFOA^-]^2_{aq}\,[CE]^x_{aq}} \tag{4.4 b}$$

Uranium distribution ratio between aqueous and supercritical phase is given by

$$D_U = \frac{[UO_2(CE)_x(NO_3)_2]_{SF} + [UO_2(CE)_x(PFOA)_2]_{SF}}{[UO_2^{2+}]_{aq}} \tag{4.5}$$

Extraction constant is related to phase distribution constant and formation constant as follows:

$$K_{ex(NO_3)} = \frac{K_{D,U\text{-}CE\text{-}NO3}\ K_{f,U\text{-}CE\text{-}NO3}}{(K_{D.CE})^X} \tag{4.6 a}$$

$$K_{ex(PFOA)} = \frac{K_{D,U\text{-}CE\text{-}PFOA}\ K_{f,U\text{-}CE\text{-}PFOA}}{(K_{D.CE})^X} \tag{4.6 b}$$

From eq.(4.4 a), (4.4 b), (4.5) and eq.(4.3 a), (4.3 b), D_U could be expressed as

$$D_U = \frac{[UO_2(CE)_x(NO_3)_2]_{SF}}{[UO_2^{2+}]_{aq}} + \frac{[UO_2(CE)_x(PFOA)_2]_{SF}}{[UO_2^{2+}]_{aq}} \tag{4.7}$$

Which gives

$$D_u = \frac{[\mathrm{CE}]_{\mathrm{SF}}^{x}}{(K_{\mathrm{D,CE}})^{X}} \{ \mathrm{K}_{\mathrm{D,U\text{-}CE\text{-}NO3}} \mathrm{K}_{\mathrm{f,U\text{-}CE\text{-}NO3}} [\mathrm{NO_3^-}]^2 + \mathrm{K}_{\mathrm{D,U\text{-}CE\text{-}PFOA}} \mathrm{K}_{\mathrm{f,U\text{-}CE\text{-}PFOA}} [\mathrm{PFOA^-}]^2 \} \tag{4.8}$$

Extraction efficiency: High solubility of uranium-crown ether complex in SC CO_2 is desirable for achieving high extraction efficiency. The solubility of crown ethers in SC CO_2 is very low e.g. the solubility of dicyclohexano-18-crown-6 is around 10^{-2} M at 100 atm and 60°C (63). Shamsipur *et al.* (58) have observed decrease in solubility of crown ethers with increasing ring size. On the other hand, solubility of fluorinated compounds is known to be very high in SC CO_2 in comparison to their non-fluorinated counter parts. Yazdi *et al.* (62) attributed this enhancement in solubility to special interaction between electron rich C-F bonds with relatively electron poor CO_2 molecules. Hence, one good strategy for extraction could be the use of counter ions consisting of several C-F bonds. We have selected HPFOA for production of counter ions, which was also employed by Wai *et al.* (63) for SFE of strontium. Because of the inductive effect from strong electron withdrawing fluorine atoms, the pKa value of HPFOA is 1. Hence, it is expected that HPFOA is present in ionic form only resulting in facile supply of $PFOA^-$ as counter ion. Drawing comparison with solvent extraction, bulky organophilic but water soluble counter ions like picrate (44, 51) have been employed for uranium extraction with crown ethers.

Solvent extraction and SFE: SFE can be compared to solvent extraction where the organic phase has been replaced by SC CO_2 and the solute gets distributed between the aqueous and SC CO_2 phase. In many cases extraction efficiencies for SFE are comparable or even higher than that with solvent extraction. This is because in SFE, supercritical fluid phase is continuously renewed (as discussed in section 3.1) and it can be assumed that instantaneous equilibrium is being established between liquid-supercritical fluid interface. Owing to the low viscosities and high diffusivities for SCFs, attainment of instantaneous equilibrium at liquid/solid and SCF interface has also been assumed in other studies (64, 65). Hence in SFE, in addition to distribution ratio, extraction efficiency is also influenced by the transport kinetics of the uranium-crown ether complex from liquid phase into SC CO_2.

Another major difference between SFE and solvent extraction is that variations in SCF density are very large, whereas in solvent extraction solvent density variations are insignificant. Solvating power of SC CO_2 is related to density. Chrastil (26) has arrived at a simple empirical correlation (eq.1.19), which relates the solubility (S) of an organic compound to the density (ρ) of supercritical fluid.

The phase distribution constant, 'K_D' of a substance (extractant, extracted complex) could be expressed in terms of its solubility in SC CO_2 and aqueous phase by eq.4.4.

$$K_D = \frac{S_{SF}}{S_{aq}} \tag{4.9}$$

On taking log of eq. 4.9 and substituting the value of 'log S' from eq. 1.19 we get:

$$\log K_D = k \log \rho + C - \log S_{aq} \tag{4.10}$$

According to eq.4.8 and eq.4.10 uranium distribution ratio is related to SC CO_2 density and solute volatility. Hence, factors influencing SC CO_2 density and solute volatility should affect the uranium distribution ratio.

In literature very few reports exist on the structure of uranium/actinides crown ether complexes. Eller *et al.* (55) have studied the structure of uranyl nitrate complex with 18-Crown-6 by X-Ray and found that uranyl group is not located inside the cavity of the crown. Rather, the structure consists of uranyl nitrate tetrahydrate unit and crown ether connected by hydrogen bonding through intermediate water molecules. Synthesis and structure elucidation of various uranyl-crown ether compounds was carried out by Roger *et al.* (56). R.M. Izatt *et al.* (52, 53) have reviewed the thermodynamic and kinetic data for macrocyclic interaction (including crown ethers) with cations and anions. P. Fux *et al.* (57) have studied the kinetics and mechanism of complex formation for the solvent extraction of uranium with crown ethers. Structure of the extracted species in solvent extraction of uranium with crown ethers has been suggested (44). In SFE, the role of SC CO_2 is similar to that of organic solvent in solvent extraction and thus may not decide the nature of the species getting extracted. It may be mentioned that even in solvent extraction the nature of species extracted is independent of organic solvent as well as the counter ion (44, 47, 49, 57). The uranium-crown ether complex species formed in SFE process may therefore be same as those formed in solvent extraction and the stoichiometry of the extracted complex should correspond to $[UO_2(\text{crown ether})_n]^{2+}.[PFOA^-]_2$.

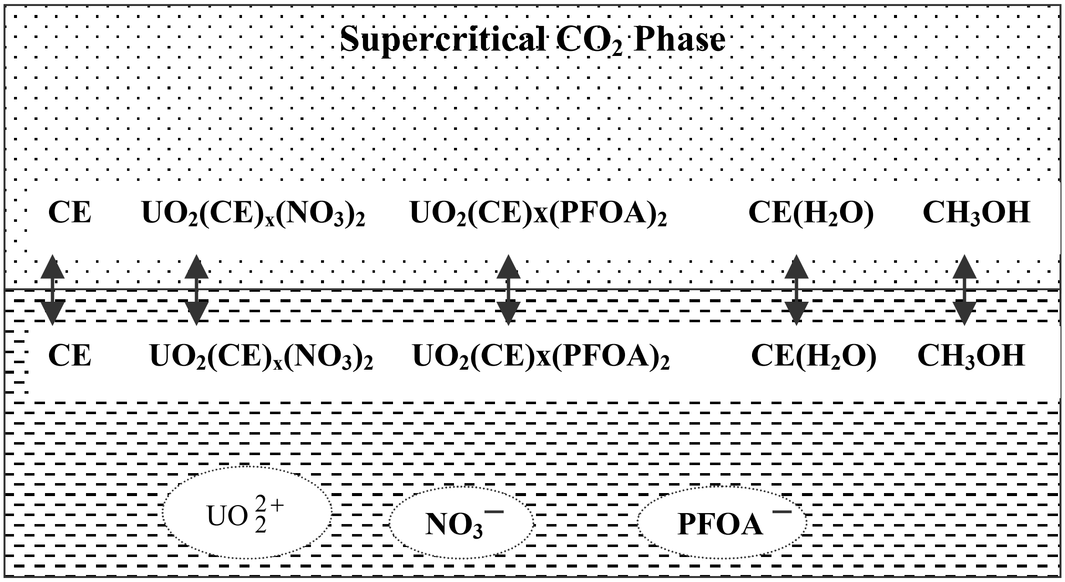


Fig.4.1. Extraction scheme for UO_2^{2+} from nitric acid medium into supercritical CO_2 employing crown ethers

4.3.2 EFFECT OF VARIOUS PARAMETERS

The effect of variation of a factor on extraction efficiency was studied by varying particular factor keeping all other factors fixed and determining corresponding uranium extraction efficiencies (27). The experimental conditions are listed in Table 4.1.

4.3.2.1 Effect of Pressure and Temperature

The experimental conditions for the study of effect of variation in pressure and temperature on extraction efficiency are listed in Table 4.1. As mentioned earlier extraction efficiency is combined effect of uranium distribution ratio and transport characteristics. For a given extraction time period, keeping constant flow rate of SC CO_2, the variation in extraction efficiency should be as per variation in uranium distribution (eq.4.3). As per eq.4.3, uranium distribution ratio is a function of distribution constant K_D, which in turn is function of SC CO_2 density (eq.4.10). The variation in extraction efficiency with pressure at temperatures 313-353 K is depicted graphically in Fig.4.2.

Table 4.1

Experimental conditions for studying the effect of various factors influencing uranium SFE

Crown ether	Ditertiarybutyldibenzo-18-crown-6	**Crown ether volume**	1 mL
Uranium conc.	64.9 µg mL^{-1}	**HPFOA volume**	1 mL
Nitric acid molarity	0.2 M	**Methanol volume**	0.5 mL
Uranium volume	1 mL	**CO_2 flow rate**	1 mL min^{-1}
Nitric acid Volume	1.5 mL	**Static time**	20 min.
U:Crown: PFOA	1:10:10	**Extraction time**	20 min.

The observed trend is complicated due to participation of many species in the extraction process. Eq.(4.8) for distribution ratio contains many pressure and temperature dependent terms, e.g. phase distribution constant of crown ether, uranium crown ether complex with nitrate as counter ion, uranium crown ether complex with PFOA$^-$ as counter ion, solubility of crown ether etc. The distribution ratio is thus combined effect of all these terms. A qualitative interpretation of the observed trend is discussed below.

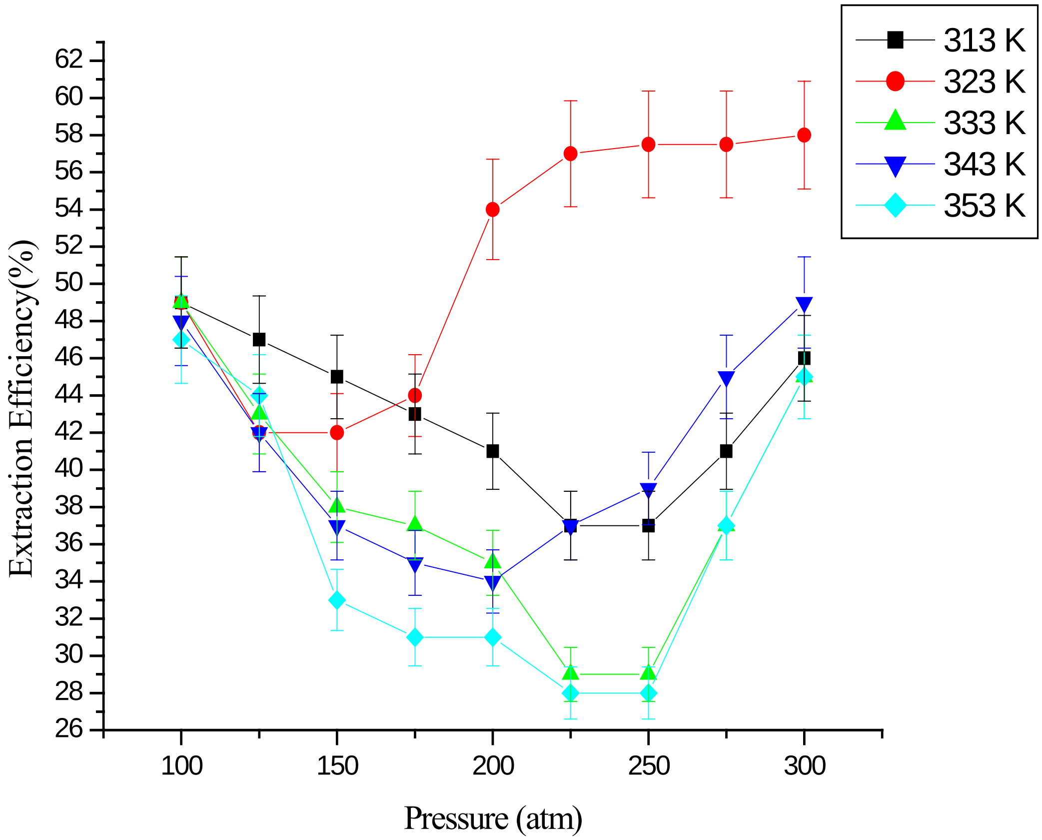


Fig.4.2. Variation of uranium extraction efficiency with pressure at various temperatures

(Error bars indicates uncertainty in the measurement;

standard deviation is 5 % of the value)

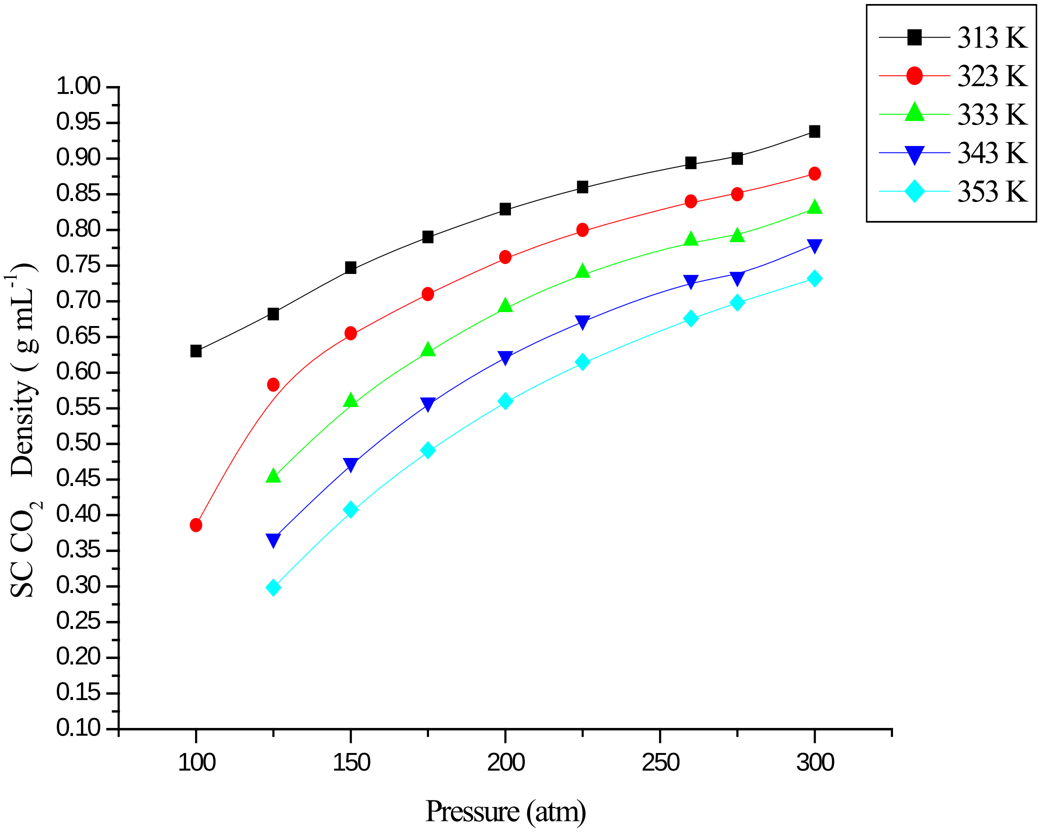


Fig.4.3. Variation of SC CO_2 density with pressure at various temperatures

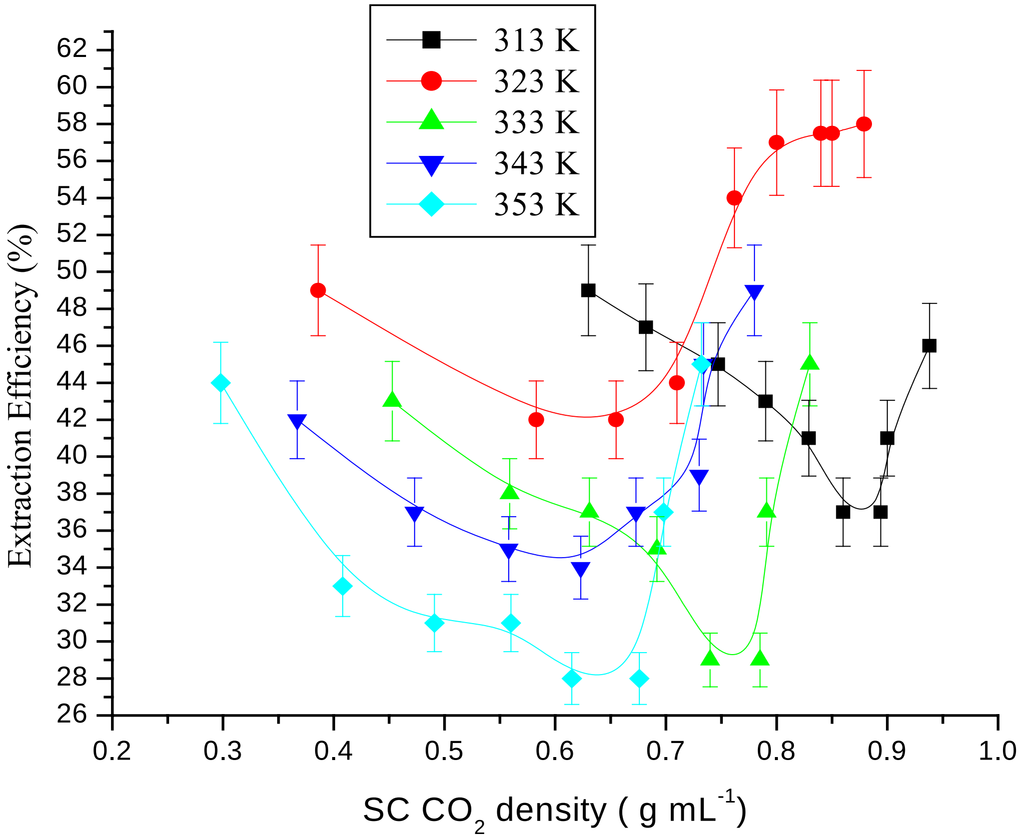


Fig.4.4. Variation of uranium extraction efficiency with SC CO$_2$ density at various temperatures

(Error bars indicates uncertainty in the measurement;
standard deviation is 5 % of the value)

Variation in SC CO$_2$ density with pressure at various temperatures is shown in Fig.4.3. SC CO$_2$ density was calculated from Peng-Robinson equation of state (15). Due to significant contribution of density variation, the graph in Fig.4.2 was transformed to extraction efficiency and SC CO$_2$ density graph (Fig.4.4). For all isotherms, the observed trend consisted of two parts, in first part extraction efficiency decreased with increasing pressure/density attained minima and subsequently increased afterwards in second part. According to eq.4.8 and eq.4.10 the efficiency should increase with increasing density. However, the observed trend matches with the expected trend in second part only. Contradictory behavior in the first part could be explained on the basis of large size cluster formation near critical point. Near critical point some properties of solutes, such as partial molar volume $\bar{V}_2^{\infty}$ and enthalpy $\bar{h}_2^{\infty}$ at infinite dilution, diverge to infinity due to the formation of large size clusters (15, 37).

From thermodynamic consideration, solvation process involves a negative enthalpy (ΔH) and a negative entropy (ΔS) due to clustering of solvent molecules. Since free energy of solvation, 'ΔG' is equal to 'ΔH-TΔS'; enthalpy factor leads to solubility enhancement while the entropy factor leads to solubility decrease. For large size clusters, the entropy losses are very high. At higher temperature, ΔG becomes less negative due to high negative value of TΔS leading to lower solubility.

As evident from Fig.4.4, in the first part, at a particular density, the observed trend in extraction efficiency was 313 K>323 K > 333 K >343 K >353 K. This could be explained on the basis of the fact that solvation is an exothermic process leading to ordering in the system. Therefore, with temperature enhancement both the enthalpy and entropy changes are expected to become less negative. Also the term 'TΔS' increases with increase in temperature. These factors result in a decrease in the free energy of solvation thereby lowering of extraction efficiency.

The critical density of SC CO_2 is 0 .47 g mL^{-1} (15). However, for all isotherms, the minima are far away from critical density. This could be attributed to the increase in critical parameters of the system due to addition of high molecular weight species such as crown ether and uranium-crown ether complex. Extraction efficiency, as discussed earlier, is influenced not only by density but also the volatility (which is again a function of temperature). If the latter influence could be corrected, the plots of extraction efficiency as a function of density might have fixed minima at all the temperatures studied.

The maximum efficiency was observed at 323 K. It is evident from Fig.4.2, for 323 K isotherm, there was no significant gain in extraction efficiency after 200 atm. Hence, pressure of 200 atm and temperature of 323 K were optimized.

4.3.2.2. Effect of variation in Uranium: Crown Mole Ratio

The variation in extraction efficiency with uranium: crown mole ratio was carried out at optimized pressure and temperature conditions (200 atm, 323 K), other experimental conditions were same as in Table 4.1 (except U: crown: HPFOA mole ratio). The solution in the extraction vessel contained a fixed uranium: HPFOA mole ratio of 1:100 and varying uranium: crown mole ratio. The variation in extraction efficiency with uranium: crown mole ratio is shown in Fig.4.5. The efficiency initially increased followed by decrease after 1:10 mole ratio. The eq.4.2.b could be rearranged as:

$$[UO_2(CE)_x(PFOA)_2]_{SF} = K_{ex(PFOA)}[UO_2^{2+}]_{aq}[PFOA^-]^2_{aq}[CE_x]^x_{SF} \quad (4.11)$$

Also, from eq.(4.3 a), $[CE]_{SF} = K_{D,CE}\,[CE]_{aq}$ (4.12)

Again, since uranium HPFOA amounts are fixed eq.4.11 could be written as

$$[UO_2(CE)_x(PFOA)_2]_{SF} = K_1[CE]^x_{aq} \quad (4.13)$$

where $K_1 = K_{ex(PFOA)}[UO_2^{2+}]_{aq}[PFOA^-]^2 K^x_{D,CE}$

As per eq.4.13, with the increase in crown amount taken, the uranium extraction efficiency would increase. The decrease with mole ratio higher than 1:10 indicates the possibility of co-extraction of some other species. Uranium is known to form 1:1 as well as 1:2 complexes with 18 member ring crown ethers (52). In present study also, the extent of formation of 1:2 complex would increase with high uranium: crown mole ratio as per Le Chatelier rule. The 1:2 complex might have lower solubility in SC CO_2 than 1:1 complex due to higher molecular weight leading to lower extraction efficiency.

Some extraction (~30%) was observed even without crown ether. Shamsipur *et al.* (60) have observed large increase in solubility of uranyl nitrate with addition of small amount of methanol, which was assigned to the formation of solvated ion pair in SC CO_2. Shamsipur *et al.* (60) observed ~ 25 % uranium extraction with methanol alone. It is most likely that some extraction might be due to ion pair formation of uranyl ion with $PFOA^-$ also.

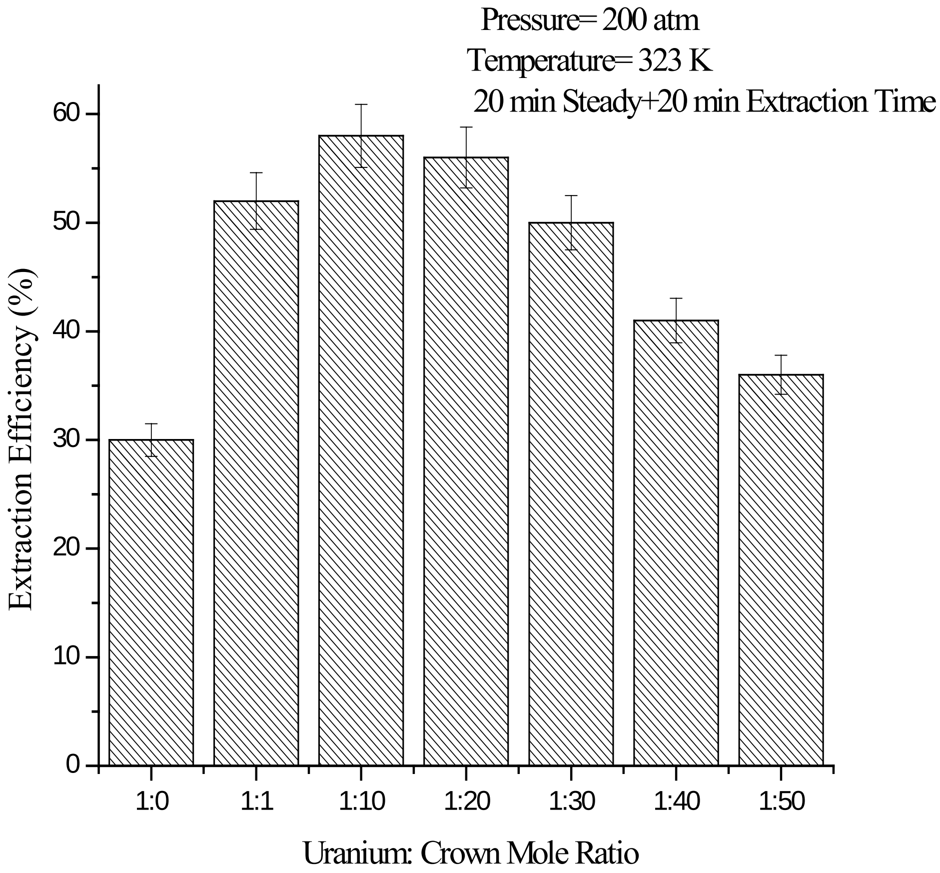


Fig.4.5. Variation of extraction efficiency with uranium: crown mole ratio

(Error bars indicate uncertainty in the measurement;
standard deviation is 5 % of the value)

4.3.2.3. Effect of Crown: HPFOA Mole Ratio

The variation in extraction efficiency with crown: HPFOA mole ratio was carried out at optimized pressure and temperature conditions (200 atm, 323 K), other experimental conditions were same as in Table 4.1 (except U: crown mole ratio). In the extraction vessel solution was taken which contained fixed uranium: crown mole ratio of 1:10 but varying crown: HPFOA ratio. The variation in extraction efficiency with crown: HPFOA mole ratio is shown in Fig.4.7. Initially extraction efficiency increased with increasing mole ratio.

The eq.4.2.b could be rearranged as eq.4.11. Since in the experiment uranium and crown ether amount are fixed, the eq.4.12 could be modified to

$$[UO_2(CE)_X(PFOA)_2]_{SF} = K_2[PFOA^-]^2_{aq} \qquad (4.14)$$

where $K_2 = K_{ex(PFOA)}[UO_2^{2+}]_{aq}[CE_X]^x_{SF}$

Because of the inductive effect from strong electron withdrawing fluorine atoms, the pKa value of HFOA is 1. Hence, it is expected that HPFOA is present in ionic form only. From eq.4.14 it is evident that higher concentration of HPFOA would lead to higher extraction efficiency. After the mole ratio of 1:10, efficiency was found to decrease which might be due to the competitive extraction of H_3O^+ (due to dissociation of HPFOA) with crown ether. Complexation of hydronium ion with crown ethers has been reported in solvent extraction (46). The crown: HPFOA ratio was selected as 1:10 for further study.

As evident from graph, even without HPFOA the extraction efficiency was ~ 30% which corresponds to uranium-crown ether complex with nitrate as counter ion. Efficiency enhancement with addition of HPFOA shows the favorable effect of fluorinated counter ion.

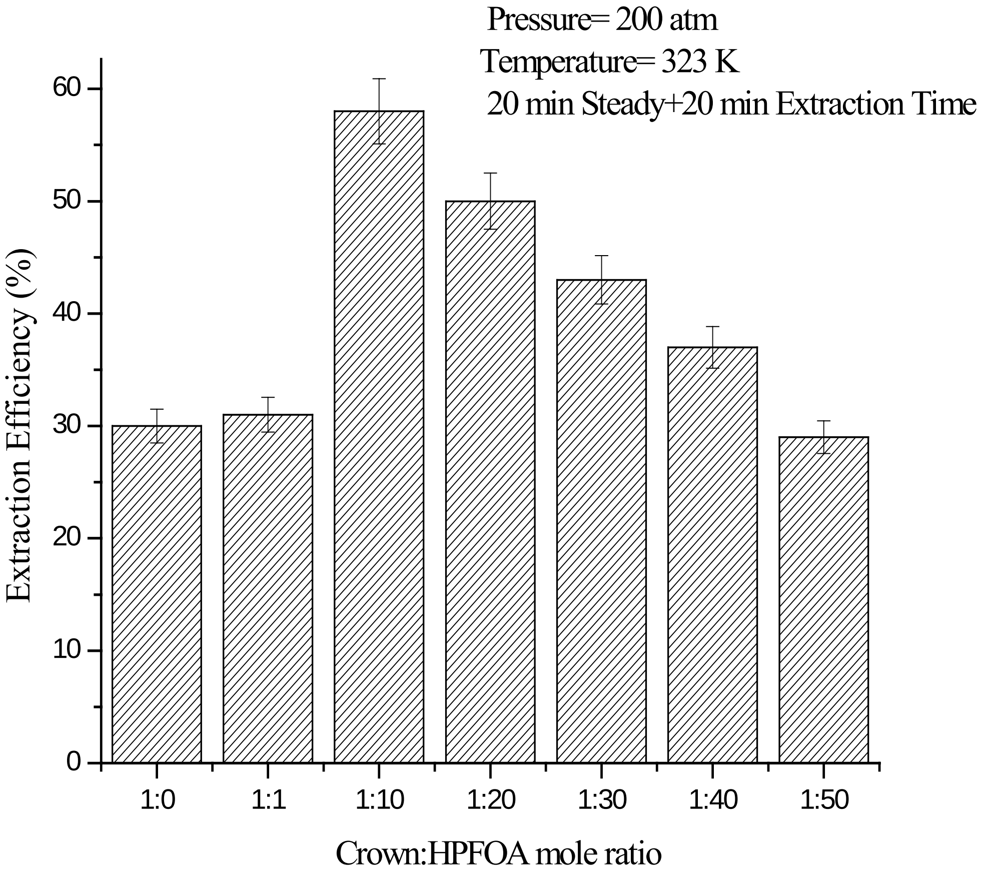


Fig.4.6. Variation of extraction efficiency with crown: HPFOA mole ratio

(Error bars indicate uncertainty in the measurement;
standard deviation is 5 % of the value)

4.3.2.4 Effect of Time Period

Under optimized conditions of pressure and temperature (200 atm, 323 K) and experimental conditions as per Table 4.1, the study on extraction time period was performed. After achieving the desired pressure and temperature conditions, the system was allowed to withstand the desired pressure and temperature conditions for certain period referred to as steady time period, followed by extraction at same pressure and temperature by flowing SC CO_2 for certain time period referred to as extraction time period. Extraction efficiency was found to vary with steady time as well as dynamic time (Fig.4.7). In one study, dynamic time was fixed at 20 minutes while steady time was varied upto 40 minutes. As shown in Fig.4.7, extraction efficiency initially increased with increasing steady time and saturated afterwards. In another study, steady time period was fixed at 20 minutes and dynamic time was varied upto 40 minutes. Extraction efficiency was found to increase upto 20 minutes and got saturated afterwards. Hence, combination of 20 minutes steady time and 20 minutes dynamic time was found to be optimum.

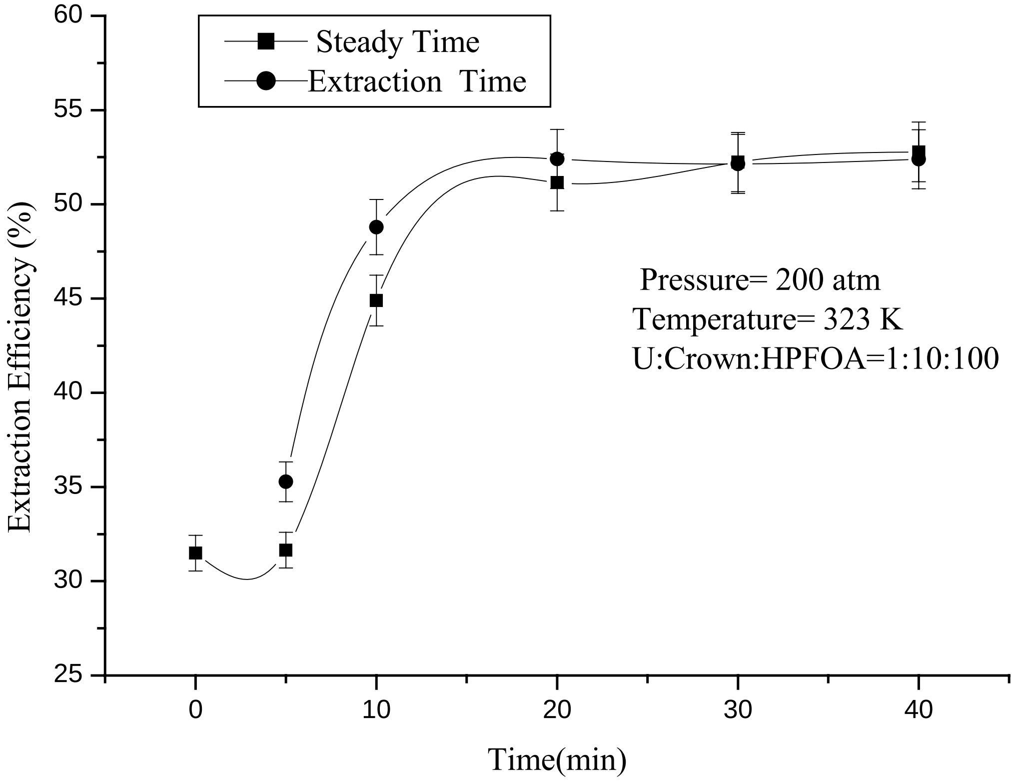


Fig.4.7. Variation of extraction efficiency with time

(Error bars indicate uncertainty in the measurement; standard deviation is 5 % of the value)

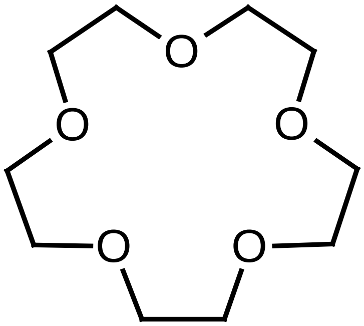
4.3.2.5. Comparision of Modes of Complexation

The uranium-crown ether complexation could be carried out in two modes viz. online and in-situ mode. These modes were studied employing ditertiarybutyldicyclohexano-18-crown-6. In the in-situ mode of complexation, crown ether solution and HPFOA solution along with uranium solution were taken in the extraction vessel. SFE was carried out at 200 atm and 323 K and experimental conditions as per Table 4.1. The extraction efficiency in in-situ complexation mode was found to be

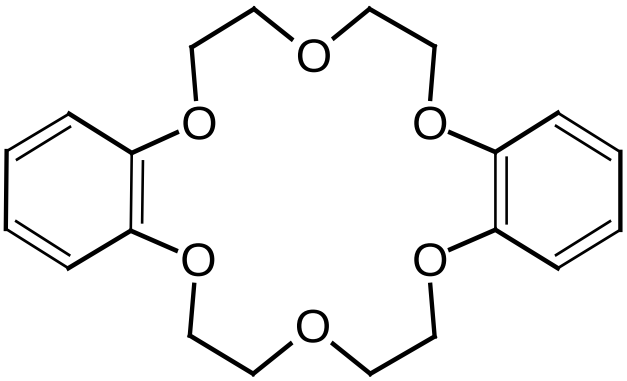
(65 ± 5) %. In online mode, CO_2 stream was mixed with stream of crown ether and HPFOA solution (1:10 mole ratio) and the resulting stream was pumped into the extraction vessel containing the uranium solution. CO_2 at 1 mL min^{-1} and crown ether plus HPFOA solution at 0.1 mL min^{-1} were pumped for 20 minutes. After extraction, system was flushed with SC CO_2 alone for 10 minutes. For online complexation mode, extraction efficiency was found to be (68 ± 5)%. The efficiencies in both modes were comparable. However, in online mode additional component viz. co-solvent pump was required. Hence, for present study in-situ mode was preferred.

4.3.3 COMPARISION AMONG VARIOUS CROWN ETHERS

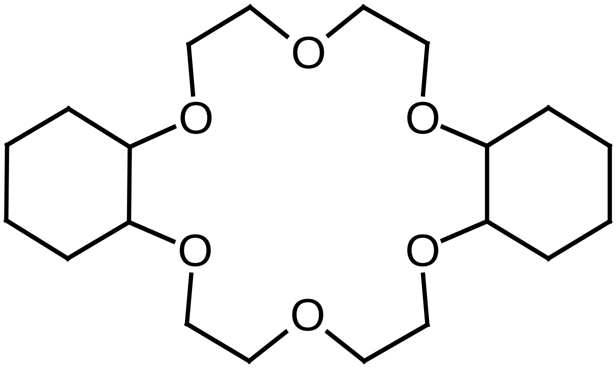
Various crown ethers were evaluated for uranium SFE. Structures of the crown ethers employed are shown in Fig.4.8. The study was carried out under experimental conditions mentioned in Table 4.1 and those obtained from section 3.2 viz. 200 atm pressure, 323 K temperature, U: crown: HPFOA mole ratio of 1:10:100, 20 minutes of steady time followed by 20 minutes of extraction time. The extraction efficiencies with various crown ethers are listed in Table 4.2. Crown ethers possess hydrophilic interior and lipophilic exterior enabling metal ion extraction. Electron-rich cavities of crown ethers have ability to complex with ions or molecules via ion-dipole or dipole-dipole stereo-selective interactions. The uranium complexation with crown ether is governed by cavity size, number of ether oxygen atoms and nature of substituents.



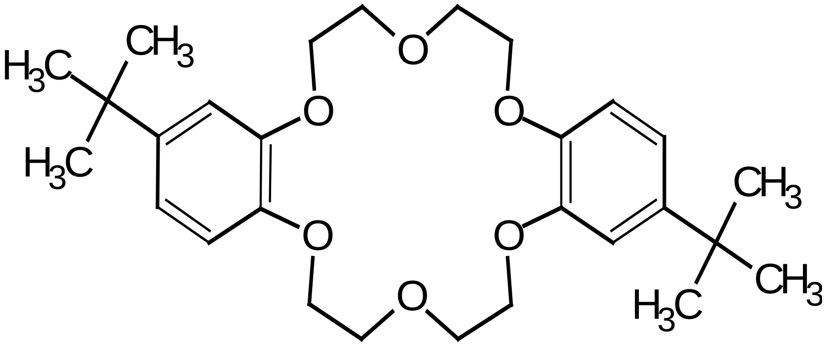
15-crown-5



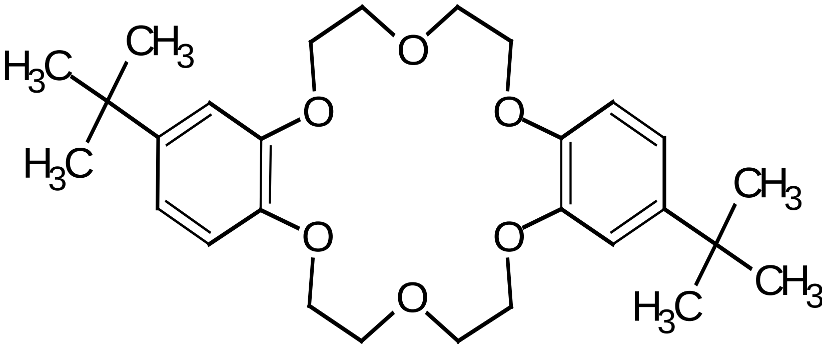
Dibenzo –18- crown-6



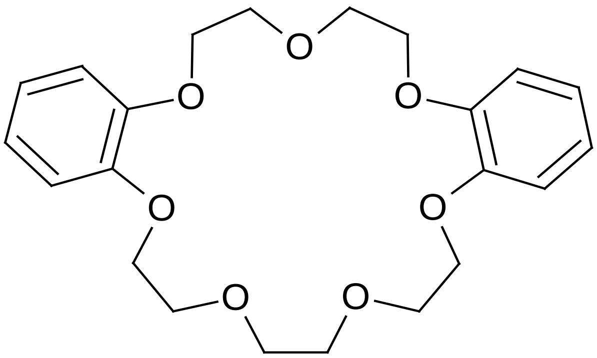
Dicyclohexano-18-crown-6



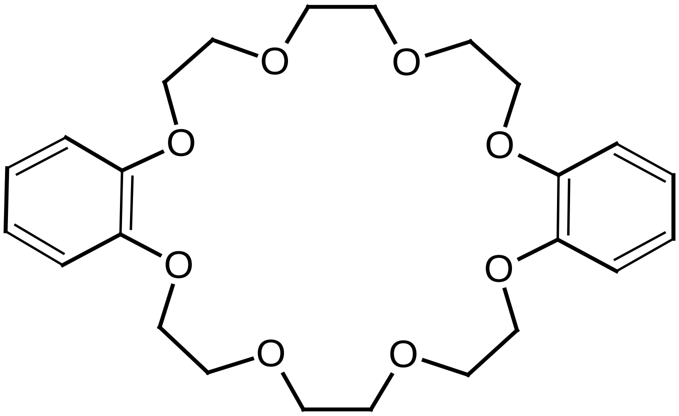
Ditertbutyldibenzo-18-crown-6



Ditertbutyldicyclohexano-18-crown-6



Dibenzo-21-crown-7



Dibenzo-24-crown-8

Fig.4.8. Structure of crown ethers employed in study

The effect of substituents is reflected while comparing efficiency for crown ethers of same ring size i.e. 18-crown-6 series:
ditertbutyldicyclohexano-18-crown-6>ditertbutyldibenzo-18-crown-6> dicylohexano-18-crown -6 > dibenzo-18-crown-6.

It is evident that cyclohexyl and/or ditertiary butyl substituents enhance the extraction efficiency. This could be attributed to the enhancement in basicity of oxygen atoms of the crown ether ring, thereby increasing bonding ability. In fact, highest extraction efficiency was observed with ditertbutyldiccyclohexano-18-crown-6. However, when two benzo groups were attached to the ring, the extraction efficiency was found to decrease. The observed decrease could be attributed to the electron withdrawing nature of benzo group. The basicity of four oxygen atoms in the ring is expected to reduce thereby decreasing the bonding ability. It may be of interest to note that cyclohexyl substituents have been found to yield higher extraction than benzo substituents in case of solvent extraction as well (47). With 15-crown-5 extractions efficiency is almost same as without crown ether indicating no complexation, which could be attributed to smaller cavity size of 15-crown-5 (1.7-2.2 ºA) than the size of UO_2^{2+} (2.4-2.5 ºA).

For crown ethers having same substituents (dibenzo) the following trend in extraction efficiency was observed:
dibenzo-24-crown-8 > dibenzo-21-crown-7> dibenzo-18-crown-6.

As observed from the trend, efficiency was found to increase with ring size. Generally, higher the molecular weight, the less soluble is the solute in supercritical CO_2. Shamsipur *et al.* (58) observed the solubility trend: dibenzo-24-crown-8>dibenzo-27-crown-9>dibenzo-30crown-10. But they have not carried out solubility measurements for dibenzo-18-crown-6 and dibenzo-21-crown-7. However, from molecular weight consideration the expected trend should be dibenzo-18-crown-6>dibenzo-21-crown-7>dibenzo-24-crown-8. The contradictory behavior in extraction efficiency indicates that structural aspects have overshadowed the solubility criterion. The enhancement with increasing ring size might be combined effect of enhanced cavity size as well as number of ether oxygen atoms.

Table 4.2

Various crown ethers studied along with their molecular weight, cavity diameter, solubility and extraction efficiency

Crown ether	**Mol. Wt.**	**Cavity[a] diameter (°A)**	**Extraction efficiency (%)**
15-Crown-5	220.20	1.7- 2.2	25
Dibenzo-18-Crown-6	360.41	2.7-2.9	33
Ditertbutyldibenzo-18-crown-6	424	-	58
Dicylohexano-18-crown-6	372.50	2.7-2.9	49
Ditertbutyldicyclohexano-18-crown-6	484.72	-	65, (86)[b]
Dibenzo-21-crown-7	404	-	45
Dibenzo-24-crown-8	448.52	4.5-4.8	63

The extraction efficiency values are mean of five repetitions.

Standard deviation = ±5%

[a] Reference (48)

[b] Uranium amount 100 μg.

4.3.4 EFFECT OF MOLARITY OF NITRIC ACID

The effect of molarity of nitric acid on extraction was investigated under experimental conditions listed in Table 4.1 and at 200 atm pressure, 323 K temperature employing ditertiarybutyldicyclohexano-18-crown-6. The uranium: crown: HPFOA mole ratio was 1:10:100. The observed trend of variation of extraction efficiency with molarity of nitric acid is depicted in Fig.4.9. Extraction efficiency was found to increase with molarity of nitric acid upto 2M and decrease afterwards. Eq.4.2.a can be rearranged as eq.4.15.

$$[UO_2(CE)_x(NO_3^-)_2]_{SF} = K_{ex(NO_3)}[UO_2^{2+}]_{aq}[NO_3^-]^2_{aq}[CE]^x_{SF} \qquad (4.15)$$

Since in the experiment, uranium and crown ether amount are fixed, the eq.4.15 could be modified to

$$[UO_2(CE)_x(NO_3)_2]_{SF} = K_3[NO_3^-]^2_{aq} \qquad (4.16)$$

where $K_3 = K_{ex(NO_3)}[UO_2^{2+}]_{aq}[CE]^x_{SF}$

It is evident from eq.4.16 that increase in NO_3^- concentration in aqueous phase should increase the concentration of uranium-crown ether complex in the supercritical fluid phase leading to higher extraction efficiency. However, for molarity greater than 2M, extraction efficiency was found to decrease. The decrease indicates the possibility of co-extraction of some other species.

Similar variation in uranium distribution ratio with molarity of nitric acid has been observed in case of solvent extraction (49). The decrease was assigned to co-extraction of CE.mHNO_3 (m =1, 2) complex. Hence, it is most likely that in case of SFE of uranium also crown-HNO_3 complex might be getting co-extracted into SC CO_2 phase leading to reduction in extraction efficiency.

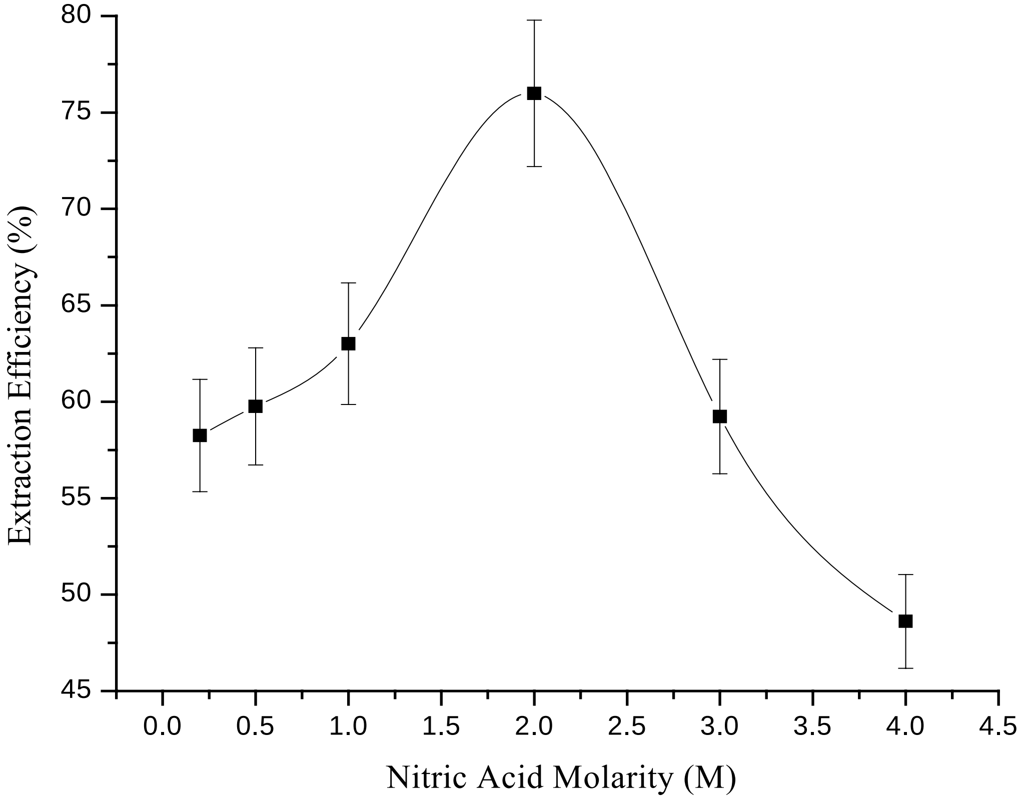


Fig.4.9. Variation of uranium extraction efficiency with molarity of nitric acid (Error bars indicate uncertainty in the measurement; standard deviation is 5 % of the value)

4.3.5 EFFECT OF URANIUM AMOUNT

Effect of uranium amount on extraction efficiency was investigated under experimental conditions listed in Table 4.1 at 200 atm pressure, 323 K temperature employing ditertiarybutyldicyclohexano-18-crown-6. The uranium: crown: HPFOA mole ratio was 1:10:100.

Total uranium amount in the SCF phase is given by:

$$[U_{total}]_{SF}=[UO_2(CE)x(NO_3)_2]_{SF}+[UO_2(CE)x(PFOA)_2]_{SF} \tag{4.17}$$

Using eq.4.11 and eq.4.15, the eq. 4.17 can be written as

$$[U_{total}]_{SF} = K_{ex(NO_3)}[UO_2^{2+}]_{aq}[NO_3^-]^2{}_{aq}[CE]_{SF}^{x} + K_{ex(PFOA)}[UO_2^{2+}]_{aq}[PFOA^-]^2{}_{aq}[CE_X]_{SF}^{x} \tag{4.18}$$

As crown ether, HPFOA and nitric acid amounts are fixed, eq.4.18 could be modified as

$$[U_{total}]_{SF}=K_4[UO_2^{2+}]_{aq} \tag{4.19}$$

where $K_4 = K_{ex(PFOA)}[PFOA^-]^2{}_{aq}[CE_X]_{SF}^{x} + K_{ex(NO_3)}[NO_3^-]^2{}_{aq}[CE]_{SF}^{x}$

The observed trend of variation of extraction efficiency with uranium amount is represented graphically in Fig.4.10. The expected trend as per eq.4.19 was observed upto uranium amount of 100 µg followed by gradual decline afterwards.

The gradual decline could be explained on the basis of the fact that uranium-crown ether complex has got certain solubility in SC CO_2 phase. At higher uranium amount (>100 µg) due to limited solubility of uranium-crown ether complex in SC CO_2 phase, higher uranium content remains in uncomplexed form in aqueous phase resulting in low uranium extraction efficiency. The maximum extraction efficiency achievable was (86±5) % for 100 µg uranium amount.

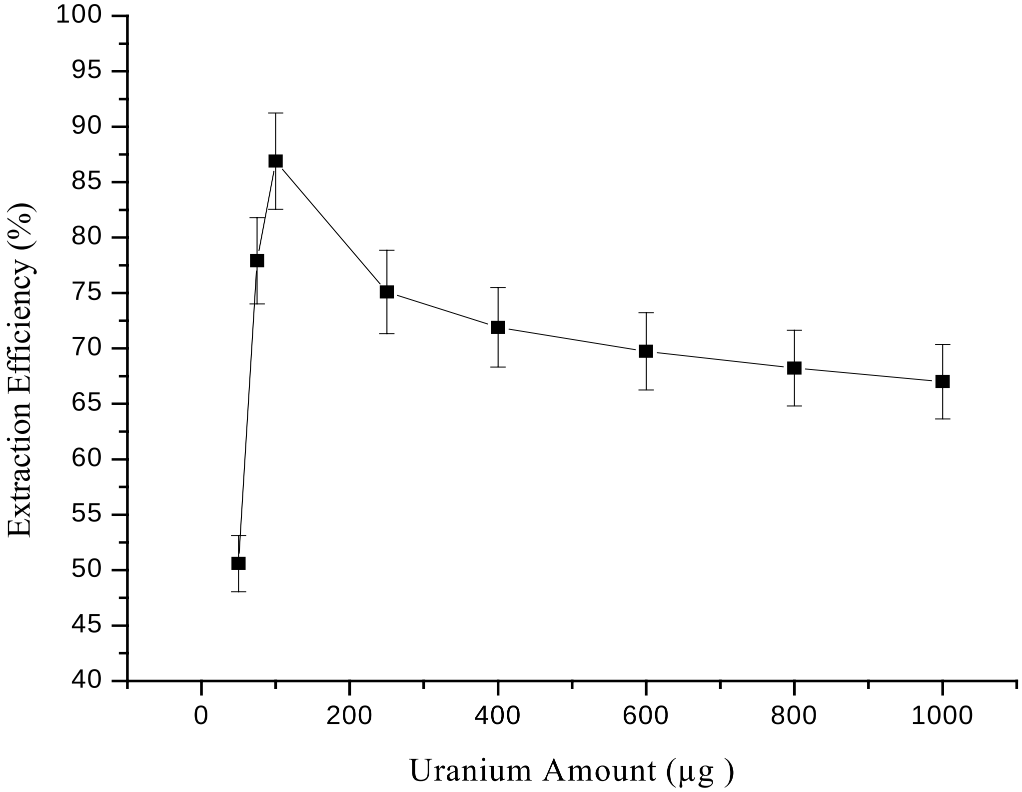


Fig.4.10. Effect of uranium loading on extraction efficiency

(Error bars indicate uncertainty in the measurement;

standard deviation is 5 % of the value)

4.3.6 EFFECT OF SOLVENTS

Effect of various solvents (methanol, ethanol, isopropanol, butanol, acetonitrile, benzonitrile, chloroform, carbon tetrachloride, hexane, toluene, xylene), for crown ether and HPFOA solution, on SFE was studied under experimental conditions listed in Table 4.1, at 200 atm pressure, 323 K temperature employing ditertiarybutyldicyclohexano-18-crown-6. The uranium: crown: HPFOA mole ratio was 1:10:100. The corresponding extraction efficiencies varied between ~70-80% and the effect of solvents, as mentioned earlier, on extraction efficiency was less pronounced.

4.4 CONCLUSIONS

Feasibility of supercritical CO_2 extraction of uranium from nitric acid medium employing various crown ethers was investigated. With crown ethers, uranyl ion gets extracted as ion pair. The uranium extraction efficiency achievable was (86±5)% for 100 µg uranium employing ditertiarybutyldicyclohexano-18-crown-6. Pressure and temperature were found to influence uranium extraction. For all isotherms, extraction efficiency decreased with increasing pressure (first part), attained minima and subsequently increased afterwards (second part). The trend in the second part was similar to density versus pressure variation trend. Contradictory behaviour in the first part could be assigned to large size cluster formation at low densities (near critical point). Free energy of solvation of complex for large size clusters would be low, as a major portion of enthalpy of solvation would be utilized in overcoming entropy losses, resulting in lower solubility. Pressure of 200 atm and temperature of 323 K was found to be optimum.

Ring size and nature of substituents were found to influence extraction efficiency. The effect of substituents was reflected while comparing efficiency for crown ethers of same ring size i.e. 18-crown-6 series:

Ditertbutyldicyclohexano-18-crown-6> ditertbutyldibenzo-18-crown-6 > dicylohexano-18- crown -6 > dibenzo-18-crown-6.

Electron donating cyclohexyl and/or ditertiary butyl substituents enhanced the extraction efficiency by increasing the basicity of ether oxygen atoms of the crown ether ring. While electron withdrawing benzo groups decreased the extraction efficiency by lowering the basicity of ether oxygen atoms of the crown ether ring. For crown ethers having same substituents (dibenzo) the trend in extraction efficiency was:

Dibenzo-24-crown-8 > dibenzo-21-crown-7> dibenzo-18-crown-6.

The enhancement with increasing ring size might be combined effect of enhanced cavity size as well as number of ether oxygen atoms.

The extraction efficiency was found to increase with molarity of nitric acid upto 2M and decreased afterwards. The decrease was attributed to co-extraction of crown-nitric acid complex. Extraction efficiency was low with nitrate as counter ion. On the addition of $PFOA^-$ as counter ion, extraction efficiency increased due to the presence of CO_2-phillic C-F bonds. Uranium: crown: HPFOA mole ratio had influence on extraction efficiency, the uranium: crown: HPFOA mole ratio of 1:10:100 was found to be optimum. Efficiency varied with extraction time. A combination of 20 minutes steady time and 20 minutes extraction time was found to be optimum. Online and in-situ complexation modes were found to be comparable in terms of extraction efficiency. Solvents had no pronounced effect on the extraction efficiency.

CHAPTER 5

SUPERCRITICAL FLUID EXTRACTION OF THORIUM FROM TISSUE PAPER MATRIX EMPLOYING ORGANOPHOSPHORUS REAGENTS AND β-DIKETONES

5.1 INTRODUCTION

India has embarked on utilization of thorium on industrial scale by designing a thorium fuelled Advanced Heavy Water Reactor (AHWR) (66). There is need to develop capabilities on all aspects of thorium fuel cycle viz. mining, fuel fabrication, reprocessing and waste management. During the fabrication of thorium based fuel, reprocessing of irradiated thorium based fuel and as a result of various radiochemical operations in laboratories significant quantity of solid as well as liquid matrix containing thorium is generated. In this context development of processes for separation and purification of thorium from various matrices, liquid as well as solid, is of utmost importance. Studies have been reported in literature on the SFE of thorium. In 1993, Lin *et al.* (12) successfully demonstrated SFE of trivalent lanthanides and uranyl ions from solid material by SC CO_2 containing fluorinated β-diketone, 2,2-dimethyl–6,6,7,7,8,8-heptafluoro-3,5-octadione (FOD). Subsequently, many studies were reported on extraction of uranium and other actinides including thorium from acid solutions as well as solid matrices (13, 30-33, 61). Lin *et al.* (13) have reported the SFE of thorium and uranium from solid and liquid materials employing β-diketones and tributyl phosphate in 1994. In 1995, Lin *et al.* (30) have also investigated organophosphorus reagents for SFE of uranium and thorium from nitric acid solutions. These authors have studied SFE of thorium in environmental samples such as filter paper, spiked with 10 μg thorium in in-situ chelation mode. Wai *et al.* (22) reviewed the supercritical fluid extraction of metals including lanthanides, actinides with various complexing agents like dithiocarbamates, β-diketones, organophosphorus reagents and macrocyclic compounds. SFE of various metals including thorium from aqueous solutions was reviewed by Erkey (21). In some studies thorium was used as mimic for plutonium (IV) (30). Mincher and Fox (67, 68) demonstrated the SFE of plutonium and americium from soil using SC CO_2 augmented with organophosphorus and β-diketone complexants.

In view of the importance of thorium, studies were initiated for evaluation of various complexing agents for thorium SFE. A few studies have been reported where adsorption/ desorption of solute (organic compounds, organometallic species) with respect to SC CO_2 has been discussed (18, 19, 69). However, in the present study of SFE of thorium from tissue paper matrix, the process has been viewed and analysed in terms of solubility of the solute, which can be correlated to the density of SCF as well as volatility of solute. Though many of the previous studies (12, 13, 27) based their choice of complexing agents and other conditions of extraction on solubility criteria, very few studies on the influence of operating parameters on extraction (hence solubility) of metal ions from solid matrix have been reported. In the present study, SFE of thorium from tissue paper employing various organophosphorus reagents (tributyl phosphate, TBP; triphenylphospahte, TPP; trioctylphosphine oxide, TOPO; triphenylphosphine oxide, TPPO and tributylphosphine oxide, TBPO) as co-solvent has been investigated. Effect of various parameters like pressure, temperature, flow rate, extraction time have been studied. By taking a combination of TBP and an organophosphorus reagent, improvement in extraction efficiency have been examined. Additionally, various solvents have been tried out for the organophosphorus reagents to investigate solvent influence on the extraction efficiency. In order to further improve efficiency and to investigate the favorable effect of fluorinated co-solvent on extraction efficiency, alternative reagents such as β-diketones (acetylacetone, AA; trifluoroacetylacetone, TFA; hexafluoroacetylacetone, HFA; thenoyltrifluoroacetone, TTA and heptaflurobutanoylpivaroylmethane, FOD) were investigated. Both online and in-situ modes of chelation were investigated. The effect of fluorination of β-diketones on the thorium extraction efficiency has been discussed. Combination of TBP and β-diketones was also studied.

5.2 METHODS AND MATERIALS

5.2.1 CHEMICAL REAGENTS

SFE experiments were performed using thorium standard solutions prepared in 4 M nitric acid by dissolving high purity ThO_2 powder. Carbon dioxide used for obtaining supercritical fluid was of 99.9% purity. TBP used was of Merck grade (for extraction analysis). TOPO (99%), TPP (98%), TPPO (98%), TBPO (95%) employed were of Sigma-Aldrich grade. TTA (99%), TFA (98%), HFA (98%), FOD (98%) of Sigma-Aldrich grade were employed. AA (99.5%) was of AR grade. Aldrich grade Arsenazo III was employed for color development. Sulphamic acid used was of Merck grade (99%). A.R. grade nitric acid was employed. Carbon tetrachloride and alcohols used to dissolve the organophosphorus reagents were of A.R. grade.

5.2.2 SUPERCRITICAL FLUID EXTRACTION PROCEDURE

In order to examine the feasibility of supercritical fluid extraction of thorium from tissue paper waste, synthetic tissue paper waste samples were prepared by loading known amount of thorium on tissue paper. Accurately weighed nuclear grade ThO_2 powder was taken in a platinum crucible. ThO_2 powder was dissolved by adding 1-2mL concentrated nitric acid and 0.5mL of 0.2 M HF and heating under IR-lamp. The clear solution thus obtained was evaporated to near dryness. 2-3 mL of 4 M nitric acid was added and again evaporated to near dryness. The evaporation process was repeated twice to ensure complete removal of HF. The final solution was made up with 4 M nitric acid. The concentrations of thorium standard were 39.3 mg g^{-1}. Accurately weighed amount of the thorium nitrate solution, containing 3 to 7 mg thorium, was sprinkled on a tissue paper kept in a petridish. The petridish was heated under IR lamp for 20 minute.

Table 5. 1

Study of thorium leaching efficiency from tissue paper

Leaching efficiency: (94.51±1.97) %

Amount of thorium Loaded on tissue (μg)	**Amount of thorium in leaching solution (μg)**	**Leaching efficiency**
3544.86	3429.69	96.75 %
4664.91	4370.25	93.68 %
4342.65	4042.73	93.09 %

Supercritical fluid extraction was performed by inserting the thorium loaded tissue paper in the extraction vessel (section 2.2). The amount of thorium left unextracted in the tissue paper was determined by leaching. Leaching study was performed to determine the amount of thorium left unextracted on the tissue paper. Known amount of thorium was loaded on tissue paper and heated with 40 mL of 4 M nitric acid for 20 minute on a hot plate. The solution left was filtered and volume was made upto 50mL with 4 M nitric acid. The amount of thorium present in the solution was determined and the corresponding leaching efficiency was calculated (Table 5.1).

$$\text{Leaching Efficiency} = \frac{\text{Thorium in leaching solution } [\mu\text{g}]}{\text{Thorium loaded on tissue paper } [\mu\text{g}]} \times 100 \qquad (5.1)$$

The amount of thorium present in the leaching solution was determined spectrophotometrically (section 2.3). The extraction efficiency was defined as follows

$$\text{Extraction efficiency} = \frac{\text{Thorium collected } [\mu\text{g}]}{\text{Thorium loaded on tissue paper } [\mu\text{g}]} \times 100 \qquad (5.2)$$

While calculating extraction efficiency, leaching efficiency was taken into consideration.

5.3 RESULTS AND DISCUSSION

5.3.1 SFE OF THORIUM WITH ORGANOPHOSPHORUS REAGENTS

5.3.1.1 Effect of various Parameters

Effects of various parameters on extraction efficiency were investigated. In a series of experiments, the parameter under consideration was varied while keeping the other parameters fixed. The parameters chosen for study were pressure, temperature, flow rate, extraction time etc. In the study, 0.2 M TOPO in CCl_4 was employed as co-solvent.

(i) Effect of Pressure

To evaluate the effect of pressure on extraction efficiency of thorium, SFE was performed at 100, 150, 200, 250 and 300 atm at a fixed temperature of 333 K. The system was maintained at desired pressure and temperature for 20 minute (static period) followed by 20 minute extraction period. The variation in extraction efficiency with pressure is depicted graphically in Fig.5.1.

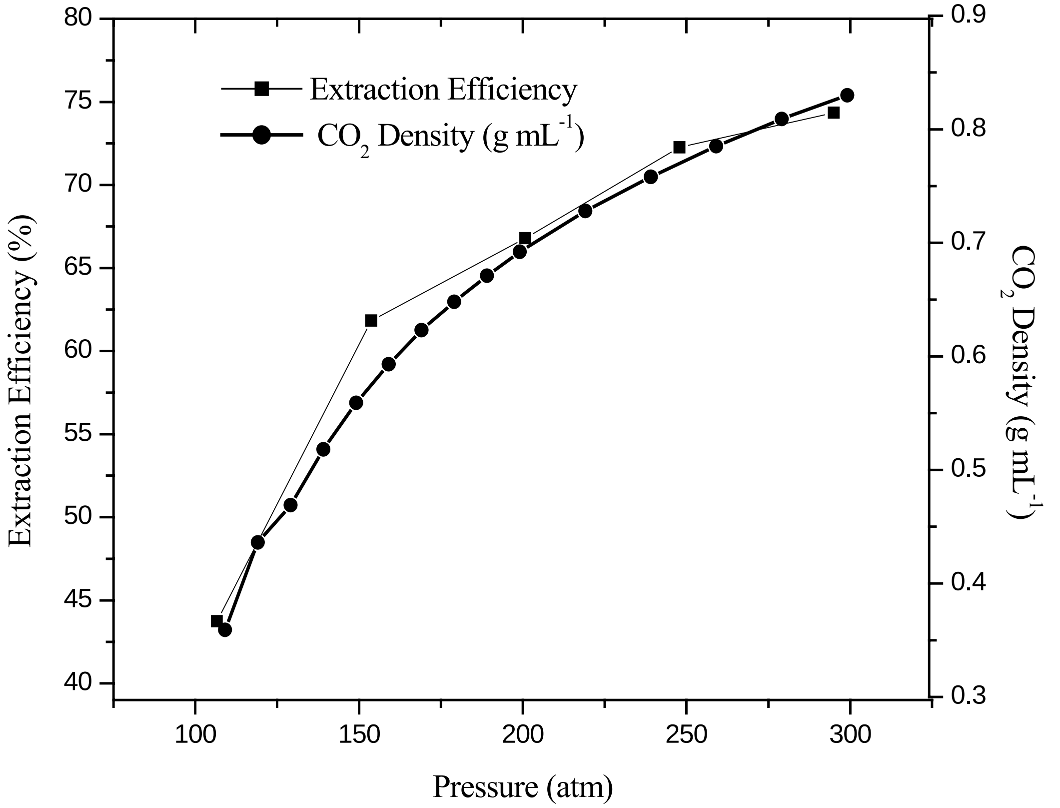


Fig.5.1. Variation of extraction efficiency with pressure

(CO_2 flow rate = 2 mL min^{-1}, Co-solvent flow rate = 0.2 mL min^{-1},

Temperature = 333 K, Static time = 20 min, Extraction time = 20 min)

The extraction efficiency is expected to be directly proportional to solubility of solute in supercritical fluid phase. The solubility of a solute is related to the SCF solvent density by the eq.1.19.The variation in supercritical CO_2 density with pressure (at 333 K) is also graphically depicted in Fig.5.1. The density of supercritical CO_2 has been calculated from Peng-Robinson equation of state (15). The graph shows increase in supercritical CO_2 density with increasing pressure. If eq.1.19 is taken into consideration one should expect increase in the extraction efficiency with increasing density and the graph between extraction efficiency versus pressure should be similar to supercritical CO_2 density versus pressure graph (at 333 K). As it can be seen from Fig.5.3, the observed trend in variation in extraction efficiency with pressure is similar to the predicted trend as per eq.1.19. Initially increase in extraction efficiency is steep. However, after 200 atm the increase is not significant, pressure of 200 atm was chosen for study.

Graph of ln (E) versus ln (D) at 333 K was a straight line (Fig5.2). ‘D’ denotes supercritical CO_2 density and ‘E’ denotes extraction efficiency. When the data was subjected to least square fitting the correlation coefficient was found to be 0.9982. The following equation fits into the graph:

$$\ln (E) = 0.540 \ \ln (D) + 4.278 \tag{5.3}$$

The graph indicates that extraction efficiency is directly proportional to density of the SC CO_2.

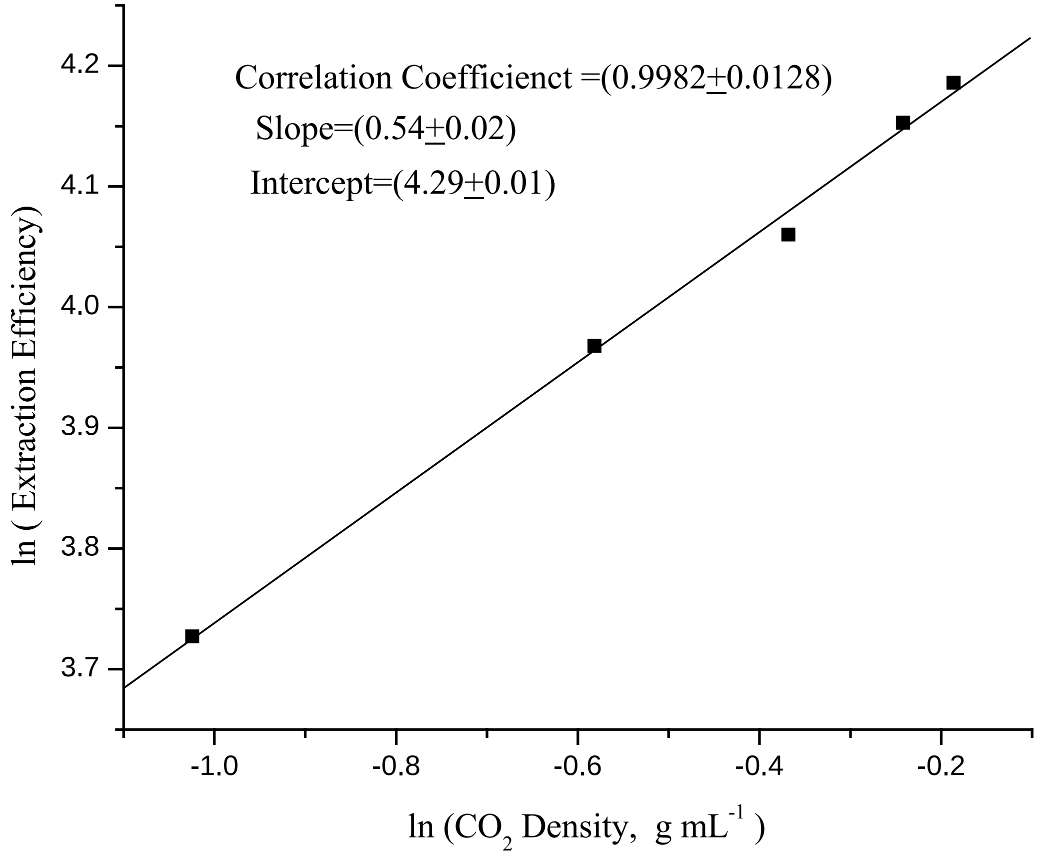


Fig.5.2. Graph between ln (Extraction efficiency) versus ln (CO_2 density)

(ii) Effect of Temperature

To investigate the effect of extraction temperature, the SFE was performed at 313, 323, 333, 343 and 353 K at extraction pressure of 200 atm for 20 minute static time followed by 20 minute dynamic time. The variation in extraction efficiency with temperature is depicted graphically in Fig.5.3. The extraction efficiency increases upto 333 K followed by decrease. In Fig.5.3, variation in supercritical CO_2 density (from Peng-Robinson equation of state) with temperature at 200 atm is also depicted.

The graph displays linear decrease in supercritical CO_2 density with increasing temperature. If only SC CO_2 density is to be taken into consideration, as per eq.1.19 one should expect similar linear decrease in the extraction efficiency with temperature. However, observed increasing trend in extraction efficiency from 313 K to 333 K clearly indicates that the increase in volatility of the metal complex not only compensates for the decrease in density but also leads to enhancement of extraction efficiency. However, after 333 K, the observed trend in extraction efficiency is similar to that of density.

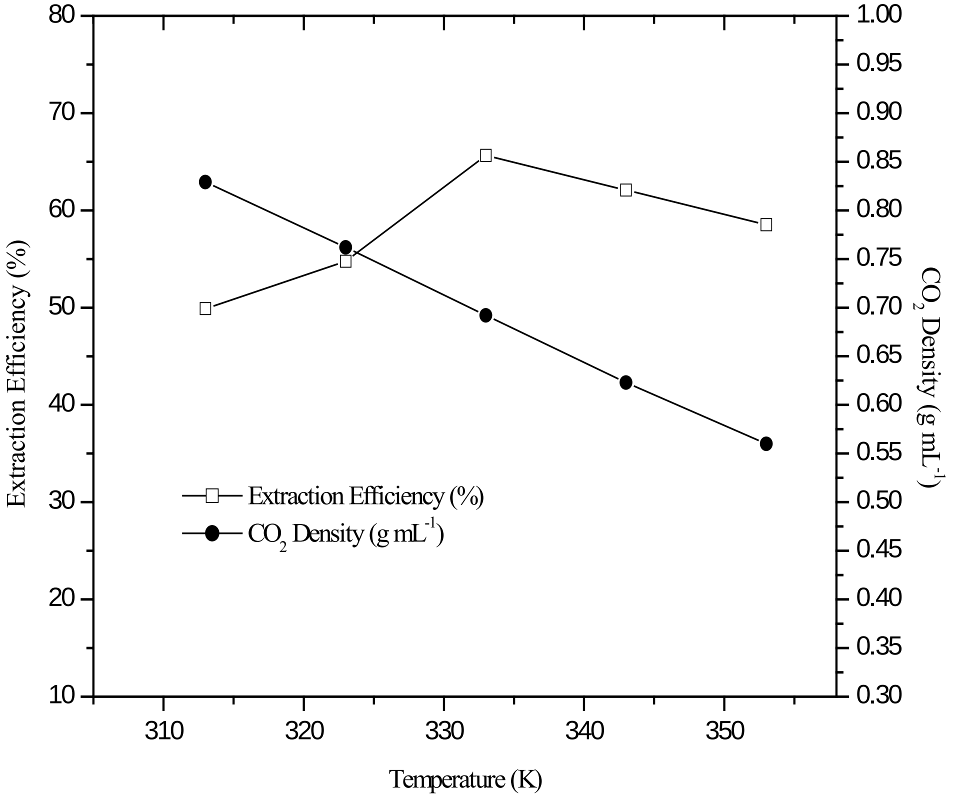


Fig.5.3.Variation of extraction efficiency with temperature

(CO_2 Flow rate =2 mL min^{-1}, Co-solvent Flow rate = 0.2 mL min^{-1},

Pressure = 200 atm,Static time = 20 min, Extraction time= 20 min static)

Assuming that extraction efficiency is a direct measure of solubility of the solute and the eq.1.19 could be modified as

$\ln E = k_E \ln D + C_E$ (5.4)

Where is 'E' extraction efficiency and 'k_E' ,'C_E' are corresponding coefficients under extraction conditions. 'C_E' is measure of volatility of metal-complex. By substituting the experimental value of 'E' , 'D' from Peng-Robinson equation of state and 'K_E' from Fig.5.2, the values of 'C_E' were calculated at various temperatures (313-373 K). The variation in 'C_E' with temperature is depicted graphically in Fig.5.4. 'C_E' increases sharply upto 333 K and gets saturated afterwards.

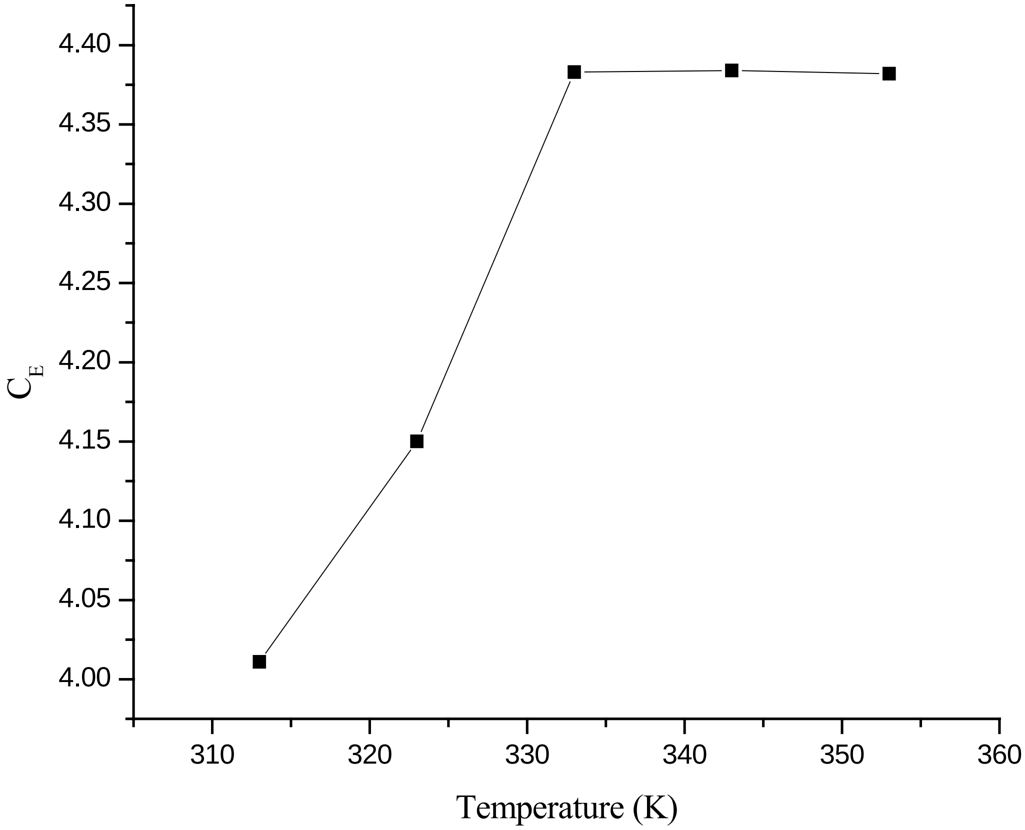


Fig.5.4. Variation of 'C_E' with temperature

(iii) Effect of CO_2 Flow Rate

In order to examine the effect of CO_2 flow rate, SFE was performed at 200 atm pressure, 333 K temperature at CO_2 flow rates of 0.5, 1, 2, 3 mL min^{-1} for 20 minute static time period followed by 20 minute dynamic extraction time. During SFE the flow rate of TOPO (co-solvent) was 10% of CO_2 flow rate. Variation in extraction efficiency with flow rate is represented in Fig.5.5. Initially extraction efficiency increases with flow rate, but after a flow rate of 1mL min^{-1} increase is very small. The flow rate of 2mL min^{-1} was selected for study.

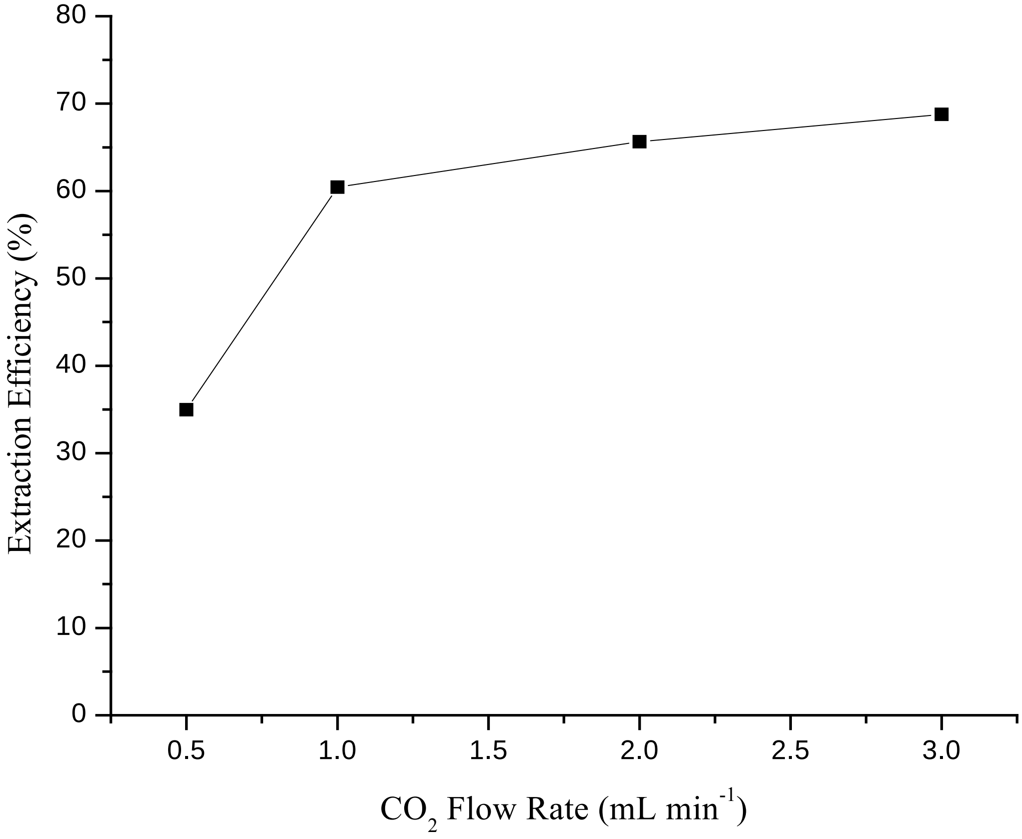


Fig.5.5. Variation of extraction efficiency with CO_2 flow rate

(Co-solvent flow rate = 0.2 mL min^{-1}, Pressure= 200 atm,

Temperature= 333 K, Static time= 20 min, Extraction time = 20 min

(iv) Effect of Extraction Time

The effect of extraction time on extraction efficiency was investigated by allowing the system to withstand particular pressure and temperature for desired period (static period) followed by dynamic time period. The effect of dynamic time was studied by keeping pressure fixed at 200 atm and temperature at 333 K for 20 minute (static period) followed by extraction for time period varying from 5 minute to 40 minute. The graph between extraction efficiency and extraction time (Fig.5.6) shows increase upto 20 minute and saturation afterwards. The extraction time of 20 minute was selected for study. The effect of static time period was investigated by maintaining the system at pressure of 200 atm and 333 K temperature for time periods varying from 0 to 40 minute followed by dynamic extraction for 20 minute under same condition of temperature and pressure. The flow rate during study was 2 mL min^{-1} and co-solvent flow rate was 0.2 mL min^{-1}. The effect of static time is represented graphically in Fig.5.7. After 20 minute the increase in extraction efficiency was not significant. From the study of effect of extraction time, it is evident that for 20 minute dynamic time period efficiency enhances significantly if extraction is preceded by a static period. The static period of 20 minute was selected.

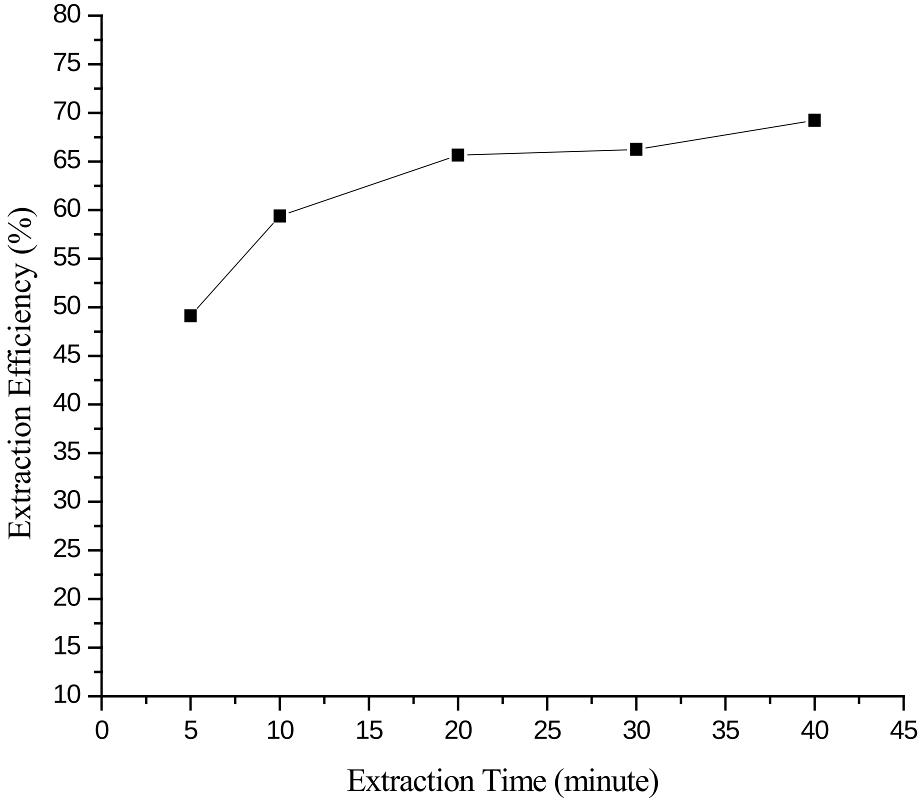


Fig.5.6. Variation of extraction efficiency with extraction time

(Pressure= 200 atm, Temperature= 333 K, CO_2 flow rate = 2 mL min^{-1}, Co-solvent flow rate = 0.2 mL min^{-1}, Static period = 20 minute)

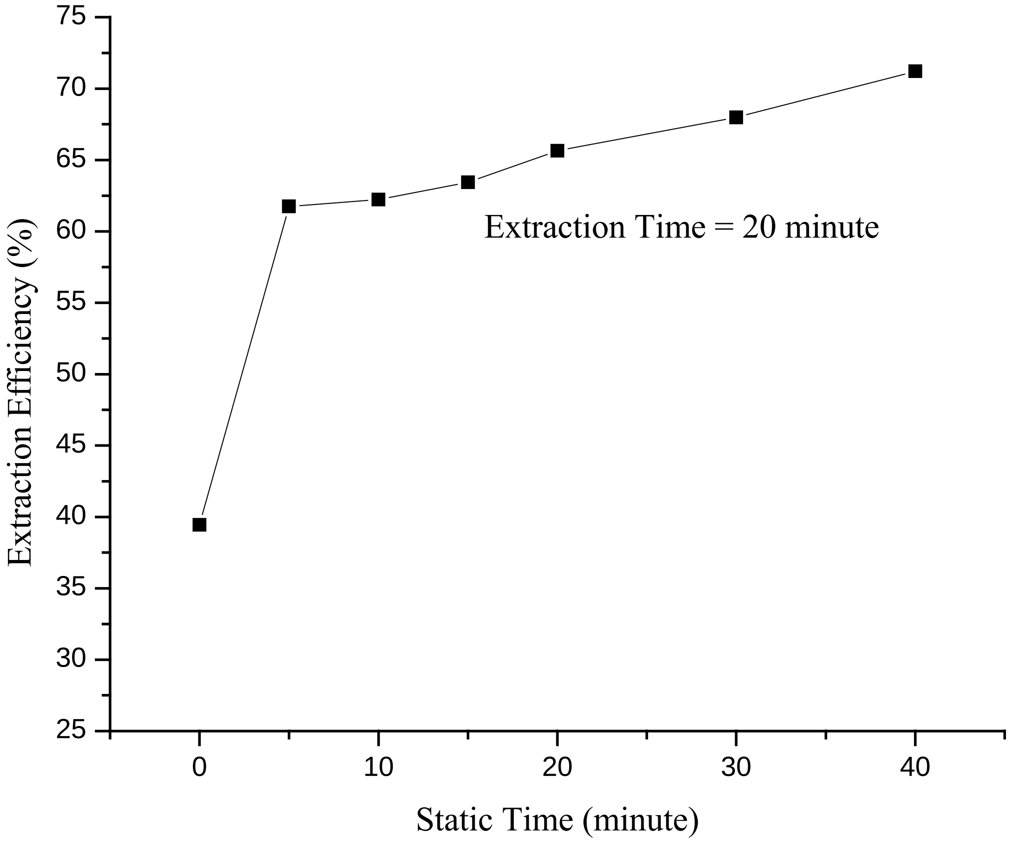


Fig.5.7. Variation of extraction efficiency with static time

(Pressure = 200 atm, Temperature = 333 K, CO_2 flow rate = 2 mL min^{-1}, Co-solvent flow rate = 0.2 mL min^{-1}, Extraction time = 20 minute)

5.3.1.2 SFE of Thorium with various Organophosphorus Reagents

Under selected conditions of pressure, temperature, CO_2 flow rate and extraction mode i.e. 200 atm, 333 K, 2mL min^{-1} and 20 minute static period followed by 20 minute dynamic extraction period respectively, SFE was carried out employing various organophosphorus reagents as co-solvent. The co-solvent flow rate was 0.2 mL min^{-1} (10% of CO_2). While studying the effects of parameters, TOPO was dissolved in CCl_4. But with other organophosphorus reagents choking in the system tubes was observed. Solvent was, thus, changed to methanol.

Table 5.2

Extraction efficiency with various organophosphorus reagents (0.2 M in methanol)

Organophosphorus reagent	**Structure**	**Extraction efficiency**
Tributylphosphate (TBP)	$(RO)_3$-P=O ($R = C_4H_9$)	(52.51 ± 7.54)%
Triphenylphospahte (TPP)	$(RO)_3$-P=O ($R = C_6H_5$)	(38.91±5.33)%
Trioctylphosphine oxide (TOPO)	R_3-P=O ($R = C_8H_{17}$)	(70.33±5.89)%
Triphenylphosphine oxide (TPPO)	R_3-P=O ($R = C_6H_5$)	(58.81±14.55)%
Tributylphosphine oxide (TBPO)	R_3-P=O ($R = C_4H_9$)	(49.58±8.39)%

(The extraction efficiency was mean of five values)

From Table 5.2, it is evident that extraction efficiency is influenced by the structure of the organophosphorus reagents. Organophosphorus reagents are known to form co-ordinatively solvated salts with actinides through P=O group. The organophosphorus reagents used in the present study can be categorized into two classes viz. phosphates and phosphine oxides.

From the present study following trends have been observed:

1. On comparing phosphates with phosphine oxides, if P is attached to aliphatic hydrocarbon the extraction efficiencies are comparable e.g. TBP and TBPO. If P is attached to aromatic ring, as in case of phosphine oxide extraction efficiency is higher than its phosphate analogue e.g. TPP and TPPO.
2. Among phosphates, if aromatic group replaces aliphatic group then extraction efficiency decreases e.g. TBP and TPP.
3. Among phosphine oxides, higher the aliphatic chain length higher is the extraction efficiency e.g. TOPO and TBPO.
4. In phosphine oxides, when phenyl group is attached to P i.e. TPPO then extraction efficiency intermediate to TOPO and TBPO was found.

5.3.1.3 Study of Effect of Combination of Organophosphorus Reagents

Effect of combination of organophosphorus reagents was studied by taking TBP and other organophosphorus reagent (0.2 M in methanol) in 1:1 volume ratio. The results are listed in Table 5.3. The combination effect is compared with individual extraction for the organophosphorus reagents graphically in Fig.5.8. In case of TOPO and TPPO there is no enhancement in extraction efficiency. Both TBPO and TPP show higher extraction efficiency.

Table 5.3

Extraction efficiency with TBP and various other organophosphorus reagents

Reagent mixture	Extraction efficiency
TBP+TOPO	(68.37±7.30)%
TBP+TBPO	(74.06±9.58)%
TBP+TPPO	(55.41±11.16)%
TBP+TPP	(60.29±9.58)%

(TBP + 0.2 M organophosphorus reagent in MeOH. The extraction efficiency was mean of five trials.)

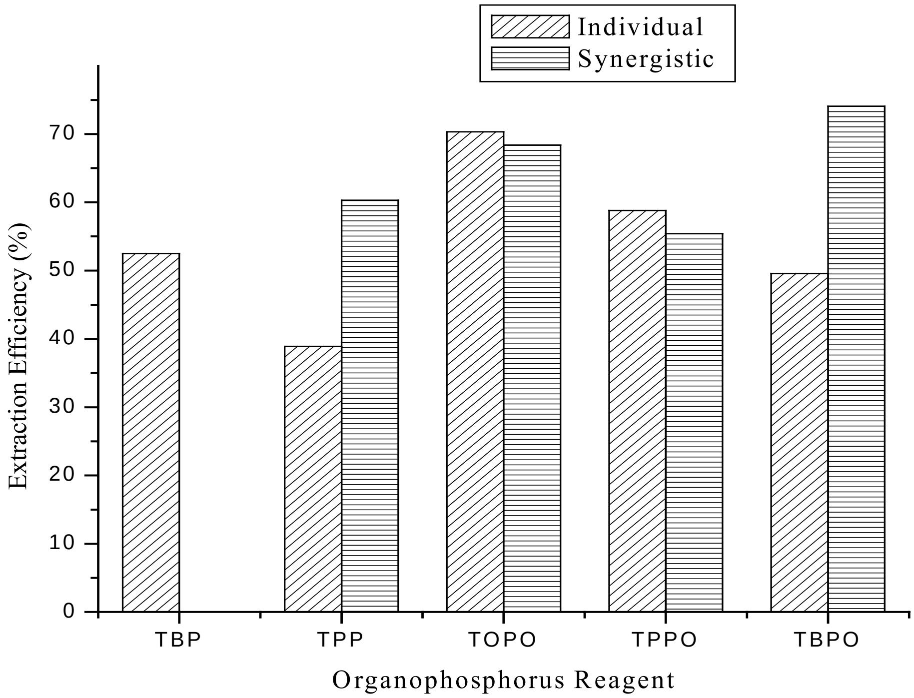


Fig.5.8. Effect of combination of organophosphorus reagents on extraction efficiency

5.3.1.4 Effect of Solvents

Effect of various solvents was studied by dissolving TOPO in various solvents and performing SFE under optimized conditions employing the TOPO solution as co-solvent (Table 5.4). With respect to the present study, methanol as solvent yields slightly better extraction efficiency than carbon tetrachloride. Amongst the alcohols, as the aliphatic chain length increases the extraction efficiency has been found to decrease. This indicates that solvent affects the stability and solubility of thorium-organophosphorus complex.

Table 5.4

Extraction Efficiency with TOPO in various solvents

Solvent	Thorium extraction
Carbon tetrachloride	(65.65 ±7.78)%
Methanol	(68.34 ±3.65)%
Ethanol	(67.38± 8.79)%
iso-Propanol	(58.96± 8.51)%
n-Butanol	(56.51± 9.77)%

(Extraction efficiency is mean of five values)

5.3.2 SFE OF THORIUM WITH β-DIKETONES

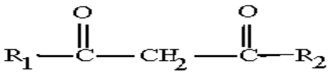
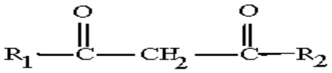
The general formula for β-diketones is  $R_1-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-R_2$. The conditions for SFE are as optimized for the organophosphorus reagents and are listed in Table 5.5. β-diketones evaluated for supercritical extraction of thorium from tissue paper matrix are listed in Table 5.6. TTA is solid whereas all other β-diketones are liquid at room temperature. The β-diketones in solution form (0.2 M in methanol) were employed for SFE of thorium.

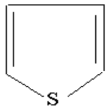
Table 5.5

Important parameters for online and in-situ chelation modes for SFE of thorium

Parameter	Online Chelation	In-situ Chelation
Pressure	200 atm	200 atm
Temperature	333 K	333 K
Static time	20 min	20 min
Dynamic time	20 min	20 min
CO_2 flow rate	2 mL min^{-1}	2 mL min^{-1}
β-diketones flow rate	0.2 mL min^{-1}	--------
Initial amount of β-diketone	-------	5 mL

Table 5.6

Structure  $R_1-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-R_2$ of β-diketones evaluated for SFE of thorium

β-diketone	**Abbreviation**	**R_1**	**R_2**
Acetylacetone	AA	CH_3	CH_3
Trifluoroacetylacetone	TFA	CH_3	CF_3
Hexafluoroacetylacetone	HFA	CF_3	CF_3
Thenoyltrifluoroacetone	TTA		CF_3
Heptaflurobutanoylpivaroylmethane	FOD	$C(CH_3)_3$	C_3F_7

5.3.2.1 COMPARISON OF MODES OF COMPLEXATION

Thorium chelation with β-diketone could be performed in two ways viz. online and in-situ chelation. In the online chelation mode, at 333 K, the supercritical mixture of CO_2 and β-diketone (0.2 M in methanol) was fed into the extraction vessel until pressure of 200 atm was reached and the system was allowed to remain at these conditions for 20 minutes followed by extraction for 20 minutes by flowing supercritical mixture at rate of 2 mL min^{-1}. In the in-situ chelation mode, 5 mL of β-diketone (0.2 M in methanol) solution was taken in the extraction vessel along with thorium-loaded tissue paper. At 333 K supercritical CO_2 was fed into extraction vessel until pressure of 200 atm was reached and the system was allowed to remain under these conditions for 20 minutes followed by extraction for 20 minutes by flowing supercritical CO_2 at 2 mL min^{-1}. The important parameters for both modes are listed in Table 5.5. Since 5 mL solution was consumed in online chelation mode, 5 mL solution was also taken in the in-situ chelation mode for adequate comparison of the two modes. The extraction efficiencies with various β-diketones in the online chelation mode and in-situ chelation mode are shown in Table 5.7. In the in-situ mode extraction efficiencies were higher than the online chelation mode with same amount of β-diketones. As evident from Table 5.6, the following trend in thorium extraction efficiency was observed in both the chelation modes for the various β-diketones:

TTA > FOD > HFA > TFA > AA

Table 5.7

Thorium extraction efficiencies with supercritical mixture of CO_2 and β-diketone

Complexing agent	**Extraction Efficiency (%) On line**	**Extraction Efficiency (%) In-situ**	**Extraction Efficiency (%) TBP+ β-diketone**
AA	29.05±2.31	34.25±6.15	43.63 ±7.72
TFA	31.48±1.97	49.93±12.40	57.76 ± 8.81
HFA	34.01±1.46	60.06±6.81	83.71±6.43
FOD	36.21±7.49	64.87±8.54	87.24±8.49
TTA	52.78±6.36	76.52±7.63	89.45±0.95

5.3.2.2 STUDY OF COMBINED EFFECT OF TBP AND β-DIKETONE

Effect of combination of TBP and β-diketone on extraction efficiency was also studied. TBP and β-diketone (0.2 M in methanol) solutions were taken in 1:1 volume ratio. Thorium extraction from tissue paper was carried out in in-situ chelation mode with 5 mL solution. The extraction efficiencies with TBP and β-diketone were higher than corresponding individual β-diketone. However, the trend in extraction efficiency was similar to that observed for the individual diketones i.e. TTA > FOD > HFA > TFA > AA. The enhancement in extraction efficiency could probably be due to adduct formation. TBP and β-diketone adduct formation is also reported in literature by Lin *et al.* (30).

5.3.2.3 DISCUSSION ON THE OBSERVED TREND

In general, extraction efficiency depends on following factors:

(i) Solubility and stability of complexing agent in SC CO_2.

(ii) Efficiency of metal-chelate formation.

(iii) Solubility and stability of metal complex in SC CO_2.

Comparison of extraction efficiencies in various modes is represented graphically in Fig.5.9. In all the modes, the same trend was observed i.e.

TTA > FOD > HFA > TFA > AA

Solubility and stability of the complexing agent are key parameters for achieving quantitative extraction in reasonable time with lesser amount of the extractant. The β-diketones do not decompose and hence are assumed to be stable under SC CO_2 conditions (22). The β-diketones under study exhibit high solubility in SC CO_2. Laintz *et al.* (70) observed that fluorination in side arm enhances the solubility of β-diketones in SC CO_2 by several orders of magnitude. For example, TFA and HFA have chelating properties similar to AA but have higher solubility in SC CO_2.

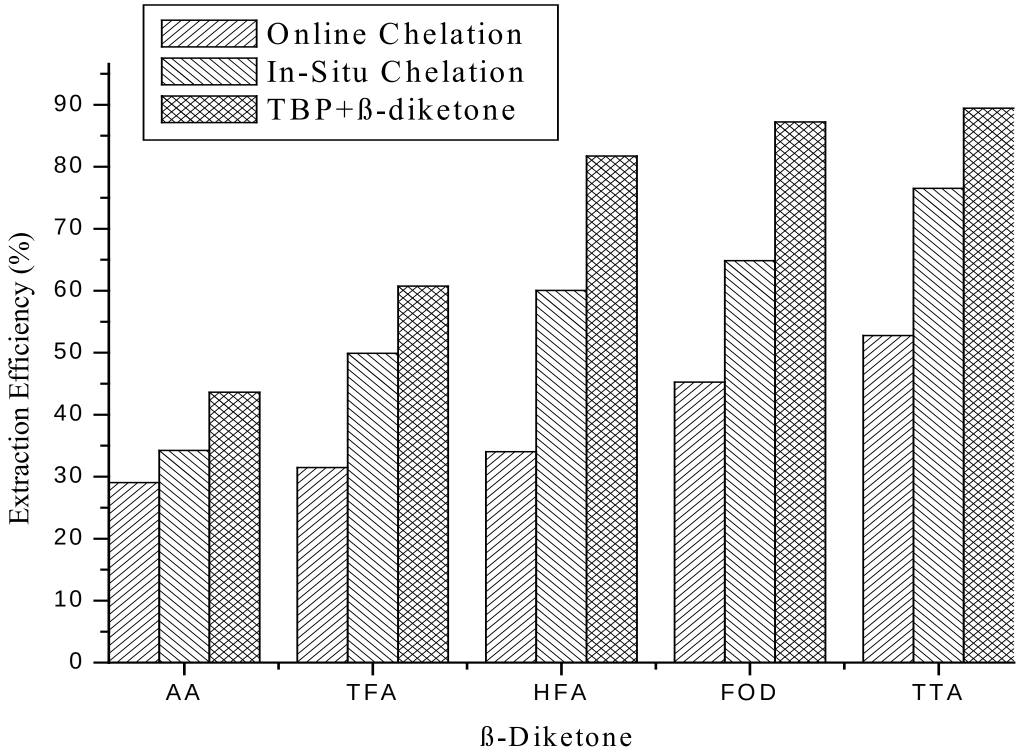


Fig.5.9.Comparison of online chelation, in-situ chelation, combined TBP + β-diketone effect on extraction efficiency

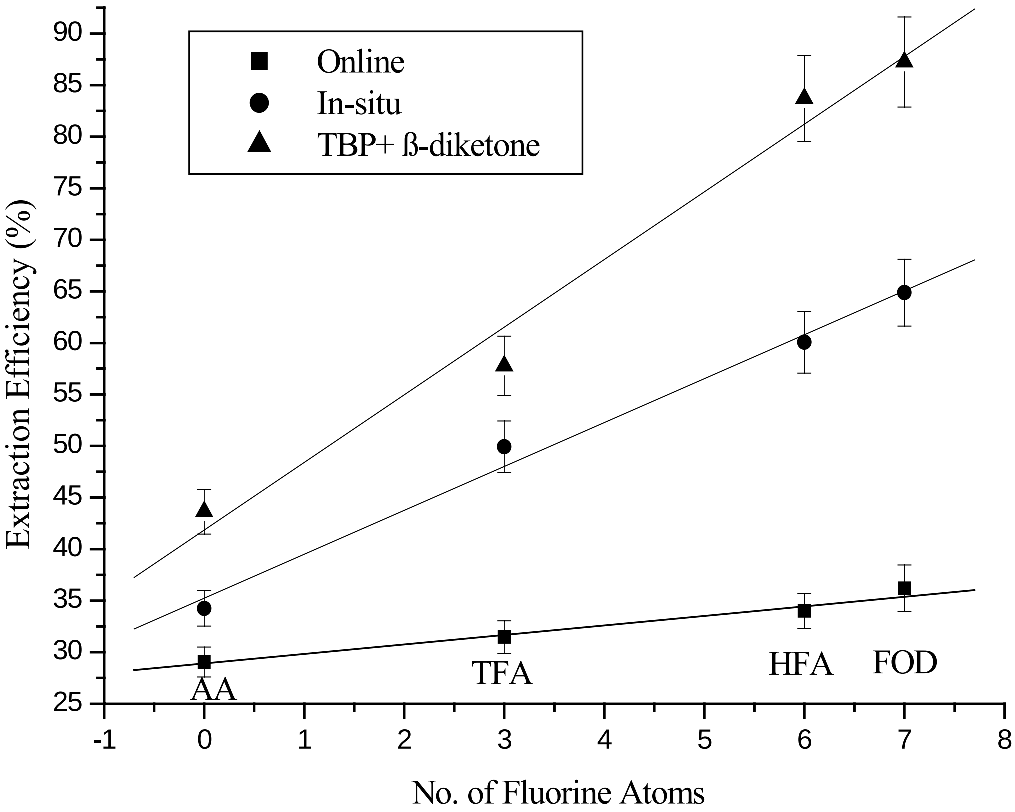


Fig.5.10. Correlation graphs between extraction efficiency and no. of fluorine atoms in the side arm of β-diketone for various modes

(Error bar is ± 5% of the value)

Table 5.8

Mol Wt, enol Content in SC CO_2 and pKa values of β-diketones

β-diketone	Mol. Wt.	Enol content (%) in SC CO_2	pKa
AA	100.12	77	8.67
TFA	154.09	98	6-6.5
HFA	208.06	~100	4.46
TTA	222.18	~100	6.5
FOD	296.18		6.7

Table 5.9

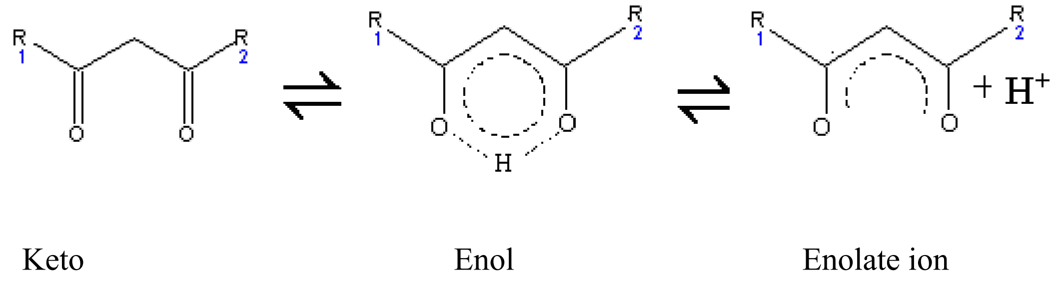
Slope, Intercept and correlation coefficient for the graphs between no. of fluorine atoms versus extraction efficiency in various modes

	Online Chelation	In-situ Chelation	TBP+ β-diketone
Slope	0.92	4.26	6.56
Intercept	28.91	35.26	41.84
ation coefficient	0.9875	0.9953	0.9909

The observed trend in extraction efficiency clearly indicates that there exists direct correlation between extraction efficiency and fluorination in the side arm of the β-diketone. In AA, where no fluorine atom is attached to the side arm, the extraction efficiency observed was least. Three fluorine atoms are attached in the side arm of TFA whereas six fluorine atoms are attached in the side arm of HFA. The graph between no. of fluorine atoms in the side arm of β-diketone versus extraction efficiency are highly linear as shown in Fig.5.10. The slope, intercept and correlation coefficients are listed in Table 5.9. Overtly, fluorination in the side arm of β-diketone influences the extraction efficiency in a regular fashion. Higher the extent of fluorination higher is the extraction efficiency. This increment in regular fashion indicates that there exists specific interaction between C-F bond and CO_2 molecules under supercritical fluid conditions. These interactions seem to be site specific. With increasing number of fluorine atoms the number of sites increases, hence solubility should also increase proportionally. In fact Dardin *et al.* (71) from NMR study have confirmed the existence of such interactions between C-F and CO_2 molecules under supercritical conditions, which were found to be higher than C-H and CO_2 interactions. Many theories have been proposed to explain these interactions but so far the exact nature of these interactions is not fully understood. However, it is well established that such interactions do exist leading to solubility enhancement.

The extraction efficiency in case of TTA is somewhat at variance of what has been mentioned above. Even though, the molecule has only CF_3 group on one side arm, the extraction efficiency is maximum amongst the β-diketones investigated. In addition, aromatic thenoyl group present in the molecule may also be responsible for efficiency enhancement. There is scope for further investigations to understand the mechanism of enhancement with TTA.

β-diketones exist as equilibrium mixture of keto and enol forms due to tautomerism. Keto form does not chelate with thorium. It is the enol form that dissociates into enolate ion, which chelates with thorium. Hence, the extent of Th-chelate formation will depend upon the extent of enolate ion formation under given supercritical fluid conditions. The extent of enolate ion formation in turn depends upon the extent of enol form present under supercritical CO_2 conditions and extent of dissociation of enol form.



(2)

NMR spectroscopy study by Spencer *et al.* (72) (in liquid) and Folkendt *et al.* (73) (in gas phase) revealed that enol form is favored energetically whereas disfavored entropically.

Wallen *et al.* (74) have extensively studied the effect of pressure and temperature on the keto and enol tautomers of AA, TFA, HFA dissolved in SC CO_2 and in the neat liquid state by ^{1}H NMR. The enol content of AA and TFA were found to be 77% and 98.3% respectively. Whereas HFA was found to be exclusively in the enol form. TTA is also found to be ~100% in enol form under supercritical CO_2 conditions (22). We have not come across data on FOD. However the observed trend in the extraction efficiencies suggest that it is logical to assume that FOD is present almost completely (~100%) in enol form in SC CO_2. Hence from keto-enol equilibrium study, it is evident that fluorination in side arm increases the stability of enol tautomer of β-diketones. Gastone *et al.* (75, 76) proposed the existence of a special type of very strong hydrogen bonding in enol form and named it as Resonance-Assisted Hydrogen Bonding (RAHB). The increased stability of enol form in SC CO_2 with increasing fluorination is due to stablization by electron-withdrawing fluorine substituents through enhanced electron delocalization in the intermolecular RAHB. Wallen *et al.* also observed that as compared to neat liquids, the enol form in supercritical CO_2 is energetically more stable relative to keto form. This is due to the fact that CO_2 being a less polar solvent than pure β-diketone itself, the keto-enol equilibrium would be shifted towards less polar tautomer of β-diketones viz. the enol form.

Thorium chelates with the enolate ion obtained as a result of removal of labile proton. Obviously, the extent of thorium chelation depends upon the amount of enolate ion present under supercritical fluid conditions. The amount of enolate ion formed depends on the dissociation constant K_a defined as:

$$K_a = \frac{[H^+][X^-]}{[HX]} \tag{5.3}$$

pKa of AA is 8.67 whereas that of HFA is 4.46 (Table 5.8). Thus, substitution by two CF_3 groups into the AA increases the acidity by four orders of magnitude. Hence, lower pKa enables HFA towards higher metal chelation. Kersch *et al.* (77) have investigated the relationship between metal-complex stability (log Km) and extractant dissociation (pka). Martin *et al.* (78) observed a linear correlation between complex stability against the extractant acidity. The solubility and stability of the metal-chelates of β-diketones in SC CO_2 influence the extraction. Data on solubility of thorium-chelate (with β-diketones) in SC CO_2 is lacking. However, reported data on solubility of transition metal-chelates with various β-diketones reveal that fluorination in side arm of β-diketone increases the solubility of metal-chelate in SC CO_2 (79, 80). On the basis of available data of solubility of transition metal-chelates in SC CO_2, prediction can be made on the thorium-chelate (with β-diketones) and solubility is expected to increase with the fluorination in side arm of β-diketone.

The discussion on observed trend in extraction efficiency could be useful in the designing of new β-diketones for enhanced extraction efficiency. The present discussion enables us to predict the extraction efficiency range of the newly synthesized β-diketone. Also, the study indicates the existence of scope for further investigation with β-diketones containing different aromatic substituents in the side arm.

5.4 CONCLUSIONS

In the present study it has been established that thorium can be extracted from tissue paper matrix by supercritical CO_2 employing various organophosphorus reagents as well as β-diketones as co-solvent. From the investigation of effects of various operating conditions on extraction efficiency, pressure of 200 atm, temperature of 333 K, CO_2 flow rate of 2 mL min^{-1}, 20 minute static period followed by 20 minute of dynamic extraction was found to be optimum. The solubility of metal complex was found to have a direct proportionality with the extraction efficiency. Also, the extraction efficiency was found to be a function of density of SCF and volatility of metal complex from the pressure and temperature variation study.

Highest extraction efficiency was observed with TOPO (0.2 M) dissolved in methanol. The extraction efficiency was found to be 70 %. Some correlation has been observed between extraction efficiency and structure of organophosphorus reagents: (i) Between phosphates and phosphine oxides, if P was attached to aliphatic hydrocarbon, the extraction efficiencies were comparable e.g. TBP and TBPO. If P was attached to aromatic ring, extraction efficiency was higher in phosphine oxides e.g. TPP and TPPO, (ii) Among phosphates, if aliphatic group attached to P, was replaced by aromatic group, then extraction efficiency decreased e.g. TBP and TPP, (iii) Among the phosphine oxides, higher the aliphatic chain length attached to P, higher was the extraction efficiency e.g. TOPO and TBPO, (iv) In case of phosphine oxides, if phenyl group was attached to P i.e. TPPO then extraction efficiency was intermediate to TOPO and TBPO.

In the study of combination of organophosphorus reagents, for TBPO and TPP (with TBP) enhancement in extraction efficiency was observed. Whereas for TOPO and TPPO there was no enhancement in extraction efficiency. Solvents have been found to affect the extraction efficiency. For alcohols extraction efficiency has decreased with increasing aliphatic chain length. Methanol was found better than carbon tetrachloride. With TOPO as co-solvent maximum extraction efficiency has been observed when methanol was employed as solvent.

Various β–diketones viz. AA, TFA, HFA, TTA and FOD were evaluated as chelating agents for the supercritical fluid extraction of thorium from tissue paper matrix. Thorium extraction efficiency was higher in in-situ chelation mode than online chelation mode. Combination of TBP and β-diketones was found to be more effective. The enhancement in combination mode was probably due to adduct formation. In online, in-situ chelation mode and in combination, the observed trend of extraction efficiency was TTA > FOD > HFA > TFA > AA. The observed trend was assigned to the degree of fluorination in the side arm of the β-diketones. Highly linear correlations were observed between extraction efficiency and degree of fluorination in the side arm of β-diketones in all the three modes of extraction. The correlation coefficients were better than 0.99. The fluorination influences the extraction efficiency in two domains. Firstly by enhancing the solubility in SC CO_2 and secondly by enhancing the chelation ability with Th. Under supercritical conditions there exists specific interaction between C-F bond and CO_2 molecules. Increase in degree of fluorination leads to enhanced number of C-F ….. CO_2 interactions thereby increasing the solubility of free β-diketones as well as Th-chelates. β-diketones exist as equilibrium mixture of keto and enol forms due to tautomerism. Enol form is stablised due to the existence of a special type of very strong hydrogen bonding viz. Resonance-Assisted Hydrogen Bonding (RAHB). The increase in stability with increasing fluorination is due to stablization of enol form by electron-withdrawing fluorine substituents through enhanced electron delocalization in the intramolecular RAHB. In SC CO_2 enol formation is favoured. The enol form dissociates into enolate ion which chelates with thorium. Also electron with drawing fluorine substituents facilitate the removal of labile H atom from enol ring promoting thorium chelation. The highest extraction efficiency was observed with TTA indicating that thenoyl group is responsible for enhanced extraction efficiency. There exist scope for further investigation to understand the role played by aromatic thenoyl group.

CHAPTER 6

DISSOLUTION AND SUPERCRITICAL FLUID EXTRACTION OF URANIUM FROM SOLID URANIUM COMPOUNDS

6.1 INTRODUCTION

Uranium dioxide is employed as fuel in boiling water reactors (BWR), pressurized water reactors (PWR) and pressurized heavy water reactors (PHWR) all over the world. Clustered tubes containing high density UO_2 pellets are loaded in the reactor. The fuel fabrication sheet adopted in India is given in Fig. 6.1. In India, the UO_2 powder is obtained from ammonium diuranate (ADU) process. This powder is not suitable for direct pelletisation and fabrication involves a pre-compaction step. The precompact pellets are crushed to large size granules. These granules are compacted into cylindrical pellets termed as green pellets. The green pellets, in turn, are sintered to achieve high density. The sintered pellets are encapsulated in zircaloy tubes (81). Solid waste is being generated at various stages of fuel fabrication. Uranium needs to be recovered from the solid waste.

Study on the SFE of uranium from nitric acid medium employing tri-n-butyl phosphate (TBP) as complexing agent has been carried out (chapter 3). An alternative and attractive method is based on direct dissolution and extraction of uranium from solid uranium compounds (82-84). Recent reports show that the adduct of TBP and nitric acid (TBP-HNO_3 adduct) (85) is capable of dissolving uranium oxides. $UO_2(NO_3)_2.2TBP$ thus formed could be extracted into SC CO_2. There have also been attempts to dissolve and extract different actinide oxides in SC CO_2 saturated with TBP-HNO_3 adduct (86-90). The possibility of dissolution of spent nuclear fuel in liquid and SC CO_2 was investigated (91).

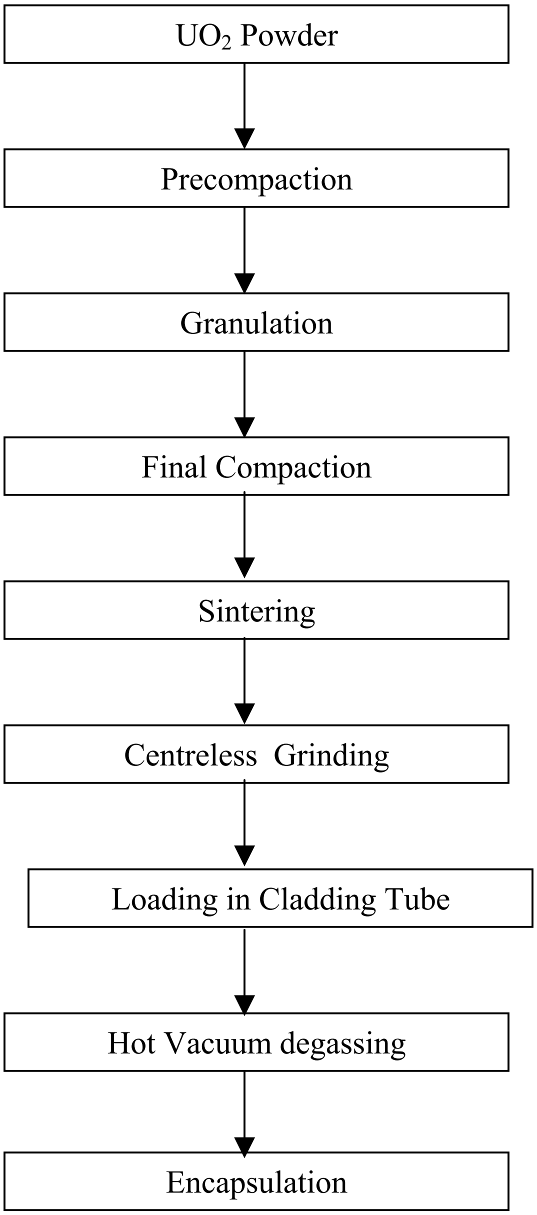


Fig. 6.1. Process flow sheet for UO_2 fuel fabrication

Present study was carried out to thoroughly investigate the feasibility employing SFE technique for the extraction of uranium directly from different solid matrices such as UO_2 (powder, granule, green pellet and sintered pellet) generated during fuel fabrication process, and from other solids like tissue paper. U_3O_8, the most stable uranium oxide which is widely used in nuclear industry as reference material for uranium analysis, was also included in the study. In fabrication process, uranium oxide loaded solid matrix is also generated. As a representative, tissue paper smeared with uranium oxides was taken for study. TBP-HNO_3 adduct was employed for dissolution thus avoiding the free nitric acid usage. Various parameters i.e. temperature, pressure, extraction time, dissolution time, volume of TBP-HNO_3 adduct and acidity of nitric acid for preparing TBP-HNO_3 adduct were found to influence the uranium extraction efficiency. Effect of addition of TBP and TTA to the SC CO_2 stream was also investigated.

6.2 METHODS AND MATERIALS

6.2.1 CHEMICAL REAGENTS

Uranium oxides were obtained from Radiometallurgy Division, BARC, Trombay. CO_2 gas employed for preparing supercritical fluid was of 99.9% purity. Tri-n-butyl phosphate (TBP) used as co-solvent was of Merck grade (for extraction analysis). Thenoyltrifluoroacetylacetone, TTA of Sigma-Aldrich grade (99%) was employed. Merck grade Arsenazo III was used for color development in the spectrophotometric determination of uranium. Sulphamic acid was of Merck grade (99%). A.R. grade nitric acid, ammonium sulphate and sodium hydroxide pellets were employed. A.R. grade methanol was used for the dissolution of TTA.

6.2.2 SUPERCRITICAL FLUID EXTRACTION PROCEDURE

TBP-HNO_3 adduct was prepared by thoroughly mixing 1:1 volume ratio of TBP and HNO_3 for one hour on a magnetic stirrer. The organic portion (TBP-HNO_3 adduct) was separated by separating funnel and used for study.

UO_2 powder, granules and U_3O_8 powder were taken as such for SFE study whereas sintered and green pellets were crushed into fine pieces by mortar and pestle. (40±4) mg of solid uranium oxide along with TBP-HNO_3 adduct was taken in the extraction vessel. After achieving the desired temperature, CO_2 was pumped into the extraction vessel until required pressure was achieved. The system was allowed to withstand the pressure and temperature conditions for certain time period (dissolution time) to ensure complete dissolution. Subsequently, at desired pressure and temperature, extraction was carried out by flowing CO_2 at constant flow rate for certain time period (extraction time) and the extract was collected in CCl_4 contained in the collection tube. In some cases, co-solvents viz. TBP/ TTA (0.2 M in MeOH) were mixed with CO_2 stream. For such cases, extraction time was followed by 10 min of flushing with SC CO_2 alone at 1mL min^{-1}. After extraction, the system was gradually depressurized to atmospheric pressure and the extraction vessel was unloaded.

The dissolution time and temperature were ascertained based on dissolution study carried out at atmospheric pressure and different temperature (323 to 353 K) with TBP-HNO_3 adduct.

For the study of extraction of solid uranium oxides from tissue paper matrix, simulated waste matrix was prepared by smearing (40±4) mg of the oxides on the tissue paper (1"x1"). This tissue paper was loaded in the extraction vessel along with TBP-HNO_3 adduct. The dissolution time was varied and optimized for different oxides keeping the extraction time fixed (as obtained from optimization study for UO_2 powder).

Uranium extraction efficiency was defined as the percentage ratio of difference of initial uranium amount taken in extraction vessel and uranium amount collected in the collection tube to the initial uranium amount in extraction vessel. Uranium thus contained in CCl_4 in the collection tube was back-extracted into aqueous phase (10% ammonium sulphate solution). Back-extraction was performed thrice with ~1:1 volume ratio of organic and aqueous phase.

Back-extraction efficiency was obtained by determining the uranium amount left unextracted in extraction vessel and uranium amount present in aqueous phase. Back-extraction efficiency was found to be (95±3) %. Uranium amount was determined spectrophotometrically (section 2.3).

For determination of acid molarity of TBP-HNO_3 adduct, 0.5 mL of the complex was shaken with 10 mL of MiliQ water followed by titration with standardized NaOH using phenolphthalein as indicator.

6.3 RESULTS AND DISCUSSION

Supercritical fluid extraction of metal ions from solid matrices could be different from the extraction from aqueous solution (chapter 3) as it involves the dissolution of the metal ions from the solid matrix. Thus, SFE of metal ions from solid matrices is a multi-step process consisting of dissolution, complexation and extraction of the metal-complex into SC CO_2. However, it is desirable if dissolution and complexation could occur preferably in a single medium, which could lead to fast kinetics and improved extraction. In the present case the single medium of TBP-HNO_3 adduct has been employed for dissolution as well as complexation. The adduct has general formula $TBP.(HNO_3)_x.(H_2O)_y$ (84). Nitric acid present in the complex oxidizes U(IV) to U(VI) forming $UO_2(NO_3)_2$. which forms $UO_2(NO_3)_2.2TBP$ with TBP.

The overall dissolution and complexation reactions of UO_2 and UO_3 in the SC CO_2 are expressed by eq.6.1, 6.2, 6.3, 6.4:

$$TBP.HNO_3 \longrightarrow TBP + HNO_3 \qquad (6.1)$$

$$UO_2 + (8/3)\, HNO_3 + 2TBP \longrightarrow UO_2(NO_3)_2.2TBP + (2/3)NO + (4/3)H_2 \qquad (6.2)$$

$$UO_2 + 4\, HNO_3 + 2TBP \longrightarrow UO_2(NO_3)_2.2TBP + 2NO_2 + 2H_2O \qquad (6.3)$$

$$UO_3 + 2HNO_3 + 2TBP \longrightarrow UO_2(NO_3)_2.2TBP + H_2O \qquad (6.4)$$

$UO_2(NO_3)_2.2TBP$ is highly soluble in supercritical CO_2. The solubility of $UO_2(NO_3)_2.2TBP$ exceeds 0.45 mol L^{-1} in SC CO_2 at 313 K and 200 atm (92).

Multiple factors are expected to influence the rate and extent of dissolution, complexation and extraction, which finally would affect the extraction efficiency. In addition to pressure and temperature, presence of nitric acid is expected to influence dissolution. Also, presence of complexing agent in SC CO_2 (TBP/TTA) should govern the extent of complexation.

6.3.1 EFFECT OF VARIOUS PARAMETERS

Various parameters affecting uranium extraction efficiency were studied and optimized. The optimization study was carried out with UO_2 powder. Dissolution study revealed that UO_2 powder was dissolvable within 5 minutes at atmospheric pressure and 323 K with 2 mL TBP-HNO_3 adduct. For the optimization study, TBP-HNO_3 adduct was prepared by using concentrated HNO_3. UO_2 powder along with 2 mL of TBP-HNO_3 adduct was taken in the extraction vessel. For SFE, dissolution time of 10 minutes was assigned to ensure complete dissolution.

6.3.1.1 Effect of Temperature

Based on our earlier experience (chapter 3), pressure was kept fixed at 150 atm and temperature was varied from 313 to 353 K. The SFE was carried out for 30 minutes by flowing SC CO_2 at 1 mL min^{-1} and extraction efficiency was calculated (Fig. 6.2).

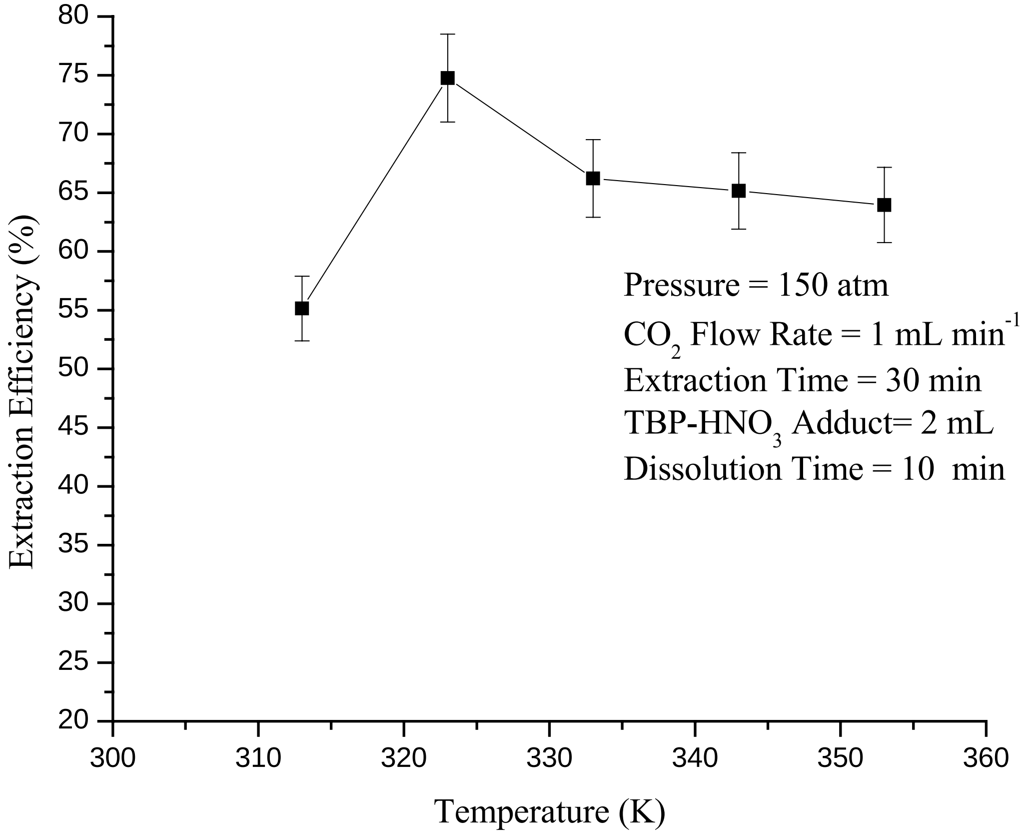


Fig. 6.2. Variation of extraction efficiency with temperature at 150 atm

(Error bars indicate uncertainty in the measurement;
standard deviation is 5 % of the value)

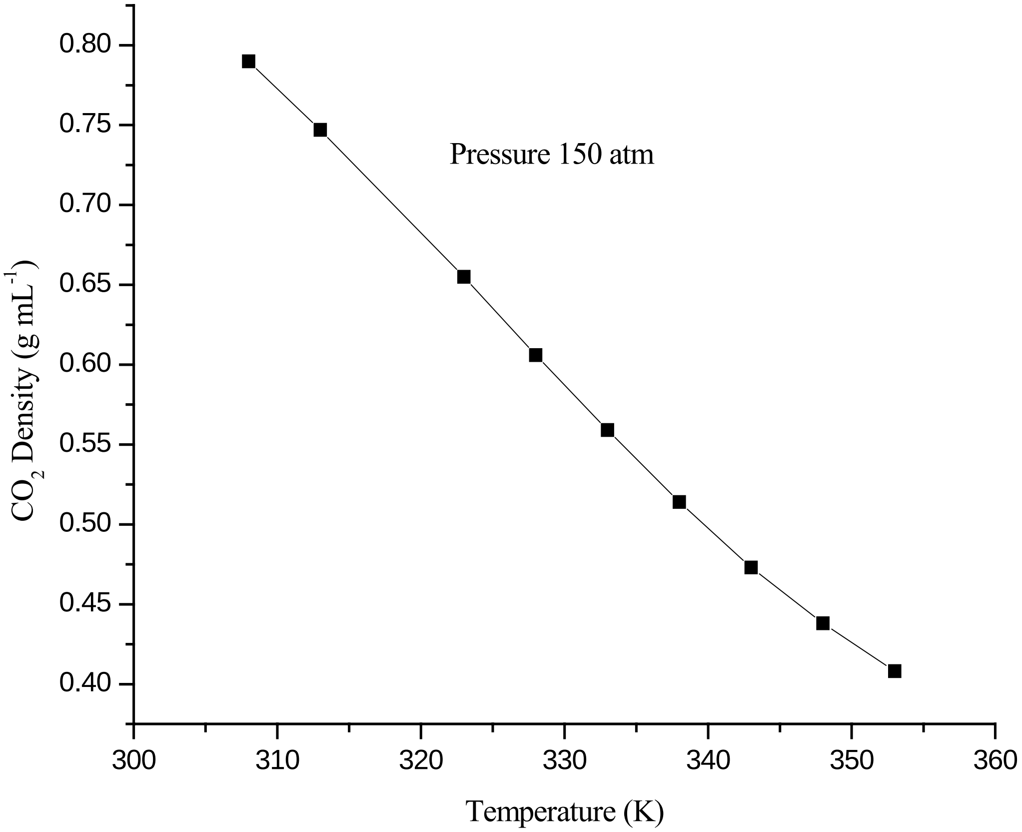


Fig. 6.3. Variation of SC CO_2 density with temperature at 150 atm

According to Chrastil's empirical correlation (26), the solubility of a solute is related to density of supercritical fluid by the eq.1.19. The density of SC CO_2 decreases with temperature as shown in Fig.6.3. The SC CO_2 density was calculated from Peng-Robinson equation of state (15). According to Chrastil's empirical correlation, solubility and hence extraction efficiency should decrease with increasing temperature. However, observed trend does not exactly tally with the trend corresponding to density decrease. Extraction efficiency increased sharply in the range 313 K to 323 K. The increase could be assigned to volatility enhancement. The volatility of $UO_2(NO_3)_2.2TBP$ increases sharply so that it not only compensates for the effect caused by density decrease but leads to an enhancement in extraction efficiency. It appears from Fig.6.2 that in the range 323 K to 353 K volatility increase is not significant and SC CO_2 density governs the extraction efficiency i.e. extraction efficiency decreased with temperature in this region. Hence, temperature was optimized at 323 K.

6.3.1.2 Effect of pressure

The effect of pressure on extraction efficiency was studied by performing SFE at 323 K for 30 minutes by flowing SC CO_2 at 1 mL min^{-1} and varying the pressure from 100 to 250 atm. The effect of pressure on extraction efficiency is depicted graphically in Fig.6.4. The density variation of SC CO_2 with pressure (at 323 K) is shown in Fig.6.5. The density of SC CO_2 was calculated from the Peng-Robinson equation of state (15). As extraction efficiency is directly proportional to solubility, extraction efficiency should vary in similar fashion as solubility. According to Chrastil's empirical correlation (eq. 1.19) at constant temperature (C constant) the solubility should vary similar to SC CO_2 density.

The graph of extraction efficiency versus pressure indicates that pressure variation has no significant effect on extraction efficiency in the range of 100 to 250 atm. In earlier study of SFE of uranium from acidic medium, a sharp increase in efficiency was observed in the range 100-150 atm (section 3.3.2.1). Since in both the cases the common species is $UO_2(NO_3)_2.2TBP$ complex, which is easily soluble in SC CO_2, the difference in behavior might be due to the fact that in current investigations with solid uranium oxide, $UO_2(NO_3)_2.2TBP$ is already formed in TBP-HNO_3 medium in the extraction vessel, which then gets directly extracted into SC CO_2. Thus it is envisaged that the complexation and uranium extraction occur from a single medium. Whereas in case of extraction from acidic medium, uranium is present in the aqueous medium while TBP is present in SC CO_2 which need to interact to form $UO_2(NO_3)_2.2TBP$ followed by uranium extraction into SC CO_2. This two-step process could influence the extent of uranium extraction as a function of pressure (density) of the SC CO_2.

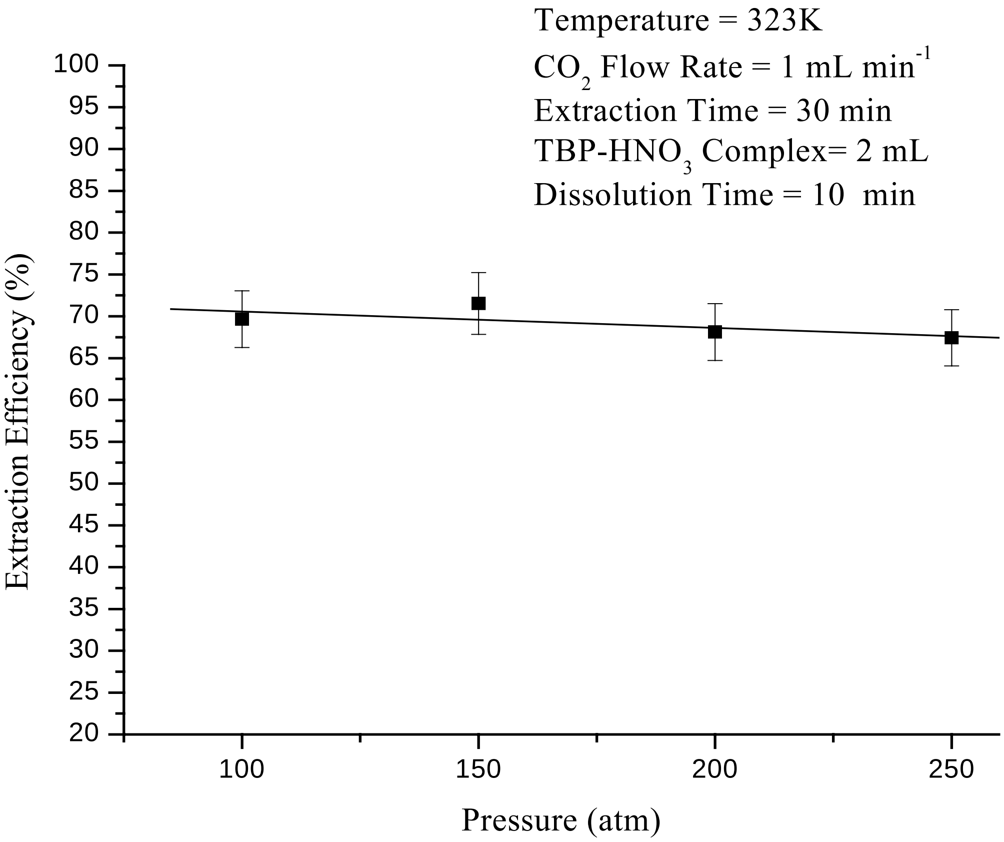


Fig.6.4. Variation of extraction efficiency with pressure at 323K

(Error bars indicate uncertainty in the measurement;
standard deviation is 5 % of the value)

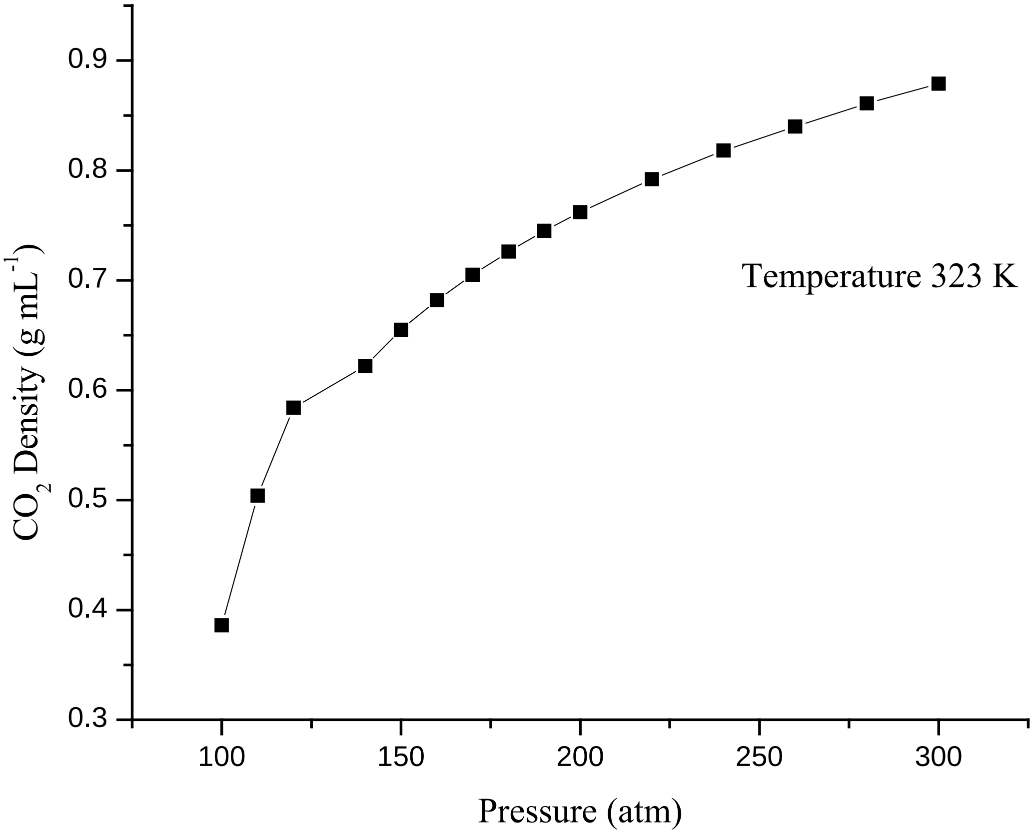


Fig.6.5. Variation of SC CO_2 density with pressure at 323 K

6.3.1.3 Effect of Extraction Time

After dissolution extraction was carried out. The effect of extraction time on extraction efficiency was studied at 150 atm and 323 K. The graph (Fig.6.6) displays that efficiency initially increased sharply with extraction time and got saturated afterwards. This might be due to diffusion of $UO_2(NO_3)_2.2TBP$ from the TBP-HNO_3 adduct into SC CO_2 phase. As diffusion depends on concentration gradient which decreases with time, efficiency is expected to be initially high, subsequently be lowered and should attain saturation afterwards. In fact, sigmoidal curve could be nicely fitted into the observed graph, having correlation coefficient of 0.9998.

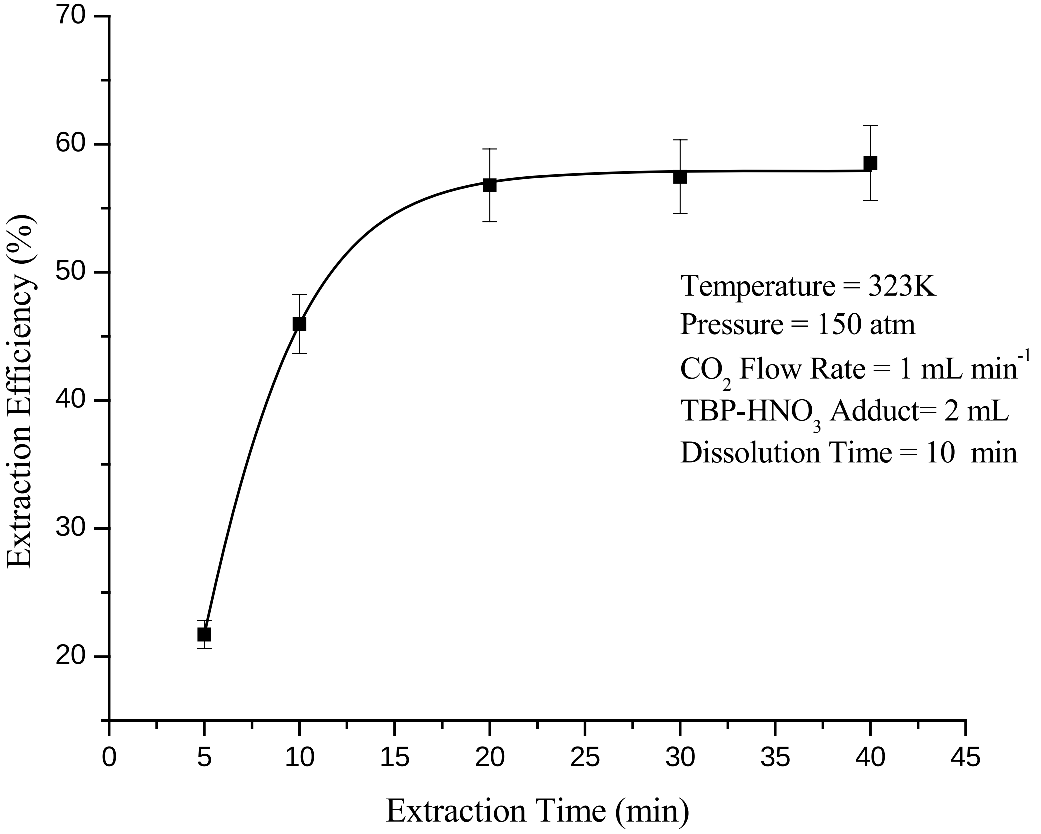


Fig.6.6.Variation of extraction efficiency with extraction time

(Error bars indicate uncertainty in the measurement;
standard deviation is 5 % of the value)

6.3.1.4 Effect of TBP-HNO$_3$ Amount

Systematic study was carried out to optimize the amount of TBP-HNO$_3$ adduct at 150 atm and 323 K. The extraction efficiency with various TBP-HNO$_3$ adduct amounts is graphically represented in Fig.6.7. SC CO$_2$ available per mL of TBP-HNO$_3$ is also represented in the same graph.

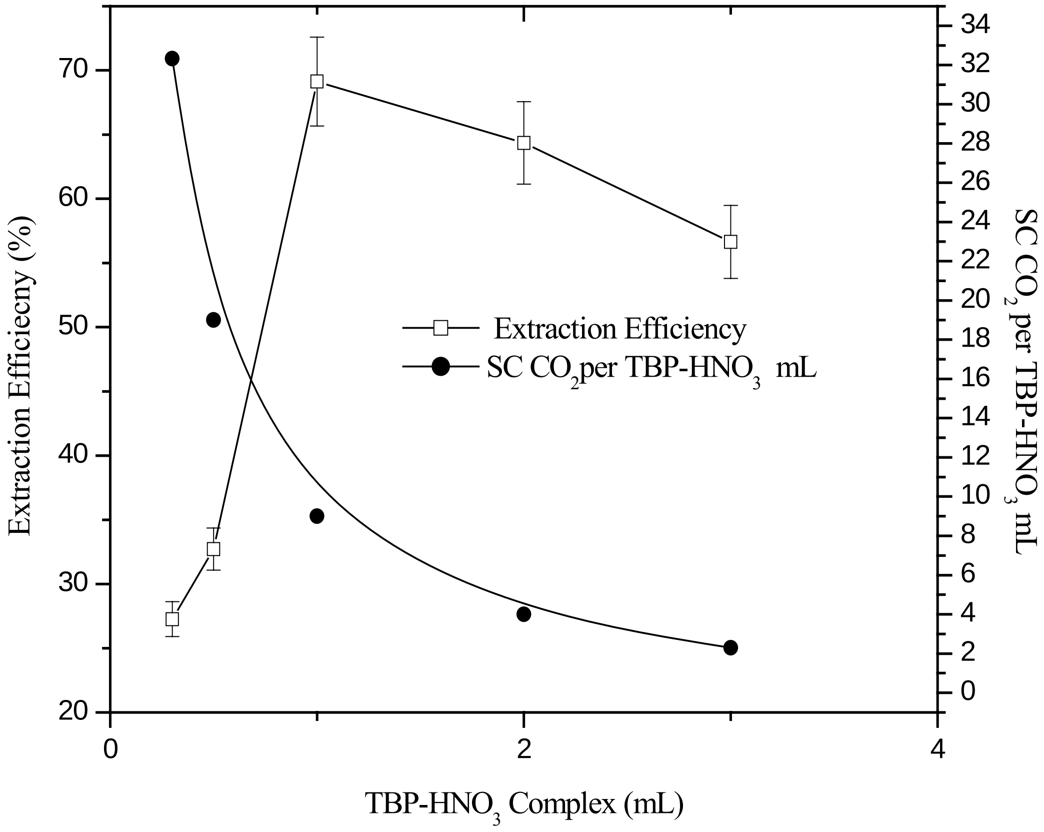


Fig.6.7. Variation in extraction efficiency with TBP-HNO$_3$ amount

(Error bars indicate uncertainty in the measurement;

standard deviation is 5 % of the value)

The efficiency initially increased sharply with TBP-HNO_3 adduct amount reached maxima at 1mL and gradually decreased afterwards. Initially sharp rise in efficiency is obvious from Le Chatelier rule i.e. as per eq.6.1, 6.2, 6.3, 6.4 higher the amount of TBP-HNO_3 adduct higher would be efficiency. However, efficiency was found to decrease gradually after 1 mL which could be explained taking into consideration the fact that with the increasing TBP-HNO_3 adduct amount, SC CO_2 volume available per mL of TBP-HNO_3 would decrease as volume of the of extraction vessel is fixed (10 mL). Hence, extraction efficiency would decrease with enhancement in amount of TBP-HNO_3 above 1 mL.

6.3.1.5 Effect of Molarity of Nitric Acid

TBP-HNO_3 adduct was prepared by shaking with nitric acid having different molarity between 1 to 16 M. The graph between extraction efficiency versus molarity of the nitric acid used for preparing TBP-HNO_3 adduct is shown in Fig.6.8.

The variation of acid molarity of TBP-HNO_3 adduct with acid molarity of nitric acid taken in aqueous phase for preparation of organic complex is shown graphically in Fig. 6.9. For 1-8 M of aqueous acidity the organic phase acidity increases sharply. Afterwards saturation was observed i.e. the extent of nitric acid loaded onto the organic phase remains almost constant for aqueous acidity above 8M. As expected from Le Chatelier rule and eq.6.2, 6.3 and 6.4 higher concentration of HNO_3 in organic complex should result in higher extraction efficiency. In fact, the trend in uranium extraction efficiency for UO_2 (Fig.6.8) is exactly identical to Fig.6.9. The observed trend in uranium extraction efficiency for U_3O_8 is also similar. The slight mismatch between the graphs for UO_2 and U_3O_8 may be assigned to the difference in number of moles of HNO_3 required for the formation of $UO_2(NO_3)_2$ for same amount of UO_2 and U_3O_8.

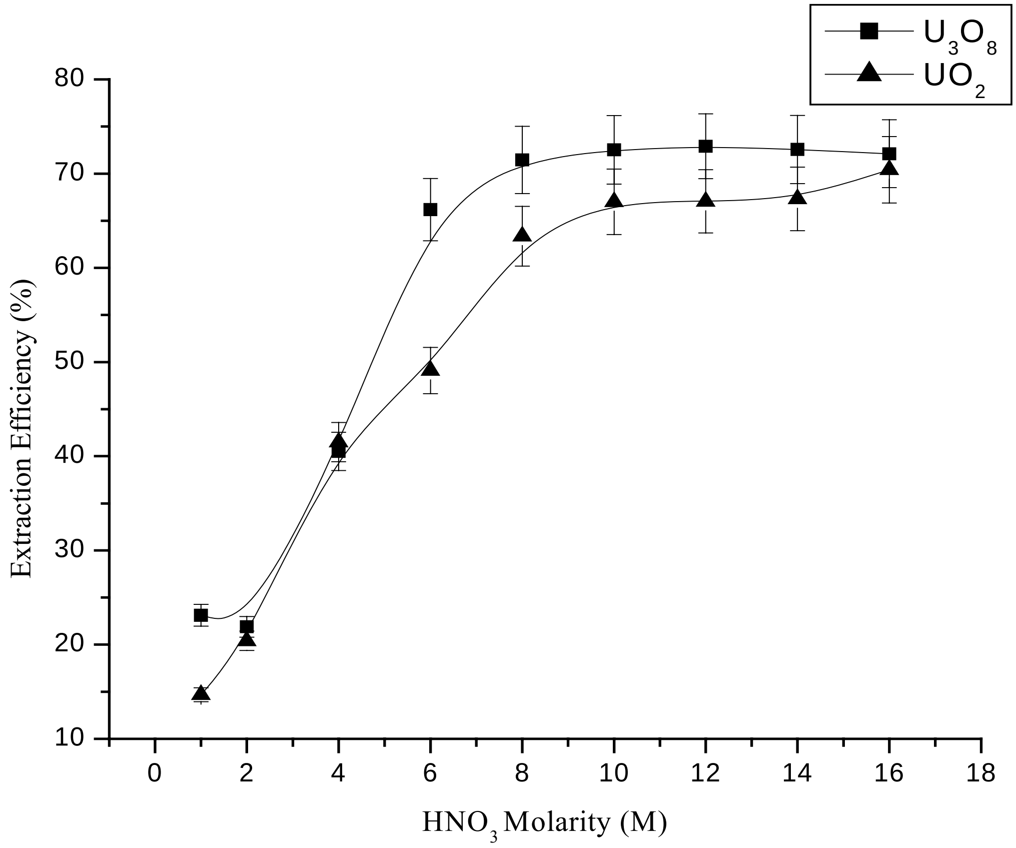


Fig.6.8. Variation of extraction efficiency with nitric acid molarity

(Error bars indicate uncertainty in the measurement;
standard deviation is 5 % of the value)

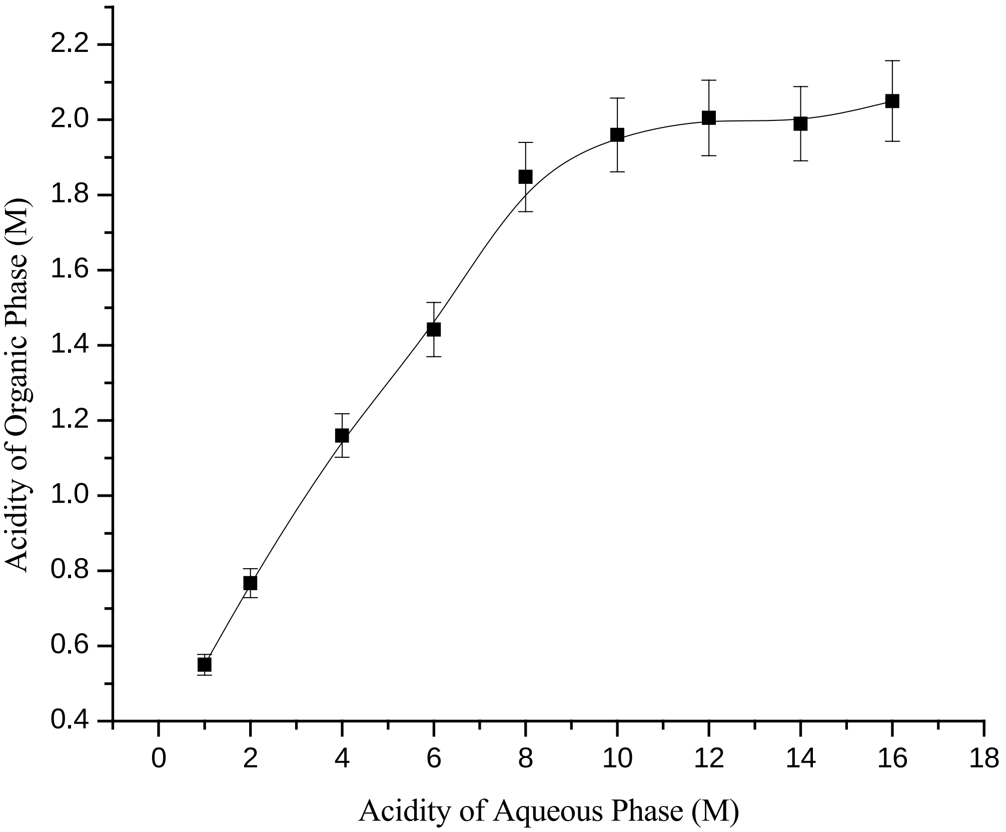


Fig.6.9. Variation of acid molarity of TBP-HNO_3 adduct with molarity of nitric acid taken in aqueous phase for preparation of organic complex

(Error bars indicate uncertainty in the measurement;
standard deviation is 5 % of the value)

6.3.1.6 Effect of TBP

In order to improve the efficiency, TBP was mixed in SC CO_2 stream during uranium extraction. Arguing on the similar lines as was done in the case of effect of nitric acid acidity, higher TBP percentage would lead to higher extent of formation of $UO_2(NO_3)_2.2TBP$ resulting in higher uranium extraction efficiency. Similar enhancement of uranium extraction efficiency with TBP percentage has also been observed (section 3.3.2.4). The effect of variation in uranium extraction efficiency with TBP percentage is depicted graphically in Fig 6.9. With addition of 2.5% TBP, 93% uranium extraction efficiency was obtained which gradually increased to 99% with addition of 20% TBP.

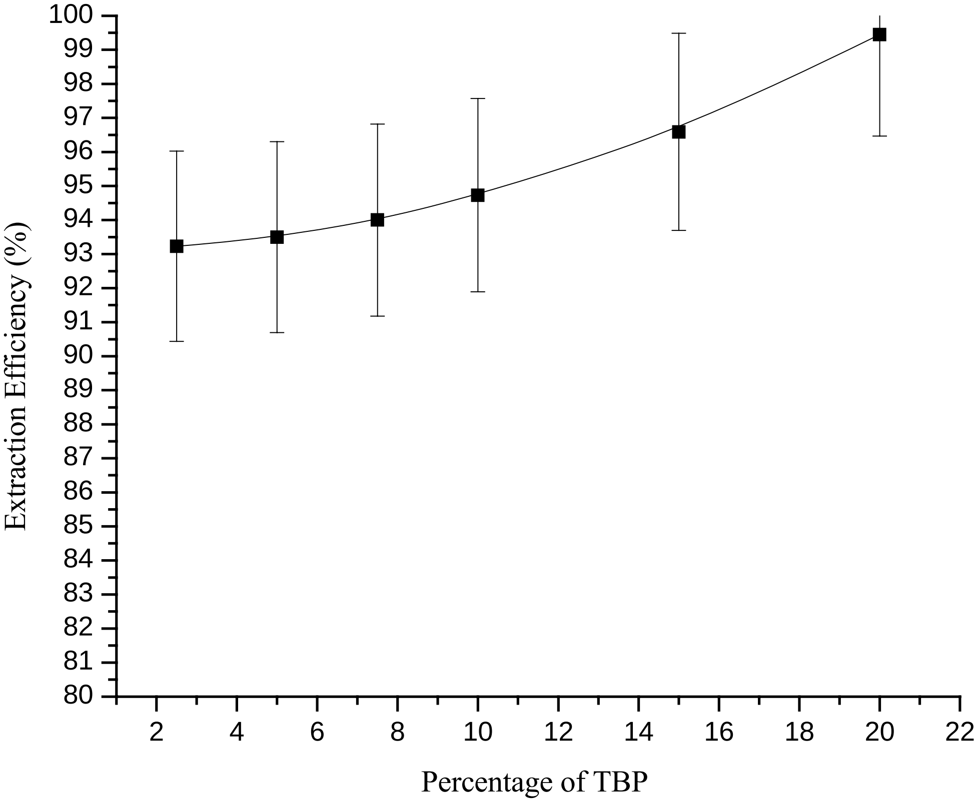


Fig.6.10. Variation in extraction efficiency with TBP percentage

(Error bars indicate uncertainty in the measurement;
standard deviation is 5 % of the value)

6.3.2 SFE OF U_3O_8, UO_2 POWDER, GRANULE, GREEN PELLET, SINTERED PELLET

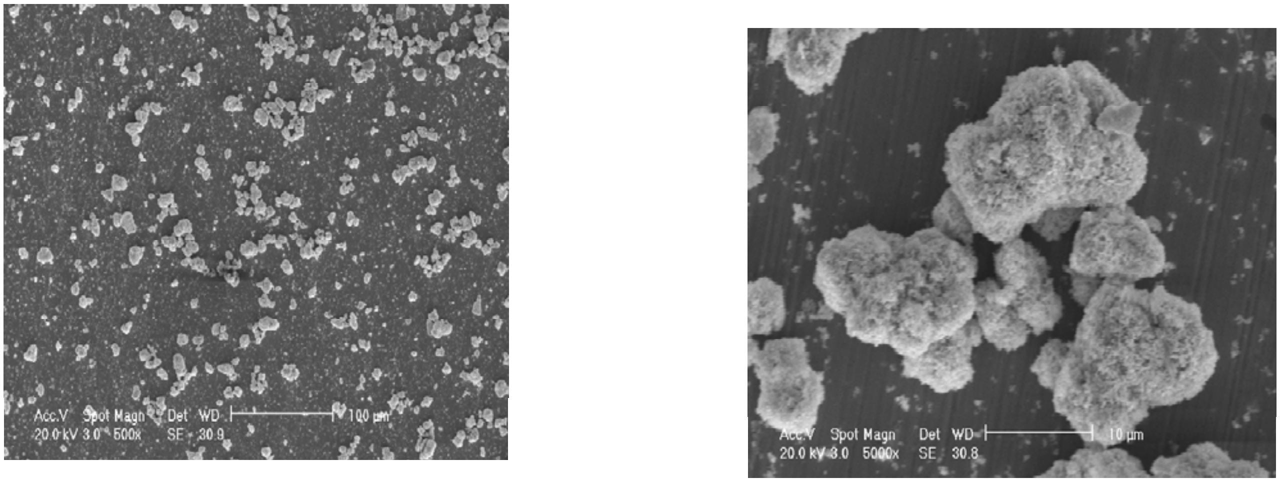
SFE consists of dissolution of solid uranium oxides in TBP-HNO_3 adduct. Dissolution time for SFE was assigned based on study at atmospheric pressure to examine the dissolution behavior of various solids. The results of study are given in Table 6.1. The microstructures of solids obtained from scanning electron microscope (SEM) are shown in Fig 6.11, which have been taken at given magnification (Magn) and accelerating voltage (Acc V). Secondary electrons (SE) are used and the detection is by wavelength dispersive (WD) mode. For each oxide, SEM has been taken at two different magnifications for better clarity and comparison.

UO_2 powder used in the study was obtained from ADU route, which is extremely fine (particle size <1 μm) having surface area in the range 2-4 m^2 g^{-1} (73). Hence, it was easily dissolvable. UO_2 and U_3O_8 powder could be easily dissolved within 5 minutes at 323 K. The granules obtained by crushing precompact have more mechanical strength and particle size of 800-1000 μm. Hence, granules took higher time i.e. 15 minutes to dissolve.

Table 6.1

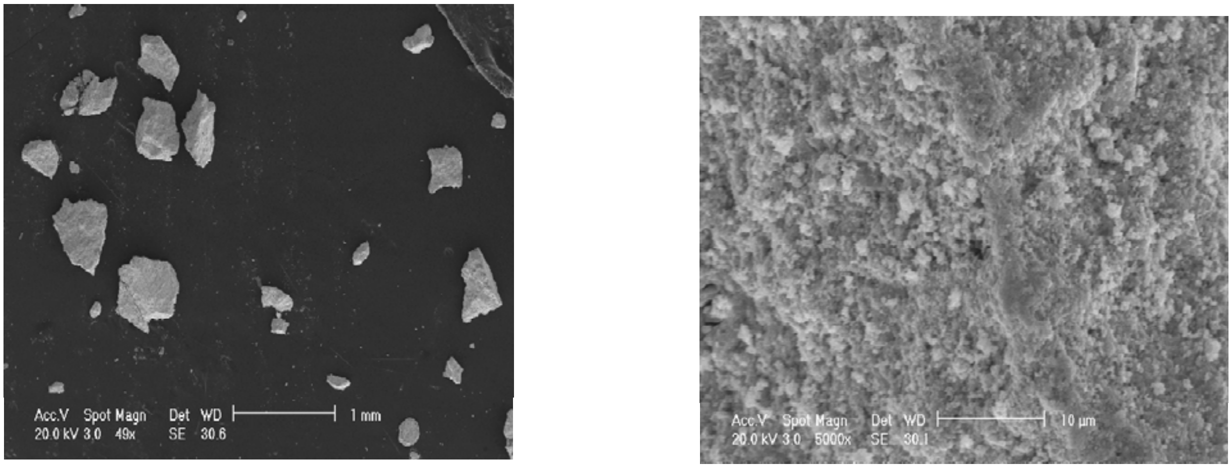
Dissolution study under atmospheric pressure conditions

Solid	**Dissolution temperature (323 K)**		**Dissolution temperature (353 K)**	
	Dissolution time (min)	**Dissolution status**	**Dissolution time (min)**	**Dissolution status**
U_3O_8 powder	5	Complete	--	--
UO_2 powder	5	Complete	--	--
UO_2 granule	15	Complete	--	--
UO_2 green pellet	50	Partial	20	Complete
UO_2 sintered pellet	50	Partial	30	Complete



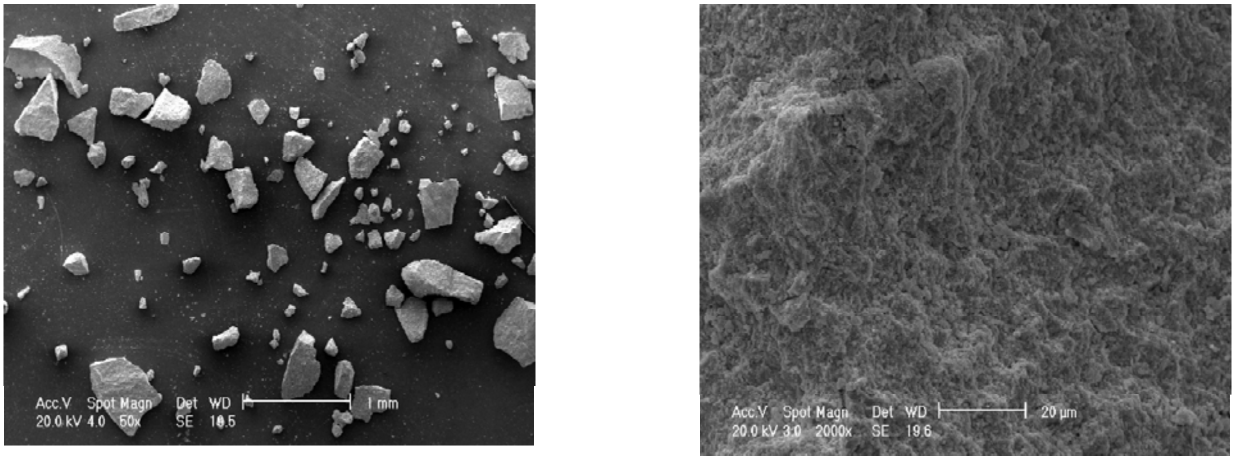
(a) (b)

UO_2 powder



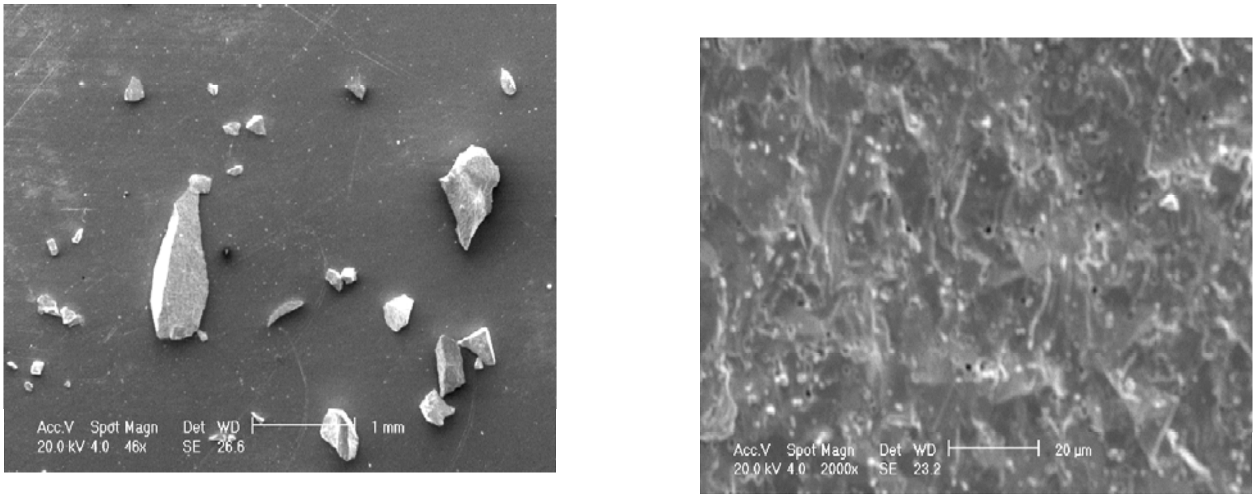
(c) **(d)**

Green UO_2 granules



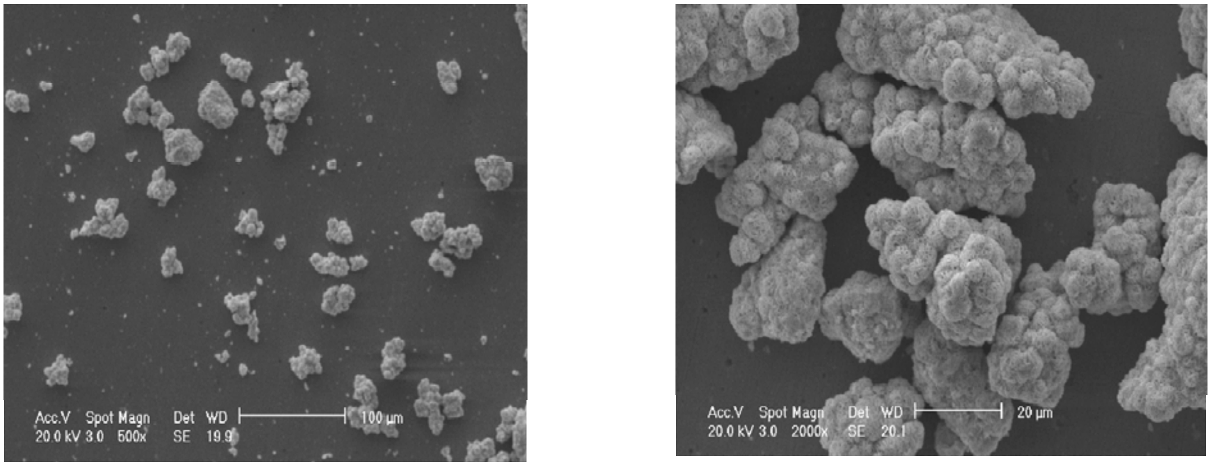
(e) (f)

UO_2 green pellet (crushed)



(g) (h)

UO_2 sintered pellet (crushed)



(i) **(j)**

U_3O_8 powder

Fig 6.11. Scanning electron microscope photographs of the different solid uranium oxides

(a), (b) UO_2 powder, (c), (d) green UO_2 granule, (e), (f) UO_2 green pellet (crushed), (g), (h)UO_2 sintered pellet (crushed), (i), (j) U_3O_8 powder

The green pellets obtained by compacting granules have got quite high strength. Green pellets have density of 40 to 55 % of theoretical density (10.96 g cm^{-3}). Sintered pellets have got still higher strength as they have 96-98 % of theoretical density. Hence, crushed powder of green pellet and sintered pellets were not dissolvable completely even after 50 minutes at 323 K. Dissolution feasibility was tested at elevated temperature of 353 K. Green pellet was dissolvable within 20 minute whereas sintered pellet within 30 minutes.

SFE was carried out under optimized conditions (Table 6.2). For UO_2, U_3O_8 powder and UO_2 granules dissolution temperature was 323 K whereas for green and sintered pellets the dissolution temperature was 353 K. It is interesting to note that with SC CO_2 alone for UO_2 and U_3O_8 powder ~70% uranium extraction efficiency was obtained (Table 6.3). With 2.5% TBP, ~93% uranium extraction efficiency was obtained. With 2.5% TTA (in methanol), for all solids nearly complete uranium extraction (99%) was obtained. TTA addition can be compared to that of using combination of TBP (in this case, TBP-HNO_3 adduct) and TTA (section 5.3.2.2). This enhanced uranium extraction efficiency with TTA might be due to adduct formation (27).

Table 6.2

Optimized parameters for SFE

Pressure	150 atm
Temperature	323 K
TBP-HNO_3 amount	1 mL
CO_2 flowrate	1 mL min^{-1}
TBP/TTA %	2.5% of CO_2 (0.025 mL min^{-1})
Extraction time	30 min
Flushing time	10 min

It is worth mentioning here that dissolution time and temperature depends on type of solid. However, once dissolution is complete uranium exists as $UO_2(NO_3)_2$ irrespective of nature of solid oxide. Hence, extraction conditions should be same for all of them. This is due to fact that after dissolution efficiency would depend upon $UO_2(NO_3)_2.2TBP$ formation and solvation into SC CO_2 . As is evident from Table 6.3, efficiency was same for all type of solids.

Table 6.3

Extraction efficiencies for different solids

Solid	**Dissolution temperature (K)**	**Dissolution time (min)**	**Extraction efficiency (%)**		
			SC CO_2	**SC (CO_2 +2.5% TBP)**	**SC (CO_2 +2.5% TTA)**
U_3 O_8 powder	323	10	72.11	91.18	98.74
UO_2 powder	323	10	70.41	93.23	98.10
UO_2 granule	323	20	--	94.92	98.44
UO_2 green pellet	353	30	--	91.80	99.26
UO_2 sintered pellet	353	40	--	94.56	98.90

(Results are mean of 3 experiments, avg. std. deviation = 4.71)

6.3.3 SFE OF SOLIDS FROM TISSUE PAPER MATRIX

Simulated tissue paper waste (prepared as described in section 6.2.1) along with 1 mL TBP-HNO_3 complex was taken in extraction vessel and was allowed to withstand 150 atm pressure and required temperature as listed in Table 4 for a given time (dissolution time). Subsequent to this the extraction was carried under optimized conditions (Table 6.2) for 30 minutes with addition of 2.5% TBP. Extraction efficiency was found to vary with dissolution time as shown graphically in Fig.6.12. ~90% extraction efficiency was obtained in 30 minutes dissolution time for UO_2 and U_3O_8 powder whereas 40 minutes dissolution time was required for UO_2 granule and green pellet. For sintered pellet ~90% extraction was achievable in 60 minute dissolution time.

Table 6.4
Extraction efficiency dependence with dissolution time for uranium SFE from tissue paper matrix with 2.5% TBP addition

Solids	**Dissolution temp. (323 K)**	**Dissolution time (min)**	**Extraction efficiency (%)**
UO_2 powder	323 K	10	52.80
		20	85.55
		30	92.80
		40	91.83
U_3O_8 powder	323 K	10	71.56
		20	86.24
		30	89.03
		40	90.92
UO_2 granules	323 K	20	87.25
		30	91.96
		40	93.86
UO_2 green pellet	353 K	20	82.41
		30	84.07
		40	94.05
		50	92.96
UO_2 sintered pellet	353 K	30	69.76
		60	89.75

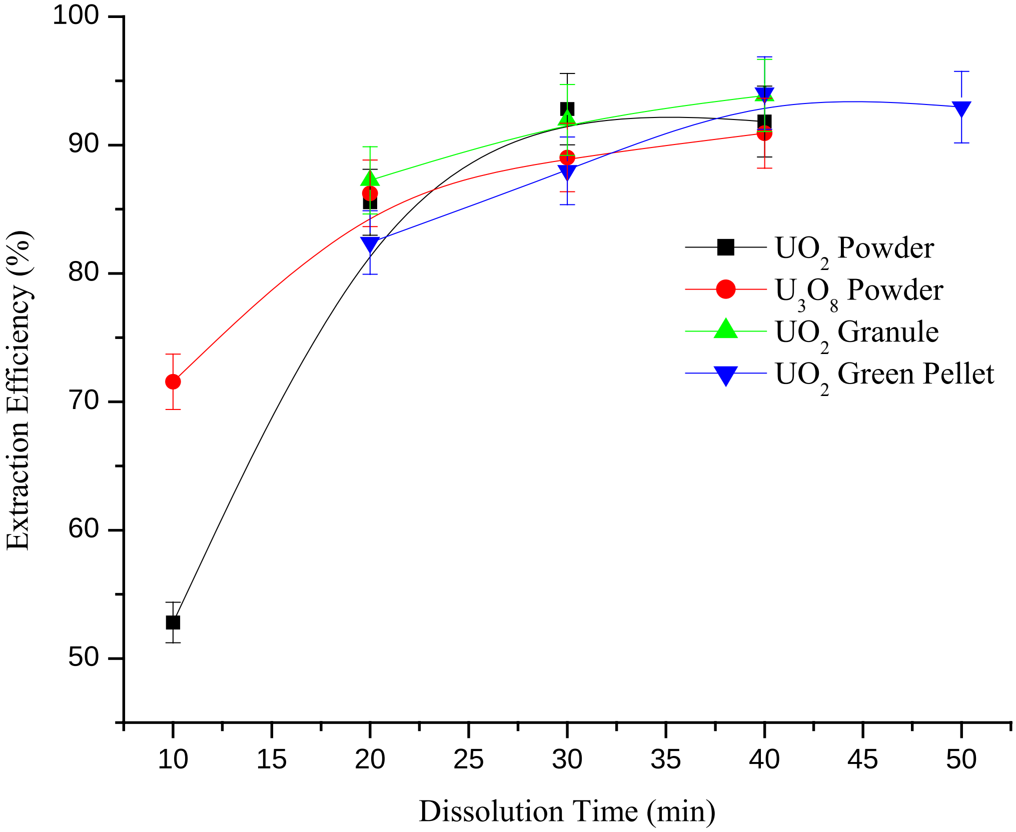


Fig.6.12. Variation of extraction efficiency with dissolution time

(Error bars indicate uncertainty in the measurement;
standard deviation is 5 % of the value)

Table 6.5

Extraction efficiencies for solids from tissue paper

Solid	**Dissolun. temp. (K)**	**Dissolun. time (min)**	**Extraction efficiency (%)**
			SC CO_2 + 2.5 % TTA
U_3O_8 powder	323	30	98.13
UO_2 powder	323	30	98.63
UO_2 granule	323	40	99.48
UO_2 green pellet	353	40	98.80
UO_2 sintered pellet	353	60	97.23

(Results are mean of 3 experiments, avg. std. deviation = 4.81)

After ascertaining the dissolution time required for different solids, extraction was carried out with 2.5 % TTA (Table 6.5). As against ~90% extraction efficiency obtained with 2.5% TBP addition, nearly complete extraction (~99%) was achievable with 2.5% TTA addition.

6.4. CONCLUSIONS

Study on supercritical fluid extraction of uranium from various UO_2 solids generated at various stages of nuclear fuel fabrication was carried out. U_3O_8 powder was also included in the study. The solids could be dissolved in TBP-HNO_3 adduct thus avoiding the use of free acid. The process minimizes the generation of liquid waste. Prior to SFE, the dissolution time and temperature for different solids was ascertained under atmospheric pressure condition by visual examination. UO_2 powder obtained from ADU route is extremely fine (<1 μm). The granules have more mechanical strength and size 800-1000 μm. At 323 K UO_2 and U_3O_8 powder were easily dissolvable within 5 minutes and UO_2 granules took 15 minutes for dissolution. The green pellets have got higher strength and density viz. 40 to 55 % of theoretical density (10.96 g cm^{-3}). Sintered pellets have got still more strength as they have 96-98 % of theoretical density. Green pellet and sintered pellet were dissolvable at elevated temperature i.e. 353 K. Green pellet was dissolvable within 20 minutes whereas sintered pellet within 30 minutes.

Temperature was found to affect extraction efficiency. Efficiency increases upto 323 K which was assigned to volatility enhancement. Efficiency decreased in the range 323 K to 353 K, which was assigned to decrease in SC CO_2 density. Extraction efficiency was found to remain uninfluenced to pressure variation. Extraction efficiency varied sharply upto 1 mL with TBP-HNO_3 amount, as according to Le Chatelier rule higher TBP amount would cause higher formation of $UO_2(NO_3)_2.2TBP$ leading to higher efficiency. The gradual decrease afterwards was assigned to decrease in amount of SC CO_2 per mL of TBP-HNO_3. The acidity of nitric acid used for preparing TBP-HNO_3 organic complex also affected extraction efficiency. The acidity of the TBP-HNO_3 organic phase was found to increase with the acidity of nitric acid used for preparing TBP-HNO_3 adduct from 1-8 M and saturation was observed afterwards. According to Le Chatelier rule, higher acidity of TBP-HNO_3 adduct should lead to higher extraction efficiency. This was indeed observed for UO_2 and U_3O_8 powder. The extraction efficiency increased with the acidity of nitric acid used for TBP-HNO_3 preparation initially which was followed by saturation.

Efficiency increased sharply with extraction time upto 20 minutes and got saturated afterwards. Under optimized conditions i.e. 323 K, 150 atm, 1 mL SC CO_2 flow rate, 1 mL TBP-HNO_3 and 30 minutes extraction time for UO_2 and U_3O_8 powder only ~ 70% extraction was obtained. With addition of 2.5% TBP efficiency was found to improve to 93% and upto 99% with the addition of 20% TBP. The efficiency was independent of type of solid. For all solids ~ 93% extraction efficiency was obtained with 2.5% TBP, whereas nearly complete (~99%) extraction efficiency was obtained with 2.5% TTA which might be due to adduct formation.

Uranium was extracted from simulated tissue paper matrix containing solid uranium oxides by 2.5 % TBP. Efficiency increased with dissolution time. ~90% extraction efficiency was obtained for UO_2 and U_3O_8 powder for 30 minutes dissolution time and for UO_2 granule and green pellet for 40 minutes dissolution time. Sintered pellet took 60 minutes of dissolution time for ~90% extraction efficiency. When extraction was carried out with 2.5 % TTA, nearly complete extraction (~99%) was achievable for all the solids contained in tissue paper. The study thus provides a basis for uranium recovery from solids generated during uranium oxide based fuel fabrication process.

SUMMARY

The thesis deals with studies on the supercritical fluid extraction of uranium and thorium from various matrices. The studies described not only establish the conditions for highest efficiency of SFE, it attempts to look into the basic reasons for the nature of parametric dependence. Various classes of complexing agents were assessed and any logical correlation with the structural feature was probed. The studies center around the objective of dealing with systems relevant to nuclear industry with an aim of minimizing the usage of complexing agents and avoiding acid treatment.

SUPERCRITICAL FLUID EXTRACTION OF URANIUM FROM NITRIC ACID MEDIUM EMPLOYING TBP AS CO-SOLVENT

Investigations on the effect of various parameters on the SFE of uranium from nitric acid medium employing TBP provided an insight for understanding the fundamental aspects of SFE process. One of the interesting observations was made while analyzing the effect of temperature on extraction efficiency at near critical density but temperature and pressure conditions far off from criticality. This study of interdependence of various parameters aided in arriving at condition for near complete extraction of uranium. Under optimised conditions (150 atm, 333 K, 1 mL/ min CO_2 flowrate, 10 % co-solvent, 7 M nitric acid and 30 minute dynamic extraction time) extraction efficiency was found to be (98 ± 2)% . Also, (100 ± 1) % mass balance was observed. 30 minutes dynamic extraction mode was found equivalent to 40 minutes static mode. Online complexation mode was more efficient than in-situ mode.

SUPERCRITICAL FLUID EXTRACTION OF URANIUM FROM NITRIC ACID MEDIUM EMPLOYING CROWN ETHERS

Feasibility was established for the SFE of uranium employing various crown ethers from nitric acid medium. Key strategy was to employ CO_2phillic fluorinated

HPFOA for providing counter ion. Pressure, temperature, nitric acid molarity, uranium amount, extraction time were found to affect extraction efficiency. Pressure of 200 atm and temperature of 323 K were found to be optimum. The observed trend in efficiency for benzo substituted crown ethers was: dibenzo-24-crown-8 > dibenzo-21-crown-7 > dibenzo-18-crown-6; reflecting ring size dependence. The enhancement was the combined effect of cavity size and number of ether oxygen. The trend in 18-crown-6 series was: ditertiarybutyldicyclohexano-18-crown-6>ditertiarybutyldibenzo-18-crown-6> dicylohexano-18-crown-6 > dibenzo-18-crown-6; which could be explained on the basis of the fact that electron withdrawing substituents (benzo group) reduce the basicity whereas electron donating substituents (tertiary butyl group) increase the basicity of ether oxygen. Efficiency increased with molarity of nitric acid upto 2M and decreased afterwards due to co-extraction of crown-nitric acid complex. Uranium: crown: HPFOA mole ratio influenced extraction efficiency, having optimum value at 1:10:100. A combination of 20 minutes of steady time followed by 20 minutes of extraction time was found to be optimum. Efficiency was also affected by uranium amount, having maximum for 100 µg. Under optimized conditions with ditertiarybutyldicyclohexano-18-crown-6 the efficiency was found to be (86 ± 5) %.

SUPERCRITICAL FLUID EXTRACTION OF THORIUM FROM TISSUE PAPER MATRIX EMPLOYING ORGANOPHOSPHORUS REAGENTS AND β-DIKETONES

For the SFE of thorium from tissue paper matrix investigations on effect of pressure, temperature, CO_2 flow rate and extraction time revealed quite different conditions for highest extraction from that of metal ion extraction from nitric acid medium. Pressure of 200 atm, temperature of 333 K, CO_2 flow rate of 2 mL min^{-1}, 20 minute static period followed by 20 minutes of extraction were found to be optimum. Evaluation of various organophosphorus reagents (TBP, TOPO, TPP, TPPO, TBPO) revealed dependence of extraction efficiency on the structural feature of the reagent. Under optimum conditions employing various organophosphorus reagents as co-solvent, extraction efficiency indicated the trends: (i) Among phosphates, if aliphatic group attached to P was replaced by aromatic group, then extraction efficiency decreased e.g. TBP (53 ± 8 %) and TPP (39 ± 5 %) (ii) Among the phosphine oxides, higher the aliphatic chain length attached to P, higher was the extraction efficiency e.g. TOPO (68 ± 4 %) and TBPO (50 ± 9 %) (iii) In case of phosphine oxides, if phenyl group was attached to P i.e. TPPO (59 ± 15 %) then extraction efficiency was intermediate to TOPO and TBPO (iv) Between phosphates and phosphine oxides, for aliphatic hydrocarbons, the extraction efficiencies were comparable e.g. TBP and TBPO. For aromatic ring, extraction efficiency was higher in phosphine oxides e.g. TPP and TPPO. Both TBPO and TPP have shown higher extraction efficiency in combination with TBP. The solvents dissolving oraganophosphorus reagents were found to influence extraction efficiency. The extraction efficiency was found to decrease slightly with increasing aliphatic chain length of the alcohol. The maximum extraction efficiency was obtained with 0.2M TOPO in methanol where thorium was extractable with 68 ± 4 % efficiency.

Various β-diketones viz. acetylacetone (AA), trifluoroacetylacetone (TFA), hexafluoroacetylacetone (HFA), thenoyltrifluoroacetylacetone (TTA) and heptafluorobutanoylpivaoylmethane (FOD) were evaluated as chelating agents for the supercritical fluid extraction of thorium from tissue paper matrix. In-situ chelation mode was found to be more effective than online chelation mode. Combination of tributyl phosphate (TBP) and β-diketones further enhanced the extraction efficiency. However, the extraction efficiency trend observed in online, in-situ chelation mode as well as with the combination of TBP and β-diketones was TTA > FOD > HFA > TFA > AA. A correlation was observed between extraction efficiency and degree of fluorination in the side arm of β-diketones. This could be attributed to the fact that in supercritical CO_2 higher fluorination results in higher percentage of enol content, greater dissociation into enolate ion of β-diketones and higher solubility and stability of β-diketones as well as Th-β-diketone chelates. Highest extraction efficiency with TTA was probably due to the presence of aromatic thenoyl group.

DISSOLUTION AND SUPERCRITICAL FLUID EXTRACTION OF URANIUM FROM SOLID URANIUM COMPOUNDS

Direct dissolution and uranium extraction from solid uranium oxides obtained from various stages of fuel fabrication could be successfully carried out. TBP-HNO_3 adduct was employed for dissolution thus avoiding free acid usage. Conditions for highest efficiency was arrived at. Temperature of 323 K, pressure of 150 atm, 1 mL TBP-HNO_3 adduct and 30 minute extraction time was found to be optimum. U_3O_8 and UO_2 powder were dissolvable within 5 minutes and UO_2 granules within 15 minutes under atmospheric pressure and 323 K temperature. Green and sintered pellet were dissolvable within 20 and 30 minutes respectively at 353 K. ~70% extraction efficiency was obtained on extraction with SC CO_2 alone which improved to 90% with the addition of 2.5% TBP in SC CO_2 stream. Extraction efficiency was found to vary linearly with TBP%, nearly complete extraction (~99%) was observed with 20% TBP. Also, nearly complete extraction was achievable with addition of 2.5 % TTA. Uranium was extracted from simulated tissue paper waste matrix smeared with uranium oxide solids. With 2.5% TBP, ~90% extraction efficiency was observed within 30 minutes dissolution for U_3O_8 and UO_2 powder. UO_2 granule and green pellet required 40 minutes whereas for sintered pellet 60 minutes of dissolution was required. Nearly complete extraction was achievable with addition of 2.5 % TTA.

FUTURE DIRECTIONS:

The studies depict the feasibility of several potential applications of Supercritical Fluid Extraction in nuclear industry. There is an enormous potential for this technique in the back-end of nuclear fuel cycle for the recovery of plutonium as well as valuable fission products like cesium, strontium, technetium etc. Future studies are envisaged for the upgradation of the extraction processes from laboratory scale to pilot and subsequently to plant scale, graduation towards the continuous, countercurrent mode of extraction from the batch mode and development of online back-extraction process subsequent to SFE. Also, once the conditions are standardized for inactive samples, studies should be directed towards development of capability for SFE of active samples.

REFERENCES

1. I. D. Wilson, Encyclopedia of Separation Science, Academic (2000).
2. D.A. Skoog, D.M. West, F.J. Holler, S.R. Crouch, Fundamentals of Analytical Chemistry, Thomson Brooks/ Cole (2004).
3. A.I. Vogel, Textbook of Quantitative Chemical Analysis, Pearson Education (2006).
4. J. Rydberg, M. Cox, C. Musikas, G.R. Choppin, Solvent Extraction Principles and Practice, Marcel Dekker (2004).
5. Advanced Separation techniques for Nuclear Fuel Reprocessing and Radioactive Waste Treatment, Report, Woodhead Publishing (Aug 2009).
6. C. Cagniard de la Tour, Ana. Chim. 22 410 (1822).
7. T. Andrews, Proc. R. Soc. London 24 455 (1875-1876).
8. J.B. Hannay, J. Hogarth, 1879. Proc. Royal Soc. London 29 324 (1879).
9. J. Lovelock, Private communication quoted in W. Bertsch, thesis, University of Houston, Texas (1958).
10. E. Klesper, A. H. Corwin and D. A. Turner, J. Org. Chem., 27 600 (1962)
11. K. E. Laintz, C. M. Wai, C.R. Yonker and R .D. Smith, Anal. Chem., 64 2875 (1992).
12. Y. Lin, R. D. Brauer, K.E. Laintz and C. M. Wai, Anal. Chem.,65 2549 (1993).
13. Y. Lin, C. M. Wai, F. M. Jean and R. D. Brauer, Environ. Sci. Technol., 28 1190- (1994).
14. M. A. Mchugh, V.J. Krukonis, Supercritical Fluid Extraction Principles and Practice, Butterworth-Heinmann (1994).
15. M. Mukhopadhyay, Natural Extracts using Supercritical Carbon Dioxide, CRC press (2000).
16. E. Kiran, P.G. Debenedetti, C.J. Peters, Supercritical Fluids Fundamentals and Applications, Kluwer Academic Publishers (1998).
17. C.A. Colina, K.E. Gubbins, Chem. Eng. Edu., 236-240 (Summer 2003).
18. G. Afrane, E.H. Chimowitz, Fluid phase Equilibria, 111 213 (1995).
19. C. Erkey, G. Madras, M. Orejuela, A. Akgerman, Environ. Sci. technol., 27 1225

(1993).

20. E.J. Beckmann, J. Supercritical fluids, 28 121 (2004).
21. C. Erkey, J. of Supercritical Fluids, 17 259 (2000).
22. C.M.Wai and S. Wang, Journal of Chromatography, 785 369 (1997).
23. N. G. Smart, T. Carleson, T. Kast, A. A. Clifford , M. D. Burford , C. M. Wai, Talanta, 44 137 (1997).
24. A.F Laglante, B. N.Hansen, T.J. Bruno, R.E. Sivers, Inorg. Chem., 34 5781 (1995).
25. W. Cross, A. Akgerman, C. Erkey, Ind. Eng. Chem. Res., 35 1765 (1996).
26. J. Chrastil, J. Phys. Chem., 86 3016 (1982).
27. P. Kumar, A. Pal, M.K.Saxena, K.L. Ramakumar, BARC Report No. BARC/2006/E/009, (2006).
28. Z. Marczenko, M. Balcerzak, Separation, Preconcentration and Spectrophotometry in Inorganic Analysis, Elsevier (2000).
29. S. B. Savvin, Talanta, 8 673 (1961).
30. Y. Lin, N.G.Smart, C.M. Wai, Environ. Sci. Technol., 29 2706 (1995).
31. Y. Meguro, S. Iso, H. Takeishi, Z. Yoshida, Radiochimic. Acta, 75 185 (1996).
32. Y. Meguro, S. Iso, H. Takeishi, Z. Yoshida, Anal. Chem., 70 1262 (1998).
33. Y. Meguro, S. Iso, H. Takeishi, Z. Yoshida, Anal. Chem., 70 774 (1998).
34. A. A. Clifford, S. Zhu, N. G. Smart, Y. Lin, , C. M. Wai, Z. Yoshida, Y. Meguro, S. Iso, Journal of Nuclear Science and Technology, 38 (No. 6) 433 (2001).
35. S. Iso, S. Uno, Y. Meguro, T. Sasaki, Z. Yoshida, Prog. in Nucl. Energy, 37 (1-4) 423 (2000).
36. R.S. Addleman, M.J. Carrot, C.M. Wai, Anal. Chem., 72 4015 (2000).
37. C.A. Eckert, B.L. Knutson, P.G. Debenedetti, Nature, 383 313 (1996).
38. T.J. Sato, J. Inorg. Nucl. Chem., 9 188(1959).
39. R. Schurhammer, G. Wipff, J. Phys. Chem. A, 109 5208 (2005).
40. C.J. Pedersen, J. Am. Chem. Soc., 89 2495 (1967).
41. C.J. Pedersen, J. Am. Chem. Soc., 89 7017 (1967).
42. C.J. Pedersen, J. Am. Chem. Soc., 92 391 (1970).

43. C.J. Pedersen, J. Am. Chem. Soc., 92 386 (1970).
44. P.K. Mohapatra, V.K. Manchanda, Talanta, 47 1271 (1998).
45. W. Wang, J. Lin, A. Wang, Inorganica Chimica Acta, 149 151 (1988).
46. W. Wang, B. Chen, Inorganica Chimica Acta., 117 81 (1986).
47. J.P. Shukla, R.K. Singh, A. Kumar, Radiochim. Acta, 54 73 (1991).
48. J.P. Shukla, A. Kumar, R.K. Singh, Radiochim. Acta, 60 103 (1993).
49. J.P. Shukla, A. Kumar, R.K. Singh, Talanta, 40 (8) 1261 (1993).
50. A.H. Bond, M.L. Dietz, R.Chiariza, Ind. Eng. Chem. Res., 39 3442 (2000).
51. P.K. Mohapatra, V.K. Manchanda, Radiochim. Acta, 55 1993 (1991).
52. R.M. Izatt, R.E. Terry, B.L. Haymore, L.D. Hansen, N.K. Dalley, A.G. Avondet, J.J. Christensen, J. of the Am. Chem. Soc., 98 (24) 7620 (1976).
53. R.M. Izatt, K. Pawlak, J.S. Bradshaw, Chem. Rev., 91 1721 (1991).
54. W. Wang, Q. Sun, B. Chen, J. Radioanal. Nucl. Chem., 110 (1) 227 (1987).
55. P.G. Eller, R.A. Penneman, Inorg. Chem. 15(10) 2439(1976).
56. R.D. Rogers, A.H. Bond, W.G. Hipple, A.N. Rollins, R.F.Henry, Inorg. Chem. 30 2671 (1991).
57. P. Fux, J. Lagrange, P. Lagrange, J. Am. Chem. Soc. 107 5927 (1985).
58. M. Shamispur, Y. Yamini, J. Hasan, Fluid Phase Equilibria, 186 39 (2001).
59. S. Wang,S. Elshani, C.M. Wai, Anal. Chem., 67 919 (1995).
60. M. Shamispur, A.R. Ghiasvand, Y. Yamini, J. of Supercritical Fluids, 20 163 (2001).
61. R. Kumar, N. Sivaraman, E.S. Vadivu, T.G. Srinivasan, P.R.V. Rao, Radiochim. Acta, 91 197 (2003).
62. A.V. Yazdi, E.J. Beckman, J. Ind. Eng. Chem.Res., 35 3544 (1996).
63. C.M. Wai, Y. Kulyako, H.K. Yak, X. Chen, S. Lee, Chem. Commun., 2533 (1999).
64. L. Ruetsch, J. Daghero, M. Mattea, Latin American Applied Research, 33 103 (2003).
65. M. Al-Jabari, J. Sep. Sci., 27 686 (2004).
66. C. Ganguly, Indian Journal of Technology, 28 296 (1990).
67. J. Mincher, R.V. Fox, R.G.G.Holmes, A. Rebecca, Robbins, C. Boardman, Radiochim. Acta., 89 613 (2001).

68. J. Mincher, R.V. Fox, ACS symposium Series, 860 (2003).
69. Y. Zhang, B. Cangul, Yves Garrabos, C. Erkey, J. of Supercrit. Fluids, 44 71 (2008).
70. K.E. Laintz, C.M. Wai, J. of Supercrit. Fluids, 4 194 (1991).
71. A. Dardin, J.M. DeSimone, E.T. Samulski, J. Phys.Chem. B, 102 1775 (1998).
72. J.N. Spencer, E.E. Holmboe, M.R. Kirshenbaum, D.W. Firth, P.B. Pinto, Can.J.Chem, 60 1178 (1982).
73. M.M. Folkendt, B.E. Weiss, J.P. Lopez, J. Chauvel, N.S. True, J. Phys. Chem., 89 3347(1985).
74. S.L. Wallen, C.R. Yonker, C.L. Phelps, C.M. Wai, J. Chem. Soc. Faraday Trans, 93 (14) 2391(1997).
75. G. Gilli, F. Bellucci, V. Ferretti, V. Bertolasi, J. Am.Chem.Soc., 111 1023(1989).
76. V. Bertolasi, P. Gilli, V. Ferretti, G. Gilli, J. Am.Chem.Soc., 113 4917(1991).
77. C. Kersch, G.J. Witkamp, Solvent Extraction and Ion Exchange, 23 189 (2005).
78. R. B. Martin, H. Sigel, Comments Inorg. Chem., 6 285 (1988).
79. R.M. Hamdi, J.F. Bocquet, K. Chlor, C. Pommier, J. of Supercritical Fluids, 4 2775 (1992).
80. M. A. Khorassani, M.T. Combs, L.T. Taylor, 7th International symposium in supercritical fluid chromatography and extraction, Indianapolis Abstract E-03, (March 31-April 4, 1996).
81. P.R. Roy, C. Ganguly, Bull. Mater. Sci., 6 No. 5 923 (September 1984).
82. O. Tomioka, Y. Meguro, S. Iso, Z. Yoshida, Y. Enokida, I. Yamamoto, J. Nucl. Sci. and Technol., 38 No.6 461 (June 2001).
83. O. Tomioka, Y. Meguro, Y. Enokida, I. Yamamoto, Z. Yoshida, J. Nucl. Sci. and Technol. 38 No. 12 1097 (December 2001).
84. Y. Meguro, S. Isho, Z. Yoshida, O. Tomioka, Y. Enokida, I. Yamamoto, J. of Supercritical Fluids, 31 141 (2004).
85. K. Sawada, K. Uruga, T. Koyamo, T. Shimada, Y. Mori, Y. Enokida, I. Yamamoto, J. Nucl. Sci. and Technol., 42 No.3 301 (March 2005).
86. Y. Enokida, O. Tomioka, S.C. Lee, A. Rustenholtz, C.M. Wai, Ind. Eng. Chem. Res.

42 5037 (2003).

87. T.I. Trofimov, M.D. Samsonov, S.C. Lee, B.F. Myasoedov, C.M. Wai, Mendeleev Commun. 129 (2001).
88. M.D. Samsonov, T.I. Trofimov, S.E. Vinokurov, S.C. Lee, B.F. Myasoedov, C.M. Wai, J. Nucl. Sci. Technol. Suppl.3 263 (2002).
89. Y.M. Kulyako, T.I. Trofimov, M.D. Samsonov, B.F. Myasoedov, Mendeleev Commun. 6 1 (2003).
90. T.I. Trofimov, M.D. Samsonov, Y.M. Kulyako, B.F. Myasoedov, C.R. Chimie, 7 1209 (2004).
91. A. Shadrin, A. Murzin, A. Lumpov, V. Romanovsky, Solvent Extraction and Ion Exchange, 26 797 (2008).
92. M.J. Carrott, B.E. Waller, N.G. Smart, C.M. Wai, Chem. Commun. 373 (1998).

PUBLICATIONS

The work described in the thesis resulted in following publications:

Journal publications:

1. "Supercritical fluid extraction of thorium from tissue paper matrix employing organophosphorus reagents", Pradeep Kumar, **Ankita Pal**, M.K. Saxena and K.L. Ramakumar, Radiochimica Acta, 95 (2007) 701-708.
2. "Supercritical fluid extraction of uranium and thorium from solid matrices", Pradeep Kumar, **Ankita Pal**, M.K. Saxena and K.L. Ramakumar, Desalination, 232 (2008) 71-79.
3. "Study of effects of different parameters on supercritical fluid extraction of uranium from acidic solutions employing TBP as co-solvent", **Ankita Rao**, Pradeep Kumar and K.L. Ramakumar, Radiochimica Acta, 96 (2008) 787-798.
4. "Supercritical fluid extraction of thorium from tissue paper matrix employing β-diketones", Pradeep Kumar, **Ankita Rao** and K.L. Ramakumar, Radiochimica Acta, 97 (2009) 105-112.
5. "Supercritical carbon dioxide extraction of uranium from acidic solution employing crown ethers", **Ankita Rao**, Pradeep Kumar and K.L. Ramakumar, Radiochimica Acta , 98 (2010) 403-412.
6. "Separation of uranium from different uranium oxide matrices employing supercritical carbon dioxide", **Ankita Rao**, Pradeep Kumar and K.L. Ramakumar, Journal of Radioanalytical and Nuclear Chemistry, 285 (2010) 245-257.

Conference publications:

1. “Supercritical fluid extraction of thorium from tissue paper matrix”, Pradeep Kumar, **Ankita Pal**, M.K. Saxena and K.L. Ramakumar, Proceedings of symposium on Emerging trends in separation science and technology, SESTEC-2006, Mumbai.
2. “Dissolution and extraction of solid uranium compounds by supercritical fluid CO_2”, Pradeep Kumar, **Ankita Pal**, M.K. Saxena and K.L. Ramakumar, Proceedings of symposium on Emerging trends in separation science and technology, SESTEC-2006, Mumbai.
3. “Supercritical fluid extraction of uranium from nitric acid medium and tissue paper matrix”, Pradeep Kumar, **Ankita Pal**, M.K. Saxena, K.L. Ramakumar, Proceedings of symposium on Role of analytical chemistry in nuclear technology”, RACNT- 2007, Mumbai.
4. “Effects of different parameters on supercritical fluid extraction of uranium from acidic solutions”, Pradeep Kumar, **Ankita Pal**, M.K. Saxena and K.L. Ramakumar, Proceedings of Nuclear and radiochemistry symposium, NUCAR-2007, Vadodara.
5. “Supercritical fluid extraction of thorium from tissue paper matrix employing β-diketones”, Pradeep Kumar, **Ankita Rao**, K.L. Ramakumar, Proceedings of the symposium on Emerging trends in separation science and technology, SESTEC-2008, Delhi.
6. “Supercritical fluid extraction of uranium from nitric acid employing crown ether”, **Ankita Rao**, Pradeep Kumar and K.L. Ramakumar, Proceedings of the symposium on Emerging trends in separation science and technology, SESTEC-2008, Delhi.
7. “Supercritical fluid extraction of thorium from tissue paper matrix employing organophosphorus reagents”, Pradeep Kumar, **Ankita Rao**, K.L. Ramakumar, Proceedings of 10th CRSI national Symposium in Chemistry, 2008, Indian Institute of Science, Bangalore.
8. “Evaluation of various crown ethers for the supercritical fluid extraction of uranium

from nitric acid medium", Pradeep Kumar, **Ankita Rao**, K.L. Ramakumar, Proceedings of Nuclear and radiochemistry symposium, NUCAR-2009, Mumbai.

9. "Direct dissolution and supercritical fluid extraction of uranium from UO_2 powder, granule, green pellet and sintered pellet", **Ankita Rao**, Pradeep Kumar, K.L. Ramakumar, Proceedings of Nuclear and radiochemistry symposium, NUCAR-2009, Mumbai.
10. Invited talk on "Supercritical fluid extraction of uranium and thorium", K.L. Ramakumar, Pradeep Kumar, **Ankita Rao**, National symposium on Recent trends and developments in analytical instrumentation and methodologies, 2009, Hyderabad.

Report/ Newsletter:

1. "Studies on supercritical fluid extraction of uranium and thorium from solid and liquid matrix", Pradeep Kumar, **Ankita Pal**, M.K.Saxena and K.L.Ramakumar BARC Report (BARC/2006/E/009).

2. "Supercritical fluid extraction of uranium and thorium from liquid and solid matrices", Pradeep Kumar, **Ankita Rao**, K.L.Ramakumar, No. 303, April 2009.