

Supercritical Fluid Extraction of Uranium, Plutonium and Thorium:

A Review

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Abstract:

In recent decades, extraction of actinides (U,Pu,Th) employing supercritical CO₂ has drawn attention owing to its inherent potential to minimize liquid waste generation. Supercritical Fluid Extraction (SFE) offers faster extraction with fine control over extraction process by means of varying pressure, temperature conditions. Supercritical Fluids have hybrid properties of liquid and gas. Liquid like solvation and gas like diffusivity enable to penetrate deep inside solid matrix, extracting component of interest, thus capable of extraction from liquid as well as solid matrix. Metal ion is complexed with suitable organic compound, which gets soluble in SC CO₂. SC CO₂ acts as a solvent and after extraction escapes as gas leaving behind extractant. Various types of ligands such organophosphorus compounds, β-diketones, macrocyclic compounds, amides, dithiocarbamates are employed. SFE offers attractive alternative to reprocessing of spent nuclear fuel and radioactive waste. In this paper, research work carried out on the SFE of actinides (U,Pu,Th) has been reviewed.

Key Words: Supercritical CO₂, Uranium, Plutonium, Thorium, Spent Nuclear Fuel

Introduction

Extraction and purification of Uranium from various matrices is of utmost importance in the nuclear industry. Conventional techniques for the separation and purification lead to generation of significant quantity of radioactive liquid waste. Liquid waste consists of used organic solvents and acids. Managing of radioactive waste is cumbersome. In the recent decades, Supercritical Fluid Extraction (SFE) has drawn attention as promising alternative to conventional solvent extraction process owing to its interesting characteristics such as inherent potential to minimize the generation of the radioactive liquid volume and

simplification of the extraction process. Supercritical Fluids (SCF) have hybrid properties of liquid and gas. SCFs can be regarded either compressed gas or expanded liquid. Their properties such as density, diffusivity, viscosity and surface tension are intermediate of liquid and gas. The unique solvating characteristic of SCFs assume significance from extraction consideration. Extraction using supercritical fluids exploits properties of both liquid as well as gas. Liquid like solvating characteristics of SCFs enable dissolution of compounds whereas gas like diffusion characteristics enable higher and faster extraction. Rapid mass transfer and faster completion of reaction is assigned to higher diffusivity than liquids whereas due to low viscosity and surface tension, SCFs can penetrate deep inside the solid matrix, efficiently extracting compound of interest. The SFE process can be finely controlled by tuning pressure and temperature according to desired requirement. Supercritical Fluids offer faster, cleaner and efficient extraction. SFE is regarded as green and clean technology.

Supercritical Fluid was discovered by Cagniard de la Tour in 1822^{1, 2}. He observed that above certain temperature which he named critical temperature, a substance exists in single phase, neither a liquid nor gas. Below critical point, gas can be liquefied by applying pressure, above critical point, the gas cannot be liquefied however large pressure might be applied. Our view of this state, now called the "Supercritical State" (a name given to it by Thomas Andrews³, who elucidated much of its nature), has not changed much in the 200 years since its discovery. This temperature is termed as the critical temperature (T_c) and the corresponding vapor pressure as the critical pressure (P_c). The values of temperature and pressure define a critical point, which is unique to a given substance. Below critical point two phases exist (biphasic system) in equilibrium with each other, above critical point liquid and gas phases merge into single phase called Supercritical Fluid (SCF), a state of continuity. In phase diagram (Fig.1) the vapor pressure versus temperature curve represents the coexistence of two phases, liquid and gas. On moving upward on the curve by increasing pressure and temperature, the liquid goes on becoming lesser dense and the gas more denser. At the critical point, the densities of the two phases become identical, the distinction between the gas and the liquid disappears, and the curve ends at the critical point. The occurrence of SCF state can be elucidated on the basis of Van der Waals equation of state for real gases⁴. $(P + a/V^2)(V-b) = RT$; where a , b are constants. P , V , T , R are pressure, volume, temperature and gas constant respectively. The equation being is cubic in V , has three values. As shown in Fig.2, for curve-I & II, three values exist, in this region

liquefaction of the gases can occur. At higher temperatures, there exists only one real root (curve-IV), other two being imaginary. At certain intermediate temperature, all the three values of V are identical (curve-III); this temperature is called critical temperature. At this point the P-V curve exhibit a horizontal inflection, hence both the first and second derivatives of the pressure with respect to volume (at constant temperature) are zero.

Conditions of criticality for one-component fluid are ⁴⁻⁶

$$(\partial P/\partial V)_T = -(\partial^2 A/\partial V^2)_T = 0 \quad \text{————— (1)}$$

$$(\partial^2 P/\partial V^2)_T = (\partial^3 A/\partial V^3)_T = 0 \quad \text{————— (2)}$$

where 'A' is the Helmholtz free energy. Isothermal thermal compressibility $K_T = (1/\rho)(\partial\rho/\partial P)_T$ is very high near critical point (diverges at critical point). The SCF can be easily compressed near critical point. K_T is proportional to mean squared density fluctuations. Moreover K_T is proportional to $\int r^2 |g(r)-1| dr$, where $g(r)$ called pair correlation function, the ratio of local to bulk density at a distance 'r' away from a fixed molecule as origin. The divergence of K_T at critical point is assigned to the fact that $g(r)$, finite quantity becomes long ranged²⁰. The term ' ζ ', called correlation length measures the range of density fluctuations. The decay of $g(r)$ near the critical point is described by the equation⁷

$$g(r) \propto \frac{\exp(-r/\zeta)}{r} \quad \text{————— (3)}$$

For CO₂, $\zeta = 55 \text{ \AA}$ at 1 K above T_c and $\zeta = 13 \text{ \AA}$ at 10 K above T_c . The average intermolecular distance at critical density is 5.4 \AA ⁷.

This phenomenon remained a matter of curiosity and was discussed in phase diagram, did not find any application in the field of chemistry. Nearly after five decades in 1879, for the first time Hanny and Hogarth⁸ reported the solvating properties of supercritical fluids in the Royal Society meeting held at London. In meeting it was a matter of great surprise and curiosity for scientists that how gas can dissolve solids. The application of SCFs remained unnoticed for nearly 8 decades until in 1958 Lovelock⁹ recognized the potential of SCF as solvating agent and suggested their use in chromatography as mobile phase enabling faster separation. However first supercritical Chromatography equipment came into existence when in 1962 Klesper et al.¹⁰ achieved separation of nickel porphyrin from nickel mesoporphyrin dimethyl ester using dichloromethane and monochlorodifluoromethane as supercritical fluids. This triggered exponential growth in separation science using

supercritical fluids. Large number of papers all over the world were published. Seeing the large number of publications, it is not possible to include all of them. We have chosen some prominent papers and review articles. This article is mainly devoted to supercritical fluid extraction of uranium, plutonium and thorium. R.M Smith^{11, 12} comprehensively reviewed the work carried out on supercritical fluids in separation science. Limited work has been carried out on SFE of uranium all over the world. The research groups engaged in Uranium SFE can be counted in fingers. Japan, USA, Russia, United Kingdom, France, Korea and India.

Most of review work is focused on SFE of transition metal ions, somewhere uranium SFE is one among various metals. Uranium, Plutonium and Thorium are basic elements used in nuclear reactors. Minimisation of radioactive liquid waste generation is a challenging task. Hence, a need was felt of a review article dedicated to SFE of Uranium, Plutonium and Thorium. Specially reprocessing of spent nuclear fuel using SC CO₂ is desirable.

CO₂ as Supercritical Fluid Gas

A large variety of substances can be employed for preparing supercritical fluid. However majority of research work uses CO₂ as supercritical fluid. It is not surprising that SFE has become synonym with supercritical CO₂ extraction. In very few and special cases and for academic research point of view other substances are investigated. More than 95% publication on SFE employ supercritical CO₂. The nearly monopoly of CO₂ emerged from its moderate critical constants, (critical pressure = 73 atm, critical temperature = 304 K and critical density 0.46 g/mL) which are easy to obtain. Moreover, CO₂ is chemically inert gas, cheap, easily available, nonflammable. Being chemically inert, it does not take part in chemical reaction and act as an inert solvent. After extraction, at atmospheric pressure it escapes as gas leaving behind the extractant. No solvent residue is left, as in case of solvent extraction where lots of acid or organic solvent is generated. Thus extractant is obtained in pure form. Hence, SFE with CO₂ is termed as "CLEAN" and "GREEN" separation. CO₂ is radiochemically stable and nicely suited for nuclear industry. Moreover CO₂ is non-toxic, recyclable, less expensive. CO₂ is generally regarded as safe (GRAS) solvent.

Solvent Behaviour of Supercritical CO₂

The solvent behavior of CO₂ is similar to dioxane. CO₂ is an excellent example of a simple, nondipolar solvent system. Although CO₂ has a zero dipole moment, it is a charge-separated molecule having significant quadrupole moment. Kauffman¹⁷ attributed dipole-quadrupole interactions with solute molecules responsible for many of the polar attributes of CO₂ and sometimes regarded as a quadrupolar solvent¹⁵⁻¹⁷. The charge separation with partial negative charges on the electronegative oxygen, considerable partial positive charge on carbon, and the overall electronic structure suggest that CO₂ can act as either a weak Lewis Acid or Lewis Base. This view suggests that CO₂ can solubilize several dipolar and nondipolar molecular systems facilitated by site-specific solute-solvent interactions. Nevertheless, the one should regard CO₂ as a polar molecule with two active and considerably strong bond dipoles. Spectroscopic study in gas-phase suggested a T-shaped dimer (C_{2v}), corresponding to a purely quadrupolar interaction. Jucks et al.¹⁸ demonstrated that, CO₂ dimer has a slipped parallel structure. CO₂ also has trimeric structure which provides insight into the three-body effects in larger CO₂ clusters as well as in liquid or SC-CO₂. Wedia and Nesbitt¹⁹ reported two trimer structures based on IR spectral studies. One of these is a cyclic structure (C₃), while the other is noncyclic (C₂), with the cyclic trimer being more abundant than the noncyclic trimer. Charge separation in CO₂ suggests the oxygen atoms can participate in hydrogen bonding with molecules of electron-deficient hydrogen atoms.

In fact Raveendran and Wallen's²⁰ by *ab initio* calculations on binary complexes of CO₂ with model carbonyl compounds, revealed existence C-H...O hydrogen bond. Raman spectroscopic studies of room-temperature gaseous mixtures of acetaldehyde and CO₂ provided experimental evidence for the presence of both the LA-LB interaction between CO₂ and the carbonyl group²¹. NMR, IR, and Raman spectroscopic studies also support the formation of weak C-H....O hydrogen bonds with CO₂¹⁵. Heldebrant and Jessop²² showed that small molecular analogues of poly(ethylene glycol) are also soluble in SC-CO₂, suggesting that the ether-CO₂ interactions result in an enthalpy driven solvation in liquid and SC-CO₂. Similar interactions are responsible for solvation in systems where Wai and coworkers⁵⁴ utilized a scheme in which a CO₂-philic Lewis base (tri-*n*-butyl phosphate) acts as a carrier to disperse a CO₂-insoluble Lewis Acid (HNO₃) in SC-CO₂ phase enabling dissolution of an ionic system (uranium dioxide).

Fluorinated compounds have very high solubility in SC -CO₂. Indeed, DeSimone^{23,24} coined the term “CO₂-philic” for such fluorinated compounds. Darr and Poliakoff²⁵ have comprehensively reviewed the Metal-organic coordination chemistry in supercritical fluids. Exact mechanism of enhanced solubility of fluorinated compounds is not clearly understood. Raveendran and Wallen²⁶ investigated in detail the mechanism, concluded the paper with the remark that the mechanism for enhanced solubility of the latter is an open question. Dardin et al.²⁸ postulated the existence of specific solute-solvent interactions between CO₂ and fluorocarbons based on density- dependent ¹H and ¹⁹F NMR studies. Several other experimental groups and theoretical studies disagree and suggested that there are no such CO₂-fluorocarbon-specific interactions in comparison with the hydrocarbon systems³⁰⁻³⁴. Whatever might be the reason, fluorinated compounds are employed for extraction taking advantage of their enhanced solubility.

SFE /SFC of Natural Products

Supercritical Fluid Extraction (SFE) and Supercritical Fluid Chromatography (SFC) have unique characteristics compared to conventional solvent extraction such as fine control over extraction process by precisely tuning pressure and temperature conditions. SCF density can be varied by changing pressure and temperature conditions. SFE and SCF are being employed in separation of natural products. Being non polar, SC- CO₂ readily dissolves organic compounds. SFE/SFC has been extensively explored for natural products, more than 95% publications address to natural products, publication on metal SFE are lesser. SFE and SFC are employed for the separation and purification of natural products. The principle of extraction is same for both SFE and SFC. In SFE process, SCF dissolves the compound and transported to a vessel at atmospheric pressure for depressurization where CO₂ escapes as gas or recycled. In SFC process SC CO₂ is employed as mobile phase and separation is performed. Thus, SFE and SFC are complementary separation processes.

Chester et al.³⁵ reviewed SFE and SFC upto 1998. SFC finds applications in separation and purification of natural products. SFC played an important role to remove fatty acids³⁶. Henry and Clement³⁷ published review article based on 300 papers published between 2003 to 2005. In the paper applications of SFE/SFC in various fields namely food, natural products, pharmaceuticals, environmental applications, energy were discussed in details. Dr. Mamata Mukhopadhyay³⁸ in her book on SFE has described in detail process and

mechanism of extraction of natural products.

In conventional solvent extraction, the natural product is dissolved or leached by acid and subsequent extraction into organic compound, thus matrix is completely destroyed. In SFE, SC CO₂ act as solvent and extractant, sample matrix is not destroyed and remains as such, also residue of solvent remains CO₂ escapes as gas. Since acid usage is eliminated, many new compounds which are destroyed by acid are discovered.

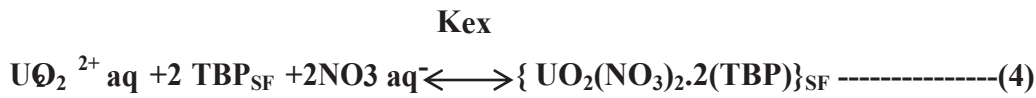
Instrumentation and Mechanism of Extraction

The SFE/SFC process consists of extraction at high pressure. A schematic diagram of a typical lab supercritical fluid extraction set-up is shown in Fig. 5^{13, 14}. Set-up consists of a CO₂ delivery pump, a modifier pump, extraction vessel, a thermostat, a back-pressure regulator and a collection vessel. Extraction vessel after sample loading is kept in the thermostat whose temperature can be varied from 258 K to ~353 K. CO₂ is delivered to the extraction vessel at a desired flow rate by the CO₂ delivery pump. From the cylinder, CO₂ gas is fed to the delivery pump, where CO₂ is liquefied by lowering the temperature to 263 K. The modifier pump is employed to add a desired percentage of the complexing agent to the liquefied CO₂ stream. The CO₂ and complexing agent streams are combined by a T-joint and fed to the extraction vessel. Prior to entry in the extraction vessel, the stream is allowed to

pass through a long spiral coil for acquiring thorough homogeneity. The desired pressure in the extraction vessel is maintained by opening/closing of a variable stroke needle valve of the back-pressure regulator. The extract coming out of the extraction vessel is collected in the collection tube at atmospheric pressure while CO₂ escapes as gas. For lab scale, pumps used for chromatography can be employed. For large scale, high-capacity pumps are used, extract containing SC CO₂ allowed to expand in a separate chamber and CO₂ can be recycled.

The complexation of metal ions can be carried out in two ways. Online complexation consists of ligand dissolution in SCF and subsequent feeding to extraction vessel. In-situ complexation consists of adding ligand directly to extraction vessel followed by flow of SC-CO₂. The extraction can be carried out essentially in two modes. In the static mode the extraction system is allowed to withstand particular temperature and pressure conditions for certain time period, followed by collection. In case of dynamic mode, collection is carried out at particular temperature and pressure. The extraction process can be understood by

typical example of uranium SFE by employing TBP. Identical to the conventional solvent extraction process employing TBP, the overall extraction reaction can be expressed by the following formula^{13, 14}



Here, K_{ex} denotes an extraction constant given by following equation:

$$K_{ex} = \frac{[\text{UO}_2(\text{NO}_3)_2 \cdot 2(\text{TBP})]_{SF}}{[\text{U}]_{aq} [\text{TBP}]_{SF}^2 [\text{NO}_3^-]_{aq}^2} \text{-----(5)}$$

The extraction reaction involves at least three elemental processes:

- (1) Distribution of TBP between aqueous and supercritical CO₂ phase
- (2) Formation of complex UO₂(NO₃)₂·2(TBP) in the aqueous phase
- (3) Distribution of the complex between aqueous and supercritical CO₂ phase

The K_{ex} can be formulated by the equation :

$$\log K_{ex} = \log K_{D, comp} - 2 \log K_{D, TBP} + \log K_f \text{-----(6)}$$

where $K_{D, comp}$, $K_{D, TBP}$ and K_f are the distribution co-efficient of the complex, the distribution co-efficient of TBP and the formation constant of the complex in the aqueous phase respectively.

Distribution ratio of a species 'j' is given by equation

$$\log K_{Dj} = j \log \rho + C_j - \log S_{j, aq} \text{-----(7)}$$

Where ' ρ ' is the density of supercritical fluid and 'S' is solubility.

SCF density increases with increasing pressure hence according to Chrastil empirical formula, solubility of substance consequently the extraction efficiency is expected to increase.

In most of cases, the extraction trend, which is followed for solids. In solution slight deviation above 80 atm pressure is observed. SC- CO₂ density decreases with temperature however, extraction efficiency is expected to decrease with temperature.

Extraction efficiency is influenced by many other factors. Solubility is combination of SC- CO₂ density and volatility of solute. The author has discussed in detail the effects of various parameters⁶⁵.

Solubility of Compounds in Supercritical CO₂

The fact that SCF can dissolve solids has fascinated chemists since the time of Hanny and Hogarth. A thumb rule is that the dissolving properties of SC- CO₂ are similar to n-hexane. Solubility of compounds in SC- CO₂ can be predicted by various models. These models are very complicated. However Smart et al.⁴⁰ compiled the data in the literature on solubility of 49 organometallic compounds and 15 free ligands in SC -CO₂. The highest solubility value reported was 56 g/L⁴⁰. The most soluble metal complexes were fluorine substituted ligands and lowest soluble were phenyl substituted ligands. The data were correlated using a model based on the relationship between ln (solubility) and ln (density) based on the earlier work of Chrastil³⁹ on correlating the solubility of complex organic molecules in SC-CO₂. The model relates the solubility of a solute to solvent density and temperature by equation $\ln S = k \ln D + C$, where 'S' being the solubility of the solute in g/L, 'D' the density of the SCF in g/L, *k* a constant for the solute–solvent system indicating the solvation of the solute in the SCF, *C* is density independent constant which varies with temperature and related to the volatility of the solute. The good agreement between experimental data and the model suggests that such a simple model can be utilized for extrapolation of limited amount of data to a wider temperature and pressure range. The equation predicts a linear relationship between ln(S) and ln (D) with a slope proportional to 'k' and intercept 'C'.

Solubility of compound can be measured either by SFE or spectroscopic methods; in SFE by static method and dynamic method. In static method, the SC CO₂ is fed to a vessel with sufficient quantity and the system is allowed to reach equilibrium condition under specific pressure and temperature conditions and the amount dissolved is measured by sampling at those conditions. In dynamic mode, SC CO₂ is allowed to flow through vessel containing the substance at particular pressure and temperature conditions and the extracted substance is collected in a vessel. In spectroscopic method the cell is maintained at desired pressure and temperature conditions and substance is measured online spectroscopically.

In 1991, Wai et al.⁴¹ was the first to report the solubilities of a number of metal dithiocarbamates in supercritical CO₂ determined by UV-VIS spectroscopy using a high-pressure view-cell with quartz window. Erkey et al.⁴² developed dynamic method to determine solubility of metal-chelate in SC- CO₂. In this technique, the supercritical fluid stream is mixed with an organic solvent stream to form a mixed phase for avoiding solid precipitation and plugging at the outlet. Yankar et al.⁴⁴ were the first to carry out NMR

study of Metal Complexes in supercritical fluids by ^1H , ^9F , and ^{129}Xe resonances, providing information about solution structure at molecular level, ligand substitution and proton position. Organophosphorus compounds are widely used for SFE of actinides, hence knowledge of their solubility in SCF is valuable from extraction point of view. Meguro et al.⁴⁵, Japan group in 1998, deeply studied solubility of various organophosphorus compounds in SC-CO₂ such as tributyl phosphate (TBP), diisodecylphosphoric acid (DIDPA), di-(2-ethylhexyl)phosphoric acid (DEHPA), dihexyl-(N,N-diethylcarbamoyl)methylphosphonate (CMP), and octyl(phenyl)(N,N-diisobutylcarbamoyl)methylphosphine oxide (CMPO). The solubility was found to increase with density of SC-CO₂ relation consistent with equation $\ln S = k \ln D + C$.

R. Schurhammer and G. Wipff⁴⁶ performed molecular dynamics study on the complexation of uranyl nitrate and the dissolution of nitric acid in SC-CO₂ by TBP. Study reveals the stronger TBP hydrogen-bonding with HNO₃ than with H₂O. Nitric acid dissolves in SC-CO₂ by TBP, nitric acid alone self aggregates via hydrogen-bonding interactions. The role of water was understood by directly measuring the pH of water in contact with supercritical CO₂ by observing the spectra of a pH indicator with a U-VIS spectrophotometer and pH was found in the range of 2.8 to 2.95 under pressure of 70-200 atm and 303-343 K temperature⁴⁷.

SFE of Uranium, Plutonium and Thorium

After the application of SCF by Lovelock in 1962, for considerably a long period, supercritical fluids were not employed for metal ion extraction. The reason being that direct extraction of metal ions by supercritical CO₂ is highly inefficient owing to charge neutralization requirement and the weak solute–solvent interactions. However, Laintz and Wai⁴⁸ in 1992 were the first to report the SFE of metal ion, Cu²⁺ from aqueous solution and from silica surface using SC-CO₂ containing Lithium diethyl dithiocarbamate (LiFDDC) as complexing agent. This opened a new realm in the field of SFE of metal ions. Subsequently SFE of various metal ions was reported. In the SFE of metal ions, choice of suitable complexing reagent plays vital role. Fascinated by attractive properties of supercritical fluids, after the demonstration of SFE of Cu, the focus was on nuclear field. Very next year in 1993, SFE knocked the door of nuclear industry when the same research group Lin et al.⁴⁹ was successful in performing SFE of lanthanides and uranyl ion from solid materials by SC-CO₂ containing a fluorinated β -diketone 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-

octanedione (FOD). The very next year, in 1994, they reported the SFE of thorium and uranium from solid and liquid materials with fluorinated β -diketones and TBP⁵⁰. These studies opened a gateway for application of SFE in nuclear industry. Kumar et al.^{52,53} carried out SFE of uranium from tissue paper matrix.

Hong Wu et al.⁵¹ carried out SFE of uranium and thorium from nitric acid solution with organophosphorus reagents. Separation and detection of lanthanide β -diketonates was carried out by adduct formation by supercritical fluid chromatography (SFC) with an open-tubular capillary column and a FID detector. Lanthanide β -diketonates decompose in SCF, but adducts of lanthanide β -diketonates with a neutral donor, tributylphosphine oxide (TBPO) or trioctylphosphine oxide (TOPO), alters their SFC behavior leading to first successful separation of lanthanide complexes of the same β -diketone ligand by SFC using SC- CO₂ as the mobile phase. Wang et al.⁵⁶ coined the term "Nuclear Laundry", described the extraction of Co, Cd, Cu, Pb, Zn by using Cyanex 302 and dithiocarbamate. Wai and Wang⁵⁷ reported separation of metal chelates and organometallic compounds by SFC and SFE. Smart et al.⁵⁸ carried out SFE of toxic metal ions using organophosphorus reagents such as Kelex 100, Cyanex 272, 301 and 302, and D2EHTPA. Toxic heavy metals such as f Cu²⁺, Pb²⁺, Zn²⁺, and Cd²⁺ are extractable from variety of matrices. Kelex 100 was found to be very selective for the extraction of Cu²⁺.

First review article on SFE of metal ions was published by Wai's group⁴³ in 1997 summarising the work on SFE of metal ions for analytical application. Till then SFE of metal ion was nicely matured and quite well understood. Wai's review article described the important parameters controlling SFE of metal species. (1) solubility and stability of chelating agents, (2) solubility of metal chelates, (3) water and pH, (4) temperature and pressure, (5) chemical form of metal species, and (6) matrix. A variety of ligands, including dithiocarbamates, β -diketones, organophosphorus reagents and macrocyclic compounds, can be utilized for SFE of metal species. Some ligands are general complexing agents and others are selective for certain metals. With proper choice of ligand and experimental conditions separation of metal ions can be achieved by SFE. In 2000 Erkey⁵⁵ extensively reviewed the SFE of metal ions from aqueous solution including uranium and thorium.

Wai and Wang⁵⁷ in 2000 reviewed separation of metal chelated and organometallic compounds by SFC and SFE/GC. Supercritical Fluid Chromatography (SFC) has dual advantages of the high diffusion properties of gas chromatography and solvating properties of liquid chromatography. Since SFC operates at lower temperatures, is nicely suited for

separation of thermally labile compounds. SFC also allows interfacing between supercritical fluid extraction (SFE) and chromatographic analysis of metal-containing compounds. SFC separation of various chelates of transition metals, heavy metals, lanthanides and actinides as well as organometallic compounds of lead, mercury, and tin was reported⁵⁸. The feasibility of separating U from nitric acid solutions of mixed actinides U, Np, Pu, and Am using tri-n-butylphosphate (TBP)-modified SC-CO₂ was investigated⁽⁶⁰⁾. The uranium was separated from plutonium at HNO₃ concentration less than 3M in the presence of acetohydroxamic acid (AHA) or oxalic acid (OA) to mitigate Pu extraction. U separation from Np was successful (<1 M HNO₃) in the presence of AHA, OA, or sodium nitrite to mitigate Np extraction. Americium was not well extracted, hence got separated.

Uranium SFE using diamide derivative was investigated by measuring distribution ratio (D_U) and extraction efficiency of uranium (VI) using N,N,N',N'-tetrabutyl-3-oxapentanediamide (TBOD)⁵⁹. D_U with TBOD was found superior to that of TBP by 2 orders of magnitude. However Uranium, fission products (Cs, Cd, Mo, Ba), and corrosion products (Ni, Fe, Cr, Co) were extracted with TBOD in SC-CO₂. Over 90% each of actinides (U,Th) and lanthanides (La, Ce, Gd) were extracted. But, fission products and corrosion products were extracted at a low efficiency of less than 20%.

Ionic liquids are considered to be a relatively recent magical chemical due their unique properties, non-volatility and non flammability. This seems to be promising field in coming future. Much work is not carried out with ionic liquids. Ankita and Tomar⁶¹ studied various amides for solvent extraction of Thorium into 1-butyl-3-methyl imidazolium hexafluorophosphate employing supercritical CO₂ for stripping, higher stripping efficiencies were observed. In the study, highest efficiency was supercritical carbon dioxide modified with DBOA-HNO₃ adduct. Keskin et al.⁴³ has reviewed the ionic liquids towards supercritical fluid application. It is noteworthy that SC-CO₂ has got solubility in ionic liquids. On the other hand ionic liquids are insoluble in SC-CO₂. On passing SC-CO₂ through the ionic liquid with organic compounds, SC-CO₂ would selectively extract organic compound. Thus the partnership of volatile and nonpolar SC-CO₂ with nonvolatile and polar ionic liquid offers a novel method to extract organic compounds from ionic liquids using SC-CO₂. Liyang et al.⁶² investigated the possibility SFE of Uranium from TRISO-coated fuel particles using supercritical CO₂ containing tri-n-butyl phosphate. Tristructural-isotropic (TRISO-) coated fuel particles are used in the high temperature gas cooled reactor

as fuel. TRSIO- coated fuel particles have four coating layers of porous carbon, inner dense pyrolytic carbon and silicon carbide for confining the fission products. The study was meant for investigating the possibility of reprocessing of spent nuclear fuel from high temperature gas cooled reactor. The extraction efficiency was higher than 98%.

Inspired by fascinating extraction properties of SC-CO₂ especially as radioactive waste minimisation, the author has also carried out research work on SFE of Uranium, Thorium and few metal ions⁶³⁻⁷³. Various organophosphorus reagents (in 2007) were studied for SFE of Thorium from simulated tissue paper matrix⁶³. The solubility trend is TBP>TBPO > TOPO>TBPO, but the extraction trend is quite different indicating the solubility of ligand alone is not the deciding factor. Among phosphates, if aromatic group is replaced by aliphatic group extraction efficiency increases, efficiency with tributyl phosphate (TBP) is higher than that with triphenyl phosphate (TPP). Among phosphine oxide, higher the aliphatic chain length, higher the extraction efficiency. In TPPO, having phenyl group, the efficiency is intermediate to TOPO and TBPO. The trend can be assigned to molecule structure, electronegativity of substituent. Electron withdrawing group decreases electron density on oxygen atom causing less solvation thereby less extraction efficiency, whereas electron donating group increases electron density on oxygen atom causing more solvation thereby enhanced extraction efficiency was observed. Various β-diketones such as acetylacetone (AA), trifluoroacetylacetone (TFA), hexafluoroacetylacetone (HFA), thenoyltrifluoroacetylacetone (TTA) and heptafluorobutanoylpivaroylmethane (FOD) were evaluated and trend observed was TTA > FOD > HFA > TFA > AA⁶⁶. The trend correlates well with the degree of fluorination in the side arms of β- diketones. A combination of TBP and β-diketones further enhances the extraction efficiency. In SC- CO₂, higher fluorination results in higher percentage of enol content, greater dissociation into enolate ion, higher solubility and stability of β-diketones as well as of Th-β-diketone chelates. Highest extraction efficiency with TTA was probably due to the presence of aromatic thenoyl group. Crown ether are versatile class of ion-selective extractant. Various crown ethers were investigated for the SFE of Uranium from acidic medium⁶⁷. HPFOA (Pentadecfluoro -n-octanoic acid) consisting of several CO₂ phillic C-F bonds was used for counter ion production. The nature of substituent attached to ring was found to affect extraction efficiency, Ditertbutldicyclohexano-18-crown-6> Ditertbutldibenzo-18-crown-6> dicyclohexano-18-crown-6> Dibenzo-18-crown-6⁶⁷.

Thus comparison for same size crown ether, electron donating group increases the basicity

of oxygen atoms of ring enhancing binding with metal ion, whereas electron withdrawing group decreases the basicity of oxygen atoms of ring lowering binding with metal ion. The size of crown ether also affects. For same substituent the observed trend in extraction efficiency was Dibenzo-24-crown-8 > Dibenzo-21-crown-7 > Dibenzo-18-crown-6, indicated increase in extraction efficiency with increasing ring size.

For nuclear industry, extraction of Uranium from solid matrix is very much desirable, since SFE process minimizes the radioactive waste generation. Supercritical Fluid Extraction of Uranium from U_3O_8 powder and also from various UO_2 solids—powder, granules, green pellet and sintered pellet—obtained from various stages of nuclear fuel fabrication was studied by single medium of TBP– HNO_3 dissolution as well as complexation, thus avoiding free acid usage and minimizing liquid waste generation⁶⁸. With SC- CO_2 alone efficiency was around 70% which increased to ~90% with 2.5% TBP in SC- CO_2 stream and nearly complete uranium extraction (~99%) with 20% TBP. Nearly complete extraction was also achieved with 2.5% TTA in methanol. The optimized procedure tested to remove Uranium from simulated tissue paper waste matrix smeared with uranium oxide solids.

Calixarenes were studied for the SFE of toxic heavy element Cd^{2+} and Pb^{2+} from acidic medium^{71,72}. With hexaacetylcalix[6]arene extraction efficiency ~ 90% was obtained and presence of HPFOA was found to enhance the extraction efficiency. Efficient extraction (~93%) of Pb(II) was observed for p-t-butylcalix(4)arene. The method was finally applied to the SFE of Pb(II) from real samples viz. batteries, paints, tobacco and industrial waste released in water.

Supercritical Fluid Extraction (SFE) and purification of Uranium, from crude sodium diuranate (SDU) containing Uranium (53%), Iron (22.2% of U) and rare earth impurities (4% of U), has been studied using adduct of TBP and HNO_3 for Uranium dissolution and extraction^{72,73}. This group also studied Uranium SFE from rock phosphates ores containing lean Uranium content (~50-100 ppm). Using SC- CO_2 , direct Uranium extraction from rock phosphate ores was studied by employing adducts of trialkyl phosphate (TBP, TiAP and TEHP) and nitric acid. The adduct fulfilled the role of dissolution as well as complexation reagent for U. With these adducts SC- CO_2 , direct extraction from yellow cake was studied, and Uranium extraction efficiency >90% was achievable. Crude yellow cake is produced in various chemical compositions such as sodium diuranate (SDU), magnesium diuranate (MDU), heat treated uranium peroxide (HTUP).

N,N-Dialkyl aliphatic amides with varying alkyl groups such as N,N-dibutyl-2-ethyl

hexaamide(DBEHA), N,N- dibutyl-3,3-dimethyl butanamide (DBDMBA), N,N-dihexyl octanamide (DBOA) were studied for SFE of Uranium and Thorium from nitric acid medium and tissue paper matrix⁷⁴. Extraction trend correlated well with structure of amides. Straight chain DBOA was found suitable for Uranium extraction whereas branched chain amide DBEHA was suitable for separation of uranium and thorium. N,N-Dialkyl aliphatic amides were used to extract Uranium into ionic liquid and stripping by SC- CO₂⁷⁰. DBEHA, DBMNA,DHOA,DBPA, DBOA were evaluated for solvent extraction of Thorium from nitric acid medium into the hydrophobic ionic liquid phase, 1-butyl-3- methyl imidazolium hexafluorophosphate. DBOA yielded highest extraction efficiency.

Mohapatra' group⁷⁵ studied extraction of Uranium from tissue paper, synthetic soil, and from its oxides (UO₂, UO₃ and U₃O₈) using SC-CO₂ modified with methanol solutions of extractants (TBP) or (DHOA). With TBP, the extraction trend was UO₃>UO₂>U₃O₈. Addition of hydrogen peroxide in the modifier enhanced the dissolution/extraction of uranium. DHOA appeared better than TBP. Direct extraction of uranium from sintered oxides UO₂, (U,Th)O₂ soil and ore samples using SC-CO₂ containing tri-n-butylphosphate and N,N-di-(2-ethylhexyl) isobutyramide was demonstrated. 80–100% extraction of Uranium from different soil/ore samples was found. The extraction of Uranium from (U,Th)O₂ samples was significantly lower for both TBP–HNO₃ (~17%) and D2EHIBA–HNO₃ (~12%) adducts in 2 hour. Employing N,N,N',N'-tetraoctyl diglycolamide (TODGA) this group also carried SFE of trivalent metal ions such as Nd(III), Eu(III) (taken as analogs of Am(III)) from solid oxide (Nd₂O₃), Thorium concentrate, tissue paper/surgical gloves (rubber), and plant waste⁷⁶.

Tessy et al.⁷⁷ carried out direct in situ supercritical fluid extraction of Neodymium ion from its oxide using thenoyl trifluoro acetone–tri butyl phosphate–methanol in carbon dioxide. Tessy et al.⁷⁸ carried out extraction of metals directly from metal oxides by SC- CO₂. Cerium as a candidate, feasibility studies along with TTA as the chelating agent was demonstrated.

Indira Gandhi Centre for Atomic Research (IGCAR) group lead by Sivraman⁷⁹⁻⁹¹ has carried out significant work on SFE of actinides (U, Pu, Th). The group has studied plutonium SFE, very limited work is reported on Plutonium SFE. It is worth mentioning that Plutonium SFE requires glove box adaptation as Plutonium is highly radiotoxic, microgram quantity of Plutonium in body is harmful. Kumar et al.⁷⁹ developed a technique for modifier free delivery of ligands in controlled manner for SFE. TBP, TOPO,TTA, D2EHIBA, CMPO

were investigated and the delivery profiles were optimised by investigating parameters such as ligand delivery vessel geometry, temperature, pressure, flow rate of SC-CO₂ and ligand content. SFE of Uranium and Thorium was demonstrated from tissue paper matrix, the extraction was comparable with that of making use of methanol or hexane modifier. Kumar et al.⁽⁸⁰⁾ used supercritical fluid to remove silicone oil from uranate microspheres prepared by sol-gel process. Silicone oil was extracted completely and the microspheres were found suitable for preparation of UO₂ spheres. SFE of Plutonium from tissue paper matrix, teflon, glass and stainless steel was demonstrated by Kumar et al.⁸¹ n-octyl(phenyl)-N,N-diisobutyl carbamoylmethyl phosphine oxide (ϕ CMPO) in methanol was used as modifier and complete extraction of Pu(III) and Pu(IV) in their nitrate was achieved for the first time. SFE of Am(III) using CMPO in methanol resulted in its complete recovery. Sujata et al.⁸² (in 2012) demonstrated nearly complete Plutonium extraction from actual Plutonium bearing cellulose matrix waste in 0.1 litre extraction vessel employing (SC-CO₂) modified with (ϕ CMPO). Next year(2014) Sujata et al.⁸³ showed recovery of Plutonium from various polymeric matrices, such as neoprene, polyvinyl chloride (PVC) and surgical gloves using SC-CO₂ modified with (ϕ CMPO) in methanol. K. C. Pitchaiah et al.⁸⁴ studied SFE of Uranium and Thorium from nitric acid medium employing various organophosphorous compounds. The extractants such as TiAP, TsBP, DAAP, DBBP, DOHP and DOPO were employed for the first time for the extraction of Uranium from HNO₃ medium and the results were compared with TBP, CMPO and TOPO. Study revealed that TOPO, CMPO are stronger extractants compared to phosphonates, which in turn are better compared to phosphates for the extraction of Uranium from nitric acid medium. K. C. Pitchaiah et al.⁸⁵ studied in detail the influence of co-solvent such as methanol, dichloromethane and n-hexane on the extraction behaviour of Uranium and Thorium with Organophosphorous reagents. The solubility of tri-iso-amyl phosphate (TiAP) in SC -CO₂ was determined and employed for selective extraction of Uranium (~95%) from simulated dissolver solution ⁽⁸⁶⁾. Pichaiah et al.⁸⁸ demonstrated recovery of Uranium and Plutonium from pyrochemical salt matrix using supercritical fluid extraction employing Trioctylmethylammonium chloride as ligand. Typical extraction yield of 95 and 75% was achieved for Uranium and Plutonium respectively. Deepitha et al.⁹⁰ determined solubility of pyridine-2,6-dicarboxylic acid in supercritical carbon dioxide and demonstrated removal of Lead and Nickel in simulated matrices. Deepitha et al.⁹¹ measured solubility of on 2-hydroxyisobutyric acid in SC- CO₂ and used for actinide extraction.

The evolution of the research work on SFE of actinides (U,Pu,Th) leads for exploring the possibilities of using SC-CO₂ in nuclear filed on large scale such as reprocessing of spent fuel or recovery from nuclear waste. B. F. Myasoedov, et al.⁹². Russian research group in 2009 thoroughly investigated recovery of Uranium and Plutonium from simulated spent nuclear fuel (SSNF). For actinide oxides UO₂, UO₃, U₃O₈, NpO₂, PuO₂, Uranium gets nearly quantitative extracted (>~0%) by SC-CO₂ containing TBP-HNO₃ adduct whereas Pu and Np remains unextracted. From mechanically mixed (UO₂ & PuO₂), (UO₂ & NpO₂) only Uranium gets extracted. From solid solutions of UO₂ and PuO₂ containing 6% and 26 % PuO₂, both Uranium and Plutonium nearly quantitative (>90%) extracted. The extraction of Uranium from its dioxide by the TBP-HNO₃ adduct dissolved in SC-CO₂ was found to be the same as that without SC-CO₂. This finding indicates the possibility of elimination or minimization of generation of large volumes of highly toxic aqueous and organic radioactive wastes getting accumulated as a result of the use of conventional technologies of spent nuclear fuel (SNF) reprocessing. They studied direct extraction of the actinides from their solid dioxides by TBP, MIBK and DMDO-HEMA adducts with HNO₃, Uranium is nearby quantitatively extracted from the solid actinide compounds (PuO₂, NpO₂) . In the case of the solid solutions of NpO₂ and PuO₂ in UO₂, Np and Pu are extracted along with Uranium by the TBP-HNO₃ and DMDOHEMA- HNO₃ adducts practically quantitatively. MIBK extracts U(VI) only, whereas Pu remains in the residue. Thus Uranium can be selectively extracted from the solid solution of PuO₂ in UO₂ and separated from Pu using the MIBK-HNO₃ adduct. U and Pu were separated by counter current chromatography (CCC) under the conditions of concentration gradients both of TBP in the stationary phase and of HNO₃ in the mobile phase⁹³. The system “30% TBP in white spirit-0.5 M HNO₃” enabled Uranium to be concentrated in the stationary phase, while Pu was eluted with a flow of the mobile phase and stepwise elution allowed U and Pu to be practically completely separated. The first Pu fraction contained 98.9% of total Pu and 0.07% of U, and the second U fraction contained 99.93% of total U and 1.1% of Pu. Thus CCC allows separation of U(VI) and Pu(IV) in the form of their complexes with TBP as well as separation of U(VI), Pu(IV), Am(III) and Cm(III) in the form of their complexes with DMDOHEMA^{94, 95}.

During SFE of the SSNF sample, more than 99% of U goes into the adduct phase along with bulk of ⁹⁵Zr and ⁹⁵Nb (~ 90%), ¹³¹I (100%), smaller percentages of ¹⁰³Ru (~ 30%), ⁹⁹Tc and lanthanides (~ 10%) whereas aqueous phase contains ~ 100% of ¹³⁷Cs, ⁸⁵Sr, ¹⁴⁰Ba and the bulk of ¹⁴⁰La, ¹⁴¹⁻¹⁴⁴Ce, ¹⁴⁷Nd and ⁹⁹Tc (90%–80%). Uranium separation from

fission products is desirable. In order to achieve separation from fission products the adduct phase containing U and the extracted fission products were separated from the aqueous phase using liquid CO₂ and U is effectively separated by counter current chromatography from the fission products. In the study ¹⁴⁰La, ¹⁴¹⁻¹⁴⁴Ce, ¹⁴⁷Nd, ⁹⁵Nb and ⁹⁵Zr were quantitatively eluted first followed ⁹⁹Tc and finally U.

In Russia, SFE of uranium and transuranium (Np, Pu, Am) from solid oxides and from solid surfaces has been extensively studied at the Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Science and at the Klopov Radium Institute. The research was specifically dedicated to investigate possibility of using SFE for spent nuclear reprocessing and decontamination purposes. In this paper, the SFE work by the Russian research group lead by M.D. Samsonov has been discussed upto year 2011⁹⁶. According to Study, liquid CO₂ is as efficient as SC CO₂ in dissolving complexes of Uranium and Plutonium. Based on study a schematic flowsheet for SNF reprocessing using CO₂ as diluent was suggested. Based on the data from Russia, United States, Japan, United Kingdom and India, Super-DIREX (Super Critical Fluid Direct Extraction, Mitsubishi)) process was suggested in Japan^{97,98}. In Super-DIREX, SC-CO₂ containing TBP-HNO₃ adduct is fed to extraction column containing SNF dissolving U and Pu leaving behind undissolved fission products. Russian groups suggested RELICT process (reprocessing by liquid Carbon dioxide Treatment)^{99,100}. In REFLECT is based on combining the operation of oxide SNF dissolution and actinide extraction with solution of TBP-HNO₃ adduct. Super-DIREX is performed at 200-300 atm and 298-318 K whereas RELICT is performed at 70 atm and 298-318 K . The RELICT was initially tested on simulated SNF. Also it was tested on real samples of spent fuel of RBMK-1000 and WWER- 1000 reactor^{101,102}.

Conclusion

Supercritical Fluid Extraction offers promising alternative to conventional solvent extraction process. It assumes significance in the extraction of actinides owing to its inherent potential of minimisation of radioactive liquid waste generation. SFE can be considered as high pressure extraction process. CO₂ is preferred choice because of its moderate critical constants, chemically inertness, radiochemically stability, nontoxic nature and easy availability. A thorough understanding of chemistry of compounds in SC- CO₂ is essential for designing SFE process for particular ion and matrix.

The whole SFE process is matter of choosing suitable complexing ligand which can

efficiently complex with metal ion. Solubility of ligand and metal complex in SC-CO₂ determine the outcome of extraction process.

Also instrumental parameters such as pressure, temperature, CO₂ flow rate, extraction mode static/dynamic, complexing mode online/in-situ, need to be optimised. A large number of ligands such organophosphorus compounds, β-diketones, macrocyclic compounds, amides, dithiocarbamates have been extensively investigated by many research groups. Super-DIREX (Super Critical Fluid Direct Extraction, Mitsubishi) process and RELICT process (Reprocessing by liquid Carbon dioxide Treatment) are proposed for reprocessing of Spent Nuclear Fuel. The RELICT process has been test on real samples of spent fuel from reactor. These are all lab scale demonstration. Commercial reprocessing plants are expected to become reality in future. The probable reason for hesitation for adapting on commercial scale might be the high pressure requirement. SFE of Uranium from ores appears promising and research need to be focused in this direction. SFE using ionic liquids is at infant stage and seems promising in future. Plant scale SFE for natural products exists. In nuclear field upscaling to plant level has still not matured. However SFE offers promising alternate to solvation extraction process and dedicated research in extraction of actines needs to be continued.

Acknowledgement

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Figures :

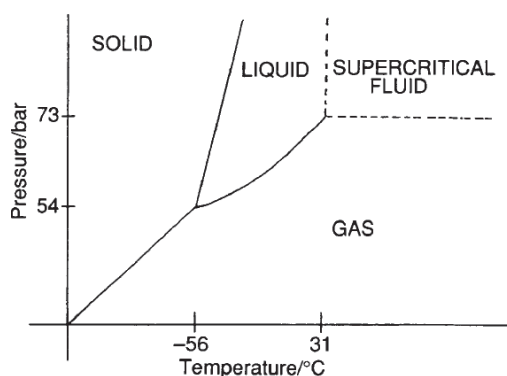


Fig. 1: Pressure –Temperature Phase Diagram for CO₂³⁸

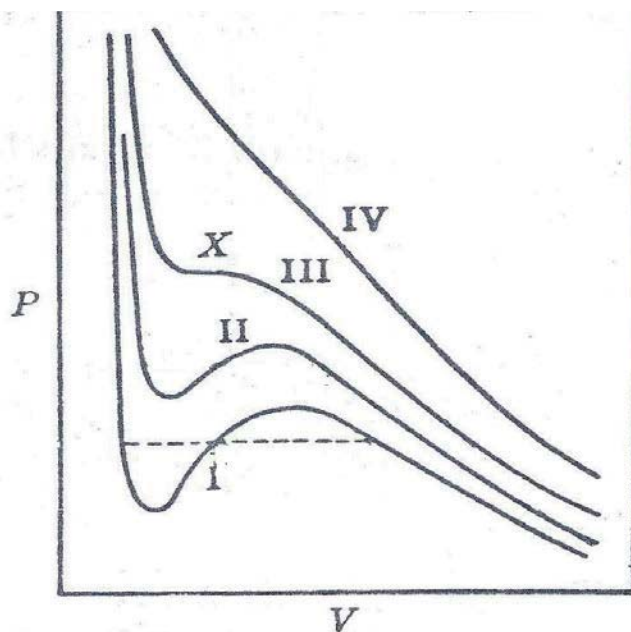


Fig. 2: Experimentally obtained P-V Isotherms for a Real Gas ⁴

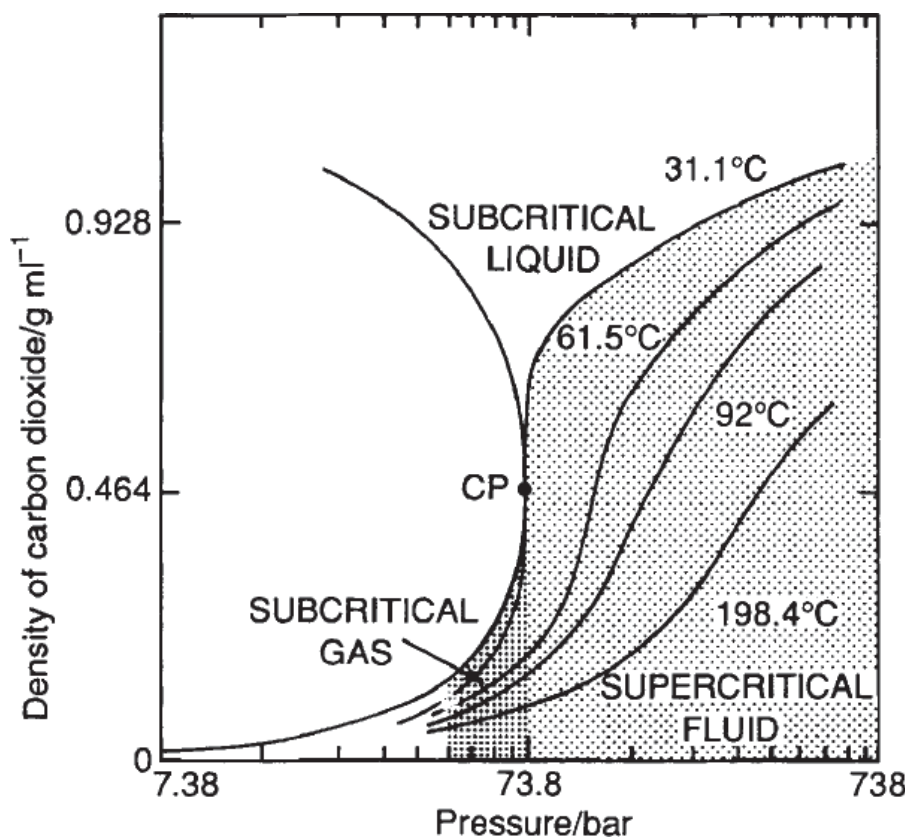


Fig. 3: Phase Diagram of supercritical and near supercritical CO₂ ³⁸.

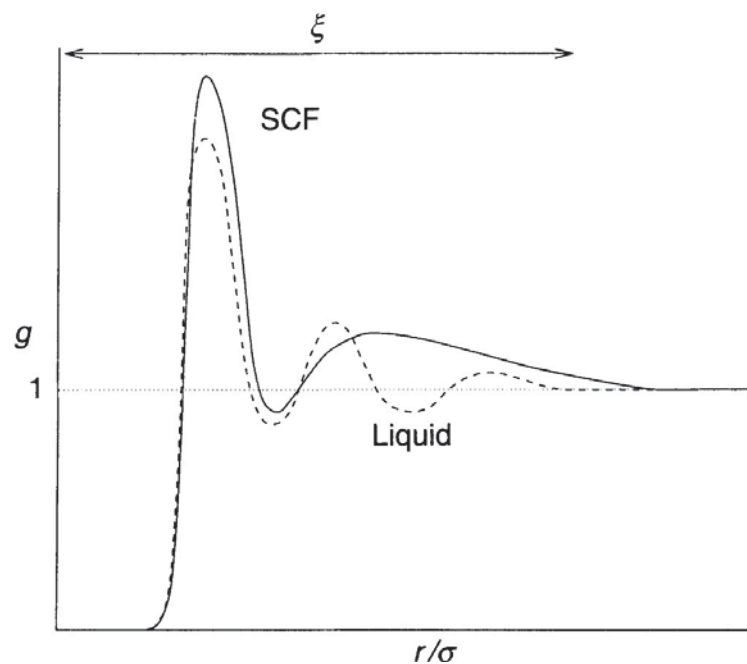


Fig. 4: Schematic representation of the pair correlation function in liquids and supercritical fluids. ζ is the correlation length, g is the ratio of local to bulk density at a distance r away from a molecule fixed at origin and σ is the molecular diameter⁷.

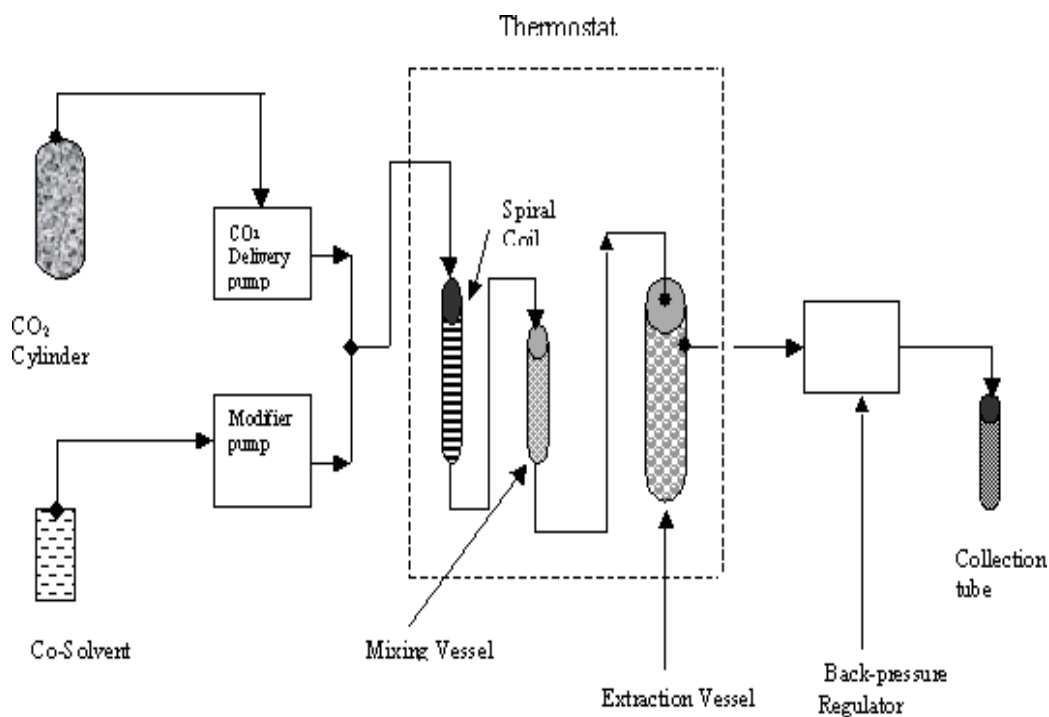


Fig. 5: A schematic diagram of SFE set-up¹⁴

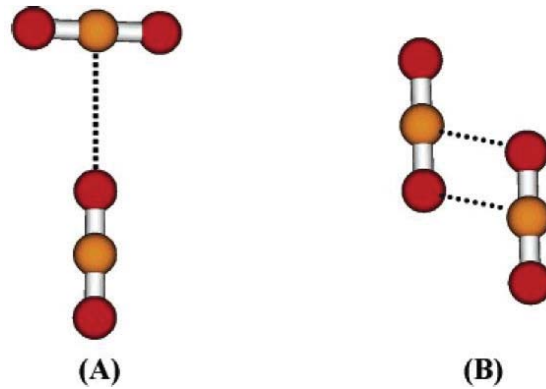


Fig. 6: Optimized geometries of the (A) T-shaped and (B) slipped parallel configurations of the CO₂ dimer¹⁸.

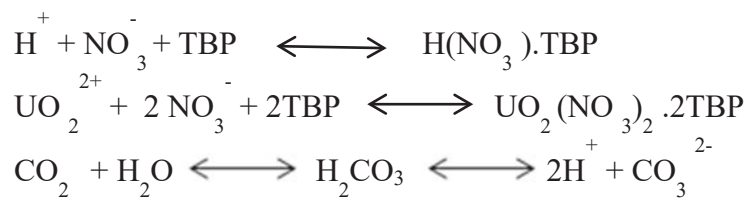
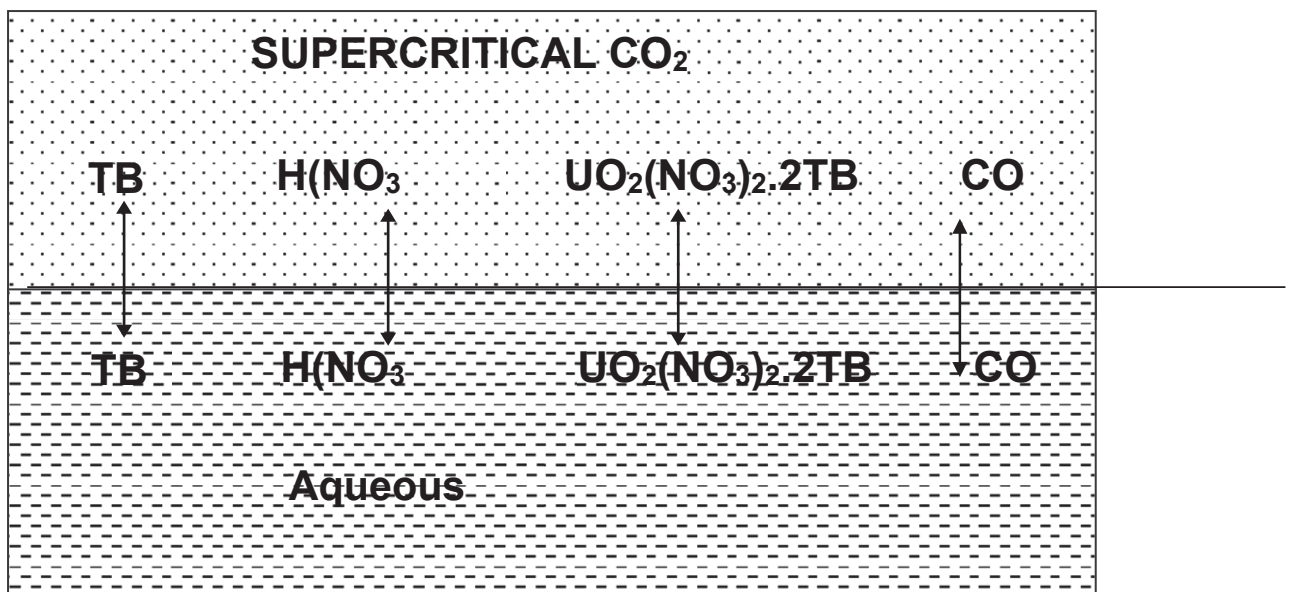


Fig. 7: Equilibria Involved in Extraction of UO₂²⁺ with Solvating Extractant¹⁴

Tables:

Table 1: Comparison of Physical Properties of Different States¹⁴

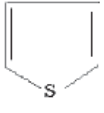
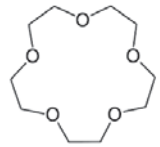
| State | Density (g mL ⁻¹) | Viscosity (poise) | Diffusivity (cm ² s ⁻¹) |
|---------------------|-------------------------------|----------------------------|--|
| Gas | 10 ⁻³ | (0.5-3.5)*10 ⁻⁴ | 0.01-1.0 |
| Supercritical Fluid | 0.2-0.9 | (0.2-1.0)*10 ⁻³ | (3.3-0.1)*10 ⁻⁴ |
| Liquid | 0.9-1.0 | (0.3-2.4)*10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

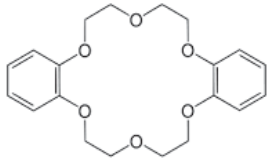

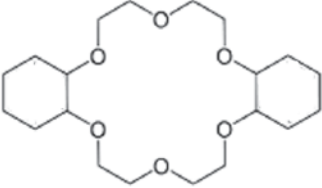
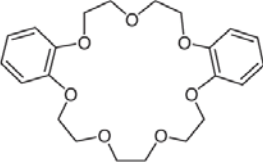
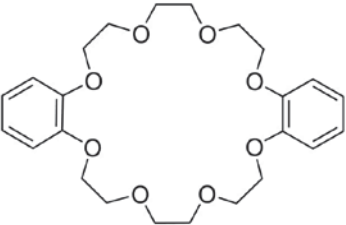
Table 2: Critical constants of some common Solvents used in SCF State¹⁴

| Fluid | Critical Temperature T _c (°C) | Critical Pressure P _c (atm) | Critical Density (g/mL) | Density at 400 atm (g/mL) |
|---------------------------------|--|--|-------------------------|---------------------------|
| CO ₂ | 31.3 | 72.9 | 0.47 | 0.96 |
| N ₂ O | 36.5 | 72.5 | 0.45 | 0.94 |
| NH ₃ | 132.5 | 112.5 | 0.24 | 0.40 |
| n-C ₅ | 196.6 | 33.3 | 0.23 | 0.51 |
| H ₂ O | 374.2 | 217.6 | 0.27 | -- |
| SF ₆ | 45.5 | 37.1 | 0.74 | 1.61 |
| Xe | 16.6 | 58.4 | 1.10 | 2.30 |
| CCl ₂ F ₂ | 111.8 | 40.7 | 0.56 | 1.12 |
| CHF ₃ | 25.9 | 46.9 | 0.52 | -- |

Table 3: Chemical Structure of various compounds employed in the SFE of Uranium, Plutonium, Thorium

| | |
|---------------------------------|---|
| Tributyl Phosphate (TBP) | (RO) ₃ -P=O, R = C ₄ H ₉ |
| Triphenyl Phosphate (TPP) | (RO) ₃ -P=O, R = C ₆ H ₅ |
| Trioctyl Phosphine Oxide (TOPO) | R ₃ -P=O, R = C ₈ H ₁₇ |

| | |
|---|--|
| Triphenyl Phosphine Oxide (TPPO) | $R_3-P=O$, $R = C_6H_5$ |
| Tributyl Phosphine Oxide (TBPO) | $R_3-P=O$, $R = C_4H_9$ |
| tri-isoamyl phosphate TiAP | $(RO_3)-P=O$, $R = (CH_3)_2CH(CH_2)_2$ |
| tri-ethyl hexyl phosphate TEHP | $(RO_3)-P=O$, $R = (CH_3)_2(CH_2)_3CH(C_2H_5)CH_2-$ |
| di-(2-ethylhexyl)phosphoric acid (DEHPA) | $(RO)_2POOH$. $R = CH_3(CH_2)_3C(CH_3)CH_2$ |
| | $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \mathbf{R_1-C=CH_2-C-R_2} \end{array}$ |
| Acetylacetone (AA) | $R_1 = CH_3$, $R_2 = CH_3$ |
| Trifluoroacetylacetone (TFA) | $R_1 = CF_3$, $R_2 = CH_3$ |
| Hexafluoroacetylacetone (HFA) | $R_1 = CF_3$, $R_2 = CF_3$ |
| Thenoyltrifluoroacetylacetone (TTA) | $R_1 = CF_3$, $R_2 =$  |
| Heptafluorobutanoylpivaroylmethane (FOD) | $R_1 = C_3F_7$, $R_2 = C(CH_3)_3$ |
| 15-Crown-5 |  |

| | |
|---|--|
| Dibenzo-18-Crown-6 |  |
| Ditertbutyldibenzo-18-Crown-6 |  |
| Dicyclohexano -18-Crown-6 |  |
| Dibenzo 21-Crown-7 |  |
| Dibenzo 24-Crown-8 |  |
| Fluorinated pentadecafluoro-n-octanoic acid (HPFOA) | $\text{CF}_3(\text{CF}_2)_6-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ |
| N,N-dialkyl amide | $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{N} \\ \quad \\ \text{R}_2 \quad \text{R}_1 \end{array}$ |
| N,N-dibutyl-2-ethylhexaanamide (DBEHA) | $\text{R}_1=\text{CH}_3(\text{CH}_2)_3(\text{C}_2\text{H}_5)\text{CH}$, $\text{R}_2,\text{R}_3 =\text{C}_4\text{H}_9$ |
| N,N-dibutyl-3,3-dimethylbutanamide (DBDMBA) | $\text{R}_1=(\text{CH}_3)_2\text{CCH}_2$, $\text{R}_2,\text{R}_3 =\text{C}_4\text{H}_9$ |

| | |
|--------------------------------------|---|
| N,N -dhexyloctanamide (DHOA) | $R_1=CH_3(CH_2)_6$, $R_2,R_3=C_6H_{13}$ |
| N,N-di-sec-butylpentanamide, DBPA | $R_1=CH_3(CH_2)_3$, $R_2,R_3=CH(CH_3)(C_2H_5)$ |
| N,N-dibutyloctnamide, DBOA | $R_1=CH_3(CH_2)_6$, $R_2,R_3=C_4H_9$ |

Table 4: Major mile stones

| | |
|------|--|
| 1822 | Supercritical Fluid was discovered by Cagniard de la Tour |
| 1879 | Hanny and Hogarth reported the solvating properties of supercritical fluids in the Royal Society meeting held at London. |
| 1958 | Lovelock suggested their use in chromatography as mobile phase enabling faster separation. |
| 1962 | Chromatography equipment came into existence by Klesper et al. |
| 1992 | Laintz and Wai were the first to report the SFE of metal ion, Cu^{2+} |
| 1993 | Lin et al. was successful in performing SFE of lanthanides and uranyl ion from solid materials |
| 1994 | Lin et al reported the SFE of thorium and uranium from solid and liquid materials with fluorinated β -diketones and TBP. |
| 1996 | Hong Wu et al ¹ carried out SFE of uranium and thorium from nitric acid solution with organophosphorus reagents |
| 1997 | First review article on SFE of metal ions was published by Wai's group |
| 2000 | Erkey extensively reviewed the SFE of metal ions from aqueous solution including uranium and thorium. |
| 2006 | M.Koh et al. investigated Uranium SFE using diamide derivative. |
| 2007 | Pradeep Kumar et al. investigated Various organophosphorus reagents for SFE of thorium from simulated tissue paper matrix. |
| 2007 | Keskin et al. reviewed the ionic liquids towards supercritical fluid application. |

| | |
|-----------|---|
| 2009 | Pradeep Kumar et al. investigated supercritical fluid extraction of thorium from tissue paper matrix employing various β -diketones |
| 2010 | Pradeep Kumar et al., investigated various crown ethers for the SFE of uranium from acidic medium. |
| 2010 | Pradeep Kumar et al. investigated Supercritical fluid extraction of uranium from U ₃ O ₈ powder granules, green pellet and sintered pellet using TBP–HNO ₃ . |
| 2010 | P.K. Mohapatra's group studied for SFE of uranium and thorium from nitric acid medium and tissue paper matrix using various N,N-Dialkyl aliphatic amides. |
| 2009-2021 | N.Sivaramn' group extensively carried out research work on SFE of plutonium, uranium, thorium and Americium employing large variety of reagents such as TBP, TOPO,TTA, D2EHIBA, CMPO. |
| 2012 | Liyang et al. investigated the possibility SFE of uranium from TRISO- coated fuel particles |
| 2014 | L.Donna et al. investigated the feasibility of separating U from nitric acid solutions of mixed actinides U, Np, Pu, and Am using tri-n-butylphosphate (TBP)-modified SC-CO ₂ . |
| 2016 | Supercritical Fluid Extraction (SFE) and purification of Uranium, from crude sodium diuranate (SDU) and rock phosphates ores |
| 2002 | Super-DIREX (Super Critical Fluid Direct Extraction, Mitsubishi)) process was suggested |
| 2005 | Russian groups suggested RELICT process (reprocessing by liquid Carbon dioxide Treatment) tested on real samples of spent fuel of RBMK-1000 and WWER- 1000 reactor |
| 2009 | B. F. Myasoedov, et al. Russian research group thoroughly investigated recovery of uranium and plutonium from simulated spent nuclear fuel(SSNF). |
| 2011 | M.D. Samsonov investigate possibility of using SFE for spent nuclear reprocessing and decontamination purposes using liquid CO ₂ . |

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