

This article was downloaded by: [Rowan University]

On: 17 December 2011, At: 12:30

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Separation & Purification Reviews

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lsp20>

A Brief Review on Solvent Extraction of Uranium from Acidic Solutions

Jyothi Rajesh Kumar ^a, Joon-Soo Kim ^a, Jin-Young Lee ^a & Ho-Sung Yoon ^a

^a Metal Recovery Department, Mineral Resources Research Division, Korea Institute of Geoscience & Mineral Resources (KIGAM), Daejeon, Republic of Korea

Available online: 16 Feb 2011

To cite this article: Jyothi Rajesh Kumar, Joon-Soo Kim, Jin-Young Lee & Ho-Sung Yoon (2011): A Brief Review on Solvent Extraction of Uranium from Acidic Solutions, *Separation & Purification Reviews*, 40:2, 77-125

To link to this article: <http://dx.doi.org/10.1080/15422119.2010.549760>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

A Brief Review on Solvent Extraction of Uranium from Acidic Solutions

JYOTHI RAJESH KUMAR, JOON-SOO KIM, JIN-YOUNG LEE,
and HO-SUNG YOON

Metal Recovery Department, Mineral Resources Research Division, Korea Institute of Geoscience & Mineral Resources (KIGAM), Daejeon, Republic of Korea

Uranium solvent extraction (SX) from aqueous acidic solutions is reviewed. First the uranium availability in earth as well as resources, mining and production reports is presented and followed by SX basic flowsheet and various important stages. Extraction, scrubbing, stripping and finally solvent equilibrium are presented in a flow-sheet form. The second half of the review discusses the various extractants used for uranium extraction and separation from acidic solutions. The extractants are divided in four types: 1) nitrogen-based extractants, 2) phosphorous-based extractants, 3) sulfur-based extractants, and 4) other extractants. Nitrogen-based extractants cover predominantly the amides and amines functional group containing extractants. The phosphorous-based extractants: tri-butyl-phosphate (TBP), di(2-ethylhexyl) phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl (PC88A), tri-n-octyl-phosphine oxide (TOPO or Cyanex 923) and bis(2,4,4-trimethyl pentyl) phosphinic acid (Cyanex 272) are the most important members of this category. Sulfur-based extractants mainly sulfoxides and other sulfur-containing extractants are discussed. Heterocyclic compounds encompass isoxazolones, pyrazolones, crown ethers and other available extractants. A compact summary of the literature on uranium SX processes as well as extraction efficiencies is given in table form.

KEYWORDS Uranium, solvent extraction, review

Received February 26, 2010; Accepted December 9, 2010

Address correspondence to Joon-Soo Kim, Metal Recovery Department, Mineral Resources Research Division, Korea Institute of Geoscience & Mineral Resources (KIGAM), 92 Gwahang-no, Yuseong-gu, Daejeon 305-350, Republic of Korea. E-mail: jskim@kigam.re.kr

INTRODUCTION

Uranium is a relatively rare metal element often found in association with other elements in earth crust. Its natural formation is from supernova explosions, along with elements having atomic weight higher than that of iron. Nowadays, all over the world the greenhouse gas-free generation of electrical power need is growing vigorously. Since nuclear power electricity generation mainly depends on uranium, the importance of this metal is also growing daily. Different processes are available for uranium extraction and separation from the associated elements in natural resources as well as from nuclear wastes. Countries like Korea have some very low-grade uranium deposits that require enriching metal values and separating from other associated elements to be usable. For this reason the upcoming researchers in developed/developing countries are establishing more research and development on extraction and separation technologies for uranium.

Resources of uranium for mining and production throughout the globe are presented in Figure 1. The worldwide production of uranium in 2006 amounted to about 40,000 metric tons, of which 25% were mined in Canada. Other important uranium mining countries are Australia (19%), Kazakhstan (13%), Niger (9%), Russia (8%) and Namibia (8%). Uranium ore is mined in several ways: by open pit, underground, in-situ leaching, and borehole mining. At the end of 2006, world uranium production provided ~60% of world reactor requirements. World annual uranium requirement amounted to 66,500 tons containing U in 2006 and is estimated to have increased to 68,700 metric tons in 2010 with 3800 tons for South Korea alone compared to 19500 tons, 10200 tons and 8000 tons for USA, France and Japan, respectively (1a).

The general flow sheet for uranium recovery from ore or natural resources is presented in Figure 2(1b). Two processes are well established for the uranium production namely the Amex and the Dopex processes. Both of them generate a final product containing 75% U_3O_8 using $0.1\text{ mol}.\text{dm}^{-3}$ amine diluted in kerosene or kerosene-alcohol diluent in the Amex process, where as in the Dopex process, 4% of D2EHPA (di-2-ethylhexyl-phosphoric acid) with an equivalent amount of TBP were added as a modifier for uranium extraction. Recovery of uranium from the loaded organic phase is carried out by using 0.75 to $1.0\text{ mol}.\text{dm}^{-3}$ Na_2CO_3 within a 1 to 4 stages as a stripping reagent in both cases (1b).

To achieve the present day demands of uranium recovering the title metal from low grade ores as well as other sources by less expensive techniques is required. Solvent extraction (SX) processes also known as liquid-liquid extraction (LLE), applied to recover and separate the metal ions from their sources is popular since very long time. When compared with other separation and extraction techniques like ion-exchange, adsorption,

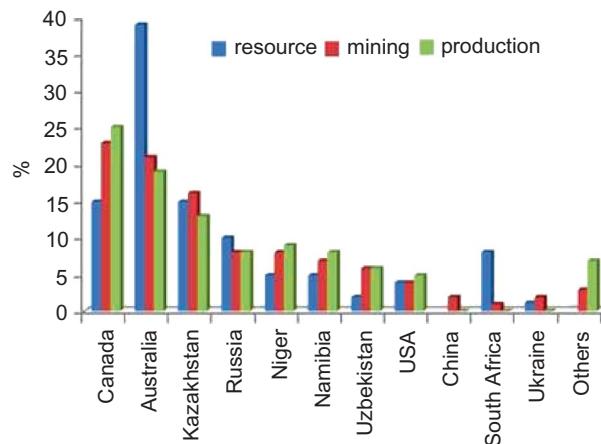


FIGURE 1 Uranium identified resources, mining (origin of the ~70,000 metric tons of uranium in 2007) and production (in 2006: 39,600 tons) all over the world (adapted from reference 1).

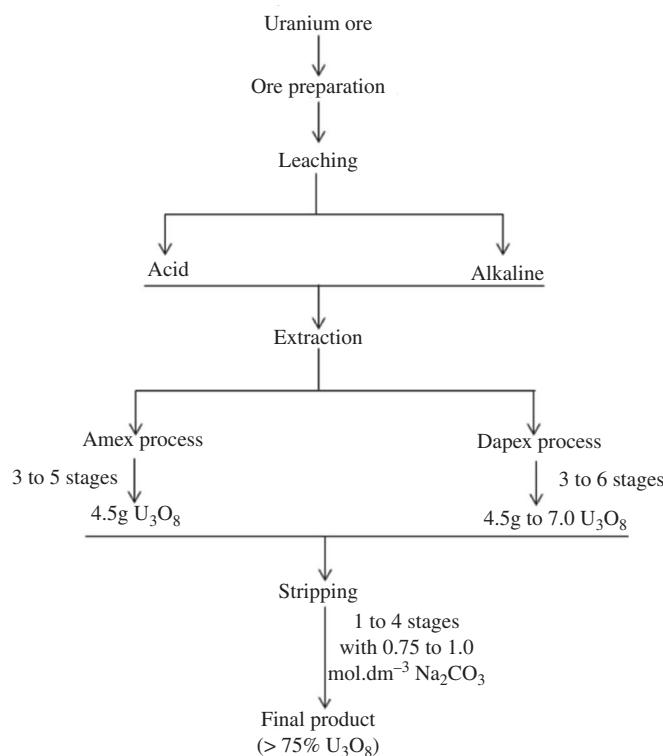


FIGURE 2 Generalized flow sheet for uranium recovery from ore or natural resources by Amex and Dapex process (1). 0.1 mol. dm^{-3} amine used for Amex process, whereas 4% phosphoric acid with same amount of TBP added as modifier used for Dapex process.

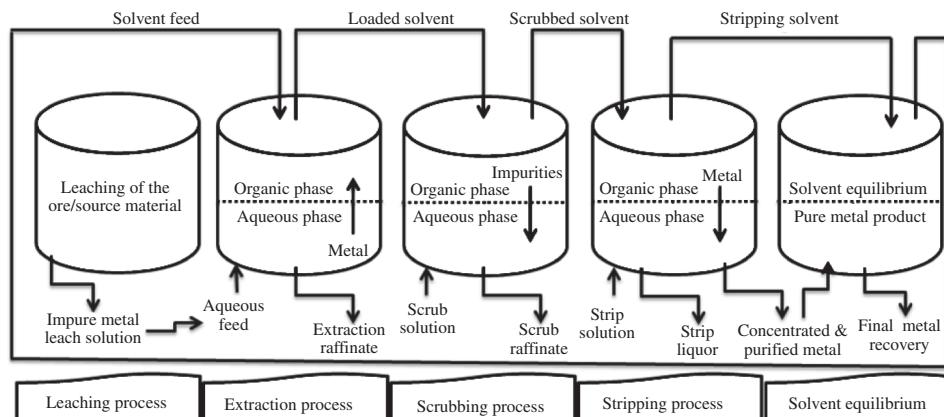


FIGURE 3 The general flow sheet of solvent extraction (SX) process (3).

or precipitation, SX process is very easy to handle and less expensive set up is required besides the possibility of zero waste generation.

In SX process extractant occupies the key role. It should be more soluble in the organic solvent volume, noted V_{org} , with a very low solubility in the aqueous phase volume, V_{aq} . The solvent should be industrially applicable, non-volatile, non-flammable and non-toxic as well as economical for pilot plant operations to produce the metal. The parameter used in SX process is the distribution ratio, D_e , defined as the ratio of [metal in organic phase] over [metal in aqueous phase]. Based on D_e , the extraction percentage, $\%E$, indicates how much metal was extracted in the organic phase. $\%E$ is calculated by following formula:

$$\%E = D_e \times 100 / (D_e + V_{aq}/V_{org}) \quad (1)$$

Next the stripping percentage, $\%S$, corresponds to the recovery in aqueous phase of the purified metal located in the organic phase. $\%S$ is simply calculated as $D_s \times 100 / (D_s + V_{aq}/V_{org})$, where D_s represents the distribution ratio of the metal loaded organic phase over its concentration in the aqueous phase. The distribution laws were established and elaborated by thermodynamic studies long time ago (4, 5). When several extractants are mixed for a given metal extraction, the improvement in extraction efficiency is measured by the synergistic coefficient factor, SC (6). A positive SC value corresponds to a positive synergistic effect. A negative SC value indicates that the mixture of extractants is not able to extract more metal than a single extractant used alone. When several metals are present, the separation factor, β , is defined as the ratio of Metal 1 distribution ratio, D_1 , over Metal 2 distribution ratio, D_2 , i.e $\beta = D_1/D_2$.

Many classes of extractants are commercially available. The phosphorous based extractants include di-2-ethyl phosphoric acid (D2EHPA), 2-ethyl hexyl phosphonic acid monoethyl hexyl ester (PC 88A), bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) and trioctylphosphine oxide (Cyanex 923). The thio-organophosphorous extractants include bis(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302) and bis(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex 301). There are also oximes (LIX reagents) and amine based extractants (Alamine series). On the other hand synthetic reagents especially heterocyclic compounds (the hetero atom must be electron donor, like oxygen, nitrogen, or sulfur) (isoxazolones, pyrazolones) are applied for base and precious/rare metal recovery from their available sources.

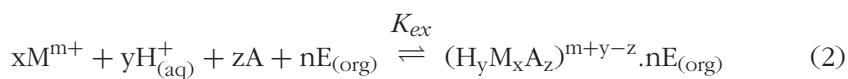
This review tries to highlight the current and future status of research and development activities on extraction and recovery of uranium from low-grade ores in acidic media, solvents as well as extractants based on nitrogen, phosphorus, oxygen and other donor atoms.

SOLVENT EXTRACTION MECHANISMS

Solvation Mechanism

Specific solvation mechanisms are involved in the case of oxygen bonded carbon type extractants such as ethers (C-O-C), esters (-COOR), alcohols (C-OH) and ketones (C=O) and those containing oxygen bonded to phosphorus such as alkyl-phosphate esters (P=O).

The metal distribution from aqueous to organic phase by solvation mechanism is a function of the metal ion concentration $[M^{m+}]$, the medium acidity (proton concentration) $[H]$, and the anion concentration $[A]$, where A can be $[Cl^-]$ or $[SO_4^{2-}]$ or $[NO_3^-]$ or any other anion found in acidic media. The ligand concentration is noted $[E]$ (7).



where K_{ex} is the equilibrium constant for the extraction process.

Chelating Mechanism

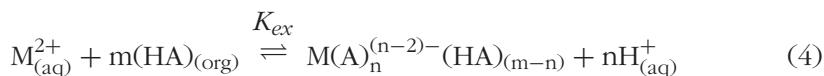
The extractants forming strong complexes with d-block elements [M] such as Ni, Co, or Cu are very selective. Back extraction, i.e., stripping, of the metal is preferably obtained with strong acids.



where RH is the oxime-based extractant.

Ion Exchange Mechanism

The acidity, i.e., the hydrogen ion concentration, plays a key role in the ion exchange mechanism. H^+ is a competitor for metal ions and extraction efficiency increases with increasing pH, which also influences organic extraction capacity.



where HA refers to the extractant (6).

Neutral Mechanism

The target metal in an oxide form can be extracted as a neutral complex. At a high acidity, un-associated acids can be removed and back extraction of the metals can be possible by water.



where HR is the extractant and AH is the acid.

AQUEOUS CHEMISTRY, HYDROLYSIS AND SPECIATION OF URANIUM

Uranium aqueous chemistry deals with the metal speciation and hydrolysis behavior in acidic solutions. Until now the reported literature demonstrates that most uranium extraction processes are developed in the following acidic or pH media: carbonate (8), hydrochloric acid (9, 21, 22, 40, 53, 59, 100, 108), sulfuric acid (12, 18, 29, 81, 111, 112, 115), nitric acid (11, 27, 33–36, 40, 47, 50, 51, 54, 56, 60–62, 68, 73, 74, 80, 83, 90, 91, 96, 100–103, 110, 114), perchloric acid (10, 31, 55, 71), phosphate (23, 25, 46, 72), hydrobromic acid (84), salicylate (43) and other low pH media (14, 28, 30, 38, 48, 67, 75, 109).

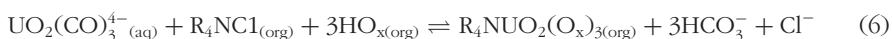
Aqueous Chemistry

The optimum stability range of uranium (V) in aqueous solutions is between pH 2 and 4. Some observations are made on the oxidation of U(V) by oxygen and other oxidizing agents and its dismutation into U(IV) and U(VI) has been studied. Near pH 2, the species U(IV): U^{4+} , $UO\text{H}^{3+}$, UO^{2+} and U(VI) as UO_2^{2+} can exist in equilibrium with each other (116, 117).

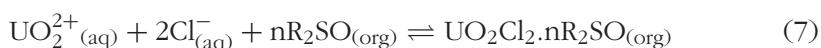
The ionic strength for perchlorate and chloride solutions obtained by using polarographic, spectrophotometric and potentiometric methods have confirmed the behavior of uranium in aqueous solutions (118). The studies

were made for establishing the behavior of uranium in trivalent state at various acidic solutions such as chloride, sulfate, perchloric solutions. The percentage of reduction is 99% in a 0.5 mol.dm⁻³ hydrochloric acid solution. Uranium was fairly stable at low concentration level in absence of atmospheric oxygen (119), but with increased acid concentration it will become unstable. The absorption spectra of trivalent uranium in the three mineral acids noted here were studied. A possibility of the formation of a chloro complex was observed due to a large change in absorption spectra at high concentrations of chloride ions (120). Aqueous solution chemistry of uranium in the binary UO_2^{2+} - SO_4^{2-} and the ternary UO_2^{2+} - SO_4^{2-} - OH^- system was investigated by using EXAFS and ^{17}O -NMR spectroscopy (121).

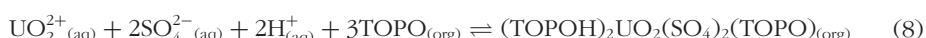
Carbonate media. The effect of concentration in the system Arquad 2C (R_4NCl) and 8-quinolinol (HO_x) dissolved in methyl isobutyl ketone (MIBK) from carbonate-bicarbonate solutions for uranium(VI) extraction phenomena can be explained quantitatively by the following equilibrium (8):



Hydrochloric acid media. The extraction of U(VI) from hydrochloric acid solutions by dihexyl sulfoxide (DHSO or R_2SO) is governed by a solvating reaction. Similar mechanism is also shown by the following extractants: tri-butyl phosphate (TBP), tri-n-octyl phosphine oxide (TOPO) (100) and benzyl octadecyldimethyl ammonium chloride (R_4NCl) (108).

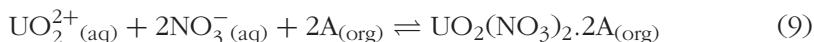


Sulfate media. Sulfuric acid media were widely used by amine based extractants for uranium extraction. Almost all systems have shown ion exchange type extraction mechanism (12, 18, 29, 115), whereas extraction of uranium(VI) from sulfuric acid solutions with tri-n-octyl phosphine oxide (TOPO) diluted in hexane showed the solvating type of mechanism (81). These results suggest that the complex of uranium(VI), H^+ and TOPO at a mole ratio of 1:2:3 is extracted into the organic phase (122). The extraction process of the preceding system can be expressed as:

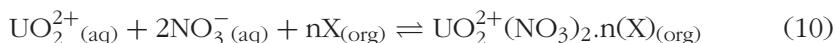


Nitric acid media with N- or P-based extractants. Extraction studies of uranium(VI) from nitric acid solutions were established by using various *N*- and *P*-based types of extractants. Nitrogen-based extractants such as amine and amide reagents predominantly appeared in the reported literature (51,

60, 62, 66–69, 73, 77, 83, 91, 101, 114). The following reaction mechanism represents the wide variety of extractants:

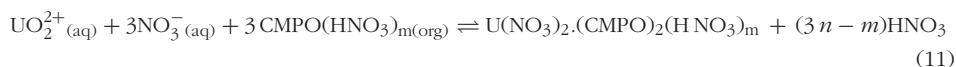


A = amide molecule = dioctyloctanamide dioctyl ethyl hexanamide (60, 62)

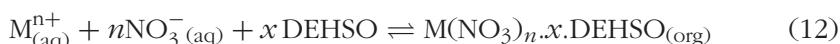


where X is an extractant such as N,N-Di-ethyl-octadecanamide (DEODA) (73) or di(2-ethyl hexyl) isobutyramide (DEHBA) (77) or N,N-di-butyl-decanamide (DBDEA) (80) or N-octanoyl-pyrrolidine (OPOD) (83) or N,N¹-dioctanoyl-piperazine (DOPEZ) (91) and/or N,N¹-dimethyl- N,N¹-dioctylsuccinylamide (DMDOSA) (101).

Several phosphorus-based extractants are also reported for uranium extraction from nitric acid solutions (11, 27, 33–36, 40, 47, 66, 74, 90, 99, 103, 113). Under the established experimental conditions, the aqueous equilibrium for the uptake uranium is expressed by:

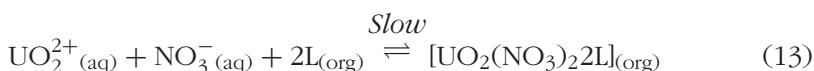


Sulfoxides and thio-substituted organophosphorus extractants were utilized for uranium extraction in nitric acid solutions. The extraction phenomena can be explained by the coexistence of the following equilibrium (56):

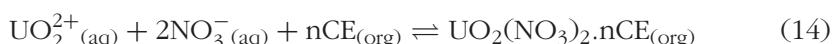


where, M is mostly U(VI) and DEHSO is the di-(2-ethylhexyl) sulfoxide.

The partial distribution of Cyanex 301 (HA) between organic phase and the interface (HA_{ads}) was reported in nitric acid solutions (96). The extraction reaction for uranium(VI) with N,N¹-dibutyl carbonyl methyl phenyl sulfoxide (L) (110, 123) can be expressed as:

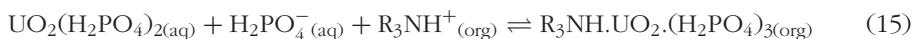


In order to study the UO_2^{2+} extraction mechanism, the dependence of uranium distribution on crown ether [CE] concentration was examined at a 4 mol. dm^{-3} nitric acid concentration (54):

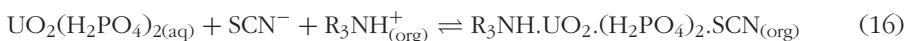


Perchlorate media. The extraction of uranium(VI) with di-2-ethyl hexyl dithiophosphoric acid (DEHDTPA) occurs via ion-exchange mechanism and complex formation in perchlorate media (31).

Phosphate media. The extraction process of U(VI) by Alamine 310 from H_3PO_4 media was established (124) recently. Orthophosphoric acid is considered as a weak acid and therefore the complex species formed in aqueous solutions are dependent on H_3PO_4 concentration and uncharged species (124). At higher H_3PO_4 concentration, more complex species $UO_2(H_2PO_4)_n^{2-n}$ exist. The following extraction mechanism is proposed with Alamine 310 as an anion-exchanger:



The influence of SCN^- ion in U(VI) extraction by Alamine 310 is as follows:



Chelate extraction data were used in investigation of the complex formation in aqueous phase by 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) mixed with TOPO for uranium(VI) extraction. The various phosphoric acid species were elucidated according to the reported literature and all possible reactions were tested. The most significant U(VI) complex formed with phosphoric acid and 2.9 to 6.33 mol. dm^{-3} U(VI) concentrations was $(U(H_5P_2O_8)_{4-n}(HPO_4)_n^{n-}$, where n was between 1 and 4. The predominant species was the neutral complex: $U(H_5P_2O_8)_4$ (29).

Other acidic media. The distribution of uranyl ion between aqueous acetate buffer (pH 5.5 to 6.5) and 7-dodecynyl-8-quinolinol (DDQ) diluted in chloroform occurred as a simple 2:1 (DDQ : UO_2^{2+}) chelate. The adverse effect of acetate ion on the uranium extraction can be explained by the formation of a series of uranyl acetate complexes from $UO_2(OAc)^+$ to $UO_2(OAc)_3^-$. The extraction data are consistent with the following reaction (30):



where HL is DDQ and OAc is the acetate ion.

By using LIX 54, TBP, or 3-methyl-4-(*p*-nitrobenzyl)-5-orophenylpyrazole (HNP), the extraction of uranium(VI), at pH 1 to 5 follows ion-exchange (reaction 4) type mechanism (38, 75).

Speciation

The speciation of uranium(VI) in micromolar aqueous solutions at ambient temperature and open atmosphere was reported (125). The solubility, mobility and bioavailability of contaminants in aquifers were controlled by the molecular interactions with solid phases (125, 126). pH solutions higher

than 8.5 are not favorable for risk of precipitation of solid uranyl hydroxides. At mildly acidic pH values, the trimer $(\text{UO}_2)_3(\text{OH})^{5+}$ is assumed to be the dominating species U(VI) whereas a further increase of the pH leads to formation of various complexes. Ultracentrifugation and acidity measurements in chloride solutions of U(VI) species were developed for hydroxyl numbers (n) up to 1.4 (128).

Hydrolysis

The hydrolysis of uranium(VI) has been investigated in various saline solutions of 0.1 and 1.0 mol. dm^{-3} Na_2SO_4 . The different uranyl hydrolysis species established were: $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_4^{2+}$, $(\text{UO}_2)_4(\text{OH})_7^+$ and $(\text{UO}_2)_5(\text{OH})_8^{2+}$. Additionally, UO_2OH^+ and $(\text{UO}_2)_3(\text{OH})_5^+$ were found in the lower 0.1 mol. dm^{-3} ionic strength only (129). The species UO_2OH^+ , $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_4^{2+}$, $(\text{UO}_2)_3(\text{OH})_5^+$ and $(\text{UO}_2)_4(\text{OH})_7^+$ have been also identified in nitrate media (130). The hydrolysis of U(VI) in tetraethyl ammonium perchlorate (0.1 mol. dm^{-3} at 25°C) was studied at different temperatures from 10 to 85°C (131). Hydrolysis of U(VI) at high temperatures and pressures via speciation analysis by time-resolved laser induced fluorescence spectroscopy was also performed (132). It found species such as $\text{UO}_2(\text{OH})^+$, $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_5^+$.

These uranyl(VI) ions indicate that the Arrhenius plot of luminescence lifetime can be an effective method for determining in-situ speciation of uranyl hydrolysis product at elevated temperatures and pressures (132). Water samples collected from different mining areas were tested for uranium speciation by laser spectroscopy. The obtained species distributions were compared with modeling predictions and were in good agreement (133).

Uranium(IV)-oxygen bonds are derived from the hydrolysis of UCl_4 . UCl_4 dissolved in H_2O (or D_2O), yields a product believed to be primarily a mixture of $[\text{U}(\text{H}_2\text{O})_6\text{OH}]_2\text{Cl}_6$ and $[\text{U}(\text{H}_2\text{O})_6(\text{OH})_x\text{Cl}_{1-x}]_2\text{Cl}_6$. U(IV) forms the following four products: $\text{UCl}_3(\text{OH}) \cdot 3\text{H}_2\text{O}$, $\text{UCl}_3(\text{OH}) \cdot 1 \cdot 5\text{H}_2\text{O}$, $\text{UCl}_{2.5}(\text{OH})_{1.5}$, and $\text{UO}_{1.15}\text{Cl}_{2.1}$ on a preparative scale, and these were examined by infrared spectroscopy in the 4000–250 cm^{-1} region (134).

LITERATURE REVIEW ON SOLVENT EXTRACTION (SX) OF URANIUM

The different extractants used for uranium recovery can be divided as 1) nitrogen-based extractants, 2) phosphorous-based extractants, 3) sulfur-based extractants and 4) other extractants. The different solvent extraction methods for uranium from acidic solutions are listed in Table 1.

TABLE 1 Summary of Uranium SX Systems

Name of the extractant	Aqueous medium and range	Diluent	Selectivity	Remarks	Ref.
<i>Nitrogen-based extractants</i>					
8-Quinolinol and a quaternary ammonium ion	Carbonate	—	—	The extraction is based upon the novel uranyl chelate $\text{UO}_2(\text{C}_9\text{H}_6\text{ON})_3^-$, formed with 8-quinolinol	8
Tri(iso-octyl)amine	Hydrochloric acid	Xylylene or methyl isobutyl ketone	Thorium, alkalies, alkaline earths, rare earths, zirconium, niobium and ruthenium	Technique for new type nuclear fuel elements produce solutions from which uranium and plutonium may be extracted as chlorides at room temperature from the fission products and particularly, from macro quantities of zirconium	9
Di-n-decyldamine sulfate	Sulfuric acid-sodium sulfate	Benzene	—	The stoichiometry of the principal organic complex is uranium:sulfate:amine = 1:4:6	12
Tri-octylamine	sulfuric acid	Benzene	U(IV)	Osmometric measurements on solutions of the uranium complex in the organic phase indicate a tendency of this complex to aggregate	18
2-n-Butyl-2-ethyl octanohydroxamic acid	—	Hexane, xylene and chloroform	Zr, Ce, Ru, Sr and Cs	The results indicate that a 1:2 complex, UO_2X_2 , is formed in solution, which has been confirmed by analysis of the isolated complex	24
Tertiary amines	Acid heap leach liquor	—	Fe	3 stages for extraction and 2 stages for stripping are required to get 98.9% uranium recovery	28
Tri-n-octylamine	Sulfate (pH 2.6 and 3.6)	Benzene	—	The dissociative reaction $\text{L}_4(\text{SO}_4) \rightleftharpoons \text{UO}_2\text{SO}_4 + \text{L}_2\text{SO}_4$ with an equilibrium constant in the region of 10^{-3} is obviously of little consequence	29
7-Dodeceny-1-8-quinolinol (HL)	Acetate	Chloroform	—	In the absence of acetate, the extracted species is the self-adduct, $\text{UO}_2\text{L}\text{-HL}$.	30

(Continued)

TABLE 1 (Continued)

Name of the extractant	Aqueous medium and range	Diluent	Selectivity	Remarks	Ref.
LIX 622	Nitrate, chloride, sulfate and phosphate (1 mol.dm ⁻³) Nitric acid (3 mol.dm ⁻³)	Benzene n-Heptane	Mo(VI) and Th(IV) Tc(VII)	Extraction of uranium(VI) by 10% (v/v) LIX 45622 in benzene was found to increase with increasing equilibrium pH (3.0 to 6.0), and becomes quantitative at pH 5.9. Stripping of Tc(VII) into 2 mol.dm ⁻³ aqueous ammonium carbonate solution was enhanced to quantitative level by repetition of the stripping procedure.	45 51 55
Primary amine					
Triisodecylamine (Alamine 310)	Phosphoric acid (1 to 10 mol.dm ⁻³)	Benzene	Mo(VI)	Extraction of U(VI) by Cyanex 301 and its mixtures studied in the range 0.2 to 1.0 mol.dm ⁻³ aqueous H ₃ PO ₄ is far from being quantitative.	55
88	N,N,N',N'-tetraalkyl-2-alkylpropane-1,3 diamides	Nitric acid	—	Pu(IV)	
				Thus, two kinds of interactions were observed: - in the inner sphere of the metal: diamide-metal ion complexation; - in the outer sphere of the metal; diamide-metallic complex interactions.	57
Tri-n-octylamine	Hydrochloric acid	Benzene	U(VI)	U(VI) was very soluble at 4 mol.dm ⁻³ HCl	59
Isomeric monoamides	Nitric acid	n-Dodecane	Pu(IV)	From the variation of distribution ratio with temperature, it was shown that the extraction reaction was enthalpy controlled in all the cases.	60
High molecular weight aliphatic monoamides	Nitric acid (5 mol.dm ⁻³)	—	Pu(IV)	U(VI) and Pu(IV) were separated by using these amides without valence adjustment was explored	62
N,N-dimethyl-N,N'-dibutylmalonamide	Nitric acid	—	Lanthanide(III)	When compared to lanthanides(III) to uranyl(VI) ins are able to extract by DMDBMA	63

Carboxylic acid amides	Nitric acid (2.5 to 6 mol.dm ⁻³)	Th(IV)	Uranium distribution ratio shows 2 nd order where as thorium distribution ratio shows 3 rd order	64
N,N-dihexyl substituted amides	Nitric acid (3.5 mol.dm ⁻³)	n-Dodecane	Pu(IV), Zr(IV), Ru(II) and Eu(III)	65
N,N,N,N-tetrabutylsuccinylamide (TBSA)	Nitric acid	Kerosene	—	68
N,N,N,N'-tetrabutyladipicamide	Nitric acid	Kerosene	Th(IV)	69
Aliquat 336 (R ₃ R'NH ₂ PO ₄)	Phosphoric acid (0.4 to 1.4 mol.dm ⁻³)	Xylene	—	71
N,N- diethyloctadecanamide	Nitric acid	—	UO ₂ A ₂ (R ₃ R'N) ₂ (H ₂ PO ₄) ₂ in the extracted organic phase was formed	71
Di(2-ethyl hexyl)isobutyramide	Nitric acid	n-Dodecane	At 3.0 mol.dm ⁻³ nitric acid concentration the phases were clear	73
N,N- dibutyldecanamide (DBDEA)	Nitric acid	Kerosene	Pu(IV)	77
N-octanoylpyrrolidine (OPOD)	Nitric acid	Toluene	IR spectra show that there is no apparent interaction between the two kinds of extractants	80
N,N-dihexyloctanamide	Nitric acid (3.5 mol.dm ⁻³)	Dodecane	The extracted species of the uranium with OPOD can be expressed as UO ₂ (NO ₃) ₂ (OPOD) ₂	83
Di(2-ethylhexyl) pivalamide	Nitric acid (4.0 mol.dm ⁻³)	n-Dodecane	At 8.5 mol.dm ⁻³ nitric acid, similar to tertiary amines, anionic species, UO ₂ (NO ₃) ₃ ⁻ extracted as [UO ₂ (NO ₃) ₃ ⁻] [HDHOA ⁺] by ion-pair formation ~98% of U could be extracted in five contacts with <1% cumulative Pu extraction.	86 95

(Continued)

TABLE 1 (Continued)

Name of the extractant	Aqueous medium and range	Diluent	Selectivity	Remarks
N,N,N',N'-tetraoctyl-3-oxapentanediamide	Nitric acid (0.002 to n-Dodecane 6.0 1 mol.dm ⁻³)	Alkali metals, Be(II), B(III), Mg(II), Al(III), Si(IV), Si(IV), V(V), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Ga(II), Ge(IV), As(III), Se(IV), Nb(V), Rh(II), Ag(I), Te(IV), Ta(V) and Ti(I)	97	The extracted chemical forms were determined to be M(TODGA) ₃ (NO ₃) _n or M(TODGA) ₄ (NO ₃) _n (M = U(VI); n = 3 or 4).
N,N'-dimethyl-N,N'-diethylsuccinylamide	Nitric acid (1.0 to 5.0 mol.dm ⁻³)	Toluene	—	The stoichiometry of the main extracted species was confirmed to be UO ₂ (NO ₃) ₂ 2DMDO-SA
Diamides of dipicolinic acid (N,N'-diethyl-N,N'-diolyl-dipicolinamide, EtIDPA)	Nitric acid	—	—	IR of loaded organic phases indicate that nitric acid is co-extracted as part of the neutral metal-ligand complex
Pyrrolidone derivatives [N-cyclohexyl-2-pyrrolidone (NCP), N-octyl-2-pyrrolidone (NOP), and N-dodecyl-2-pyrrolidone (NDP)]	Nitric acid (0.08 to 3.0 mol.dm ⁻³)	Dichloromethane	—	Extracted U(VI) as UO ₂ (NO ₃) ₂ (NRP) ₂
Alamine 336 (Modifier= 5% w/w 1-tridecanol)	Sulfate solutions (0.146 mol.dm ⁻³)	Kerosene	—	For developing the flow-sheets for uranium 111 by extraction process is improved
Di-n-octylamine	Sulfate solutions (0.146 mol.dm ⁻³)	Kerosene	—	A new route to delay the effect of chemical 112 degradation of the organic phase during uranium recovery.

N,N,N',N'-tetraoctyl diglycolamide (TODGA) and N,N-dihexyl octanamide (DHOA)	Nitric acid (3.12 mol.dm ⁻³)	Paraffinic hydrocarbons (NPH)	Fe, Mn, Ni, Ba and Cs	The extractant was tested for five cycles for 114 metal extraction
Alamine 336	Sulfate solutions (0.1 to 1.0 mol.dm ⁻³)	Ketosene	V(V)	
<i>Phosphorus-based extractants</i>				
Di-(2-ethylhexyl)-phosphoric acid (DPA)	Perchlorate	n-Hexane	—	The highest separation factor (S.F = 45.18) 115 was observed at 0.1 mol.dm ⁻³ H ₂ SO ₄ concentration with 0.005 Alamine 336.
Tri-n-octylphosphine oxide	Nitric acid	Cyclohexane	Ca(II), Cd(II), Co(II), Cr(III), Cu(II), Al(III), Y(III), La(III), Fe(II) and V(IV)	Electro micrographs were taken for DPA-hexane system of uranium Chloride interferes seriously in this method 11
Di-(2-ethylhexyl)-phosphoric acid	Sulfuric acid	Ketosene	—	IR data was recorded for organic phases 13 with different acidic conditions
Tetra-butyl-pyrophosphate (TBPP)	Nitric acid	Carbon tetrachloride	—	The molar ratio of TBPP and uranium nitrate was 10:1 reported 15
Mono-2,6,8-trimethylnonyl-4- and mono-n-butylphosphoric acids	Sulfuric acid	Benzene and carbon tetrachloride	—	The loaded organic tested for the 16 composition of the metal and extractant ratio
Di-(2-ethylhexyl)-phosphoric acid	Perchloric acid	Carbon tetrachloride	—	U(ClO ₄) ₄ (HDEHPA) _n ·2HClO ₄ complex 17 confirming the salivation mechanism in strong acidic solutions
Tri-n-octyl phosphine oxide (TOPO or Cyanex 923)	Hydrochloric acid	Ketosene	—	The absorption spectra of both the aqueous 19 and organic phases have been examined
Octa-ethyl-tetra-amidopyrophosphate	HCl and HNO ₃	Carbon tetrachloride	—	The solvation energy of the extracted 21 complexes was calculated and reported
Di-n-butylphosphate	Nitrate	Toluene	—	Synergistic effect was studied and reported 26 the factor 100 for uranium extraction process
Tri-butyl-phosphate (TBP)	HNO ₃ and HCl (1 to 4 mol.dm ⁻³)	Naphthalene	Mg, Fe, La and Al	Uranium concentrated to 1,000-fold of the 27 initial concentration in this method

(Continued)

TABLE 1 (Continued)

Name of the extractant	Aqueous medium and range	Diluent	Selectivity	Remarks
Di-2-ethylhexylthiophosphoric acid	Perchlorate	Cyclohexane	—	The enhancement of the distribution of the metal aqueous to organic was due to the long and branched alkyl chain of the extractant 31
Di-2-ethylhexylthiophosphoric acid (HEhdtp)	Nitrate, chloride, sulfate and phosphate	Benzene	—	The extracted species is a 1:2 complex of metal with extractant 33
Organophosphorus esters	Nitrate and phosphate	—	—	The species of the metal complex was reported as $\text{UO}_2\text{X}_2(\text{HX})_2$ is shown ($\text{HX} = \text{D2EHPA}$) with single extractant where as with mixture was $\text{UO}_2\text{X}_2(\text{HX})_2 \cdot \text{TOPO}$ 34
92	Cetylphenyl acid phosphate (OPAP)	Nitrate	Toluene	Ce(III), Nd(III), Gd(III) and Tb(III)
Di(2-ethylhexyl)phosphoric acid	Nitrate	—	—	Various experimental parameters like influence of diluents, acid concentration and extractant effect metal extraction was examined 36
Bis(2-ethylhexyl) phosphoric acid	Nitrate (0.111 to 6 mol. dm^{-3})	Kerosene	—	The equilibrium process was influenced by very low vicinity of the metal and acid concentrations 37
Tris-2-ethyl hexyl-phosphate	Salicylate media	Xylene	Th, Ce, Ti, Zr, Hf, Cu, V and Cr	Aqueous phase acidity was influenced the order of reaction process 39
Di (2-ethylhexyl) phosphoric acid	phosphoric acid	—	Ce and Y	Various experimental parameters like time effect, extractant concentration and metal ion effect was established for optimization of the extraction process 43
				Radioisotopes of the every element was used for this study 46

Oetyl(phenyl)-N,N-diisobutylcarbamoyl methylphosphine oxide (CMPO) and tributyl phosphate (TBP)	Nitrate	Dodecane	Pm(III), Pu(IV), Am(III), Basic experimental conditions was established by acid, extractant and metal ions influence in extraction process	47
TBP	—	n-Dodecane	Temperature influence for the extraction process was established	48
TOPO	HCl, H ₂ SO ₄ and HNO ₃	—	Extraction constants reported based on corresponding mineral acids dissociation constants	49
Trialkyl phosphates 2-Ethylhexyl 2-ethylhexylphosphonic acid (PC88A = HY) and TOPO TBP	Nitric acid Sulfuric acid	— Cyclohexane and xylene	Pu(IV) and Th(IV) —	58 61
TOPO and D2EHPA TBP	Nitric acid	Kerosene	Th(IV) and U(VI) —	66 72
Di-2-ethylhexyl phosphoric acid	Phosphoric acid	Kerosene	—	74
TOPO	Nitric acid	Kerosene	—	74
Di-n-butyl phosphoric acid	Phosphoric acid	Kerosene	Fe(II) and Fe(III)	79
TOPO	Sulfuric acid (3.5 mol.dm ⁻³)	n-Heptane	—	81
Di-n-butyl phosphoric acid	Nitric acid (0.5 to 3.0 mol.dm ⁻³)	Decane or xylene	—	82

(Continued)

TABLE 1 (Continued)

Name of the extractant	Aqueous medium and range	Diluent	Selectivity	Remarks	Ref.
N,N-dialkylcarbamoylmethyl (diphenyl)phosphine oxides	Hydrochloric acid	1,2-Dichloroethane	Sc, Ga, In, Tl, Mo, Zr, Sn, Sb, and Th	Replacement of hydrogen in the methylene bridge between the phosphinoyl and carbamoyl groups by an alkyl radical was increasing the selectivity of the title metal was extracted into xylene as $\text{UO}_2(\text{NO}_3)_2$.	85
Cyanex 923 (TRPO)	Nitric acid	Xylene	Th(IV)	The results demonstrate that title metal ion was extracted into xylene as $\text{UO}_2(\text{NO}_3)_2$.	87
PC-88A (H_2A_2 in dimeric form), TBP, TOPO and Cyanex 923 (S)	Hydrochloric acid	Dodecane	—	$\text{UO}_2(\text{HA}_2)_2$: Species with PC 88A UO_2Cl_2 : Species with TOPO or Cyanex 923 $\text{UO}_2(\text{HA}_2)_2$: S: Species with mixture At lower acidities, U(VI) was extracted as Uranium follows different aqueous mechanisms based on acidic condition.	89
Bis(2,4,4-trimethyl pentyl) phosphinic acid (Cyanex 272)	HNO_3 , HCl and HClO_4	n- <i>Dodecane</i>	—	At lower acidity: $\text{UO}_2(\text{HA}_2)_2$ by an ion exchange mechanism, whereas at higher acidities as $\text{UO}_2(\text{NO}_3)_2\cdot 2(\text{H}_2\text{A}_2)$ following a solvation mechanism	90
Diphenyl (dibutylcarbamoylmethyl) phosphine oxide	HCl (1.0 mol.dm ⁻³)	Dichloroethane	Am(III) and Pu(IV)	Aryl strengthening effect was observed in chloride solutions	94
Di-nonyl phenyl phosphoric acid (DNPPA) and tri-n-octyl phosphine oxide (TOPO)	HNO_3 , HClO_4 , H_2SO_4 , and HCl	Aliphatic hydrocarbon	Zn, Cu, Ni, Ca, and Fe	The extraction order of metal in following aqueous media follows: perchlorate > nitrate > chloride > sulfate > phosphate	98
TBP	Nitric acid (0.5 to 6.35 mol.dm ⁻³)	Kerosene	—	Two stages are enough to extract more than 98% of uranium at 5.75 mol.dm ⁻³ nitric acid concentration using 0.363 and 0.726 mol.dm ⁻³ TBP/kerosene at operating lines ($\text{V}_{\text{org}}/\text{V}_{\text{aq}} = 1/6$ and 1/3) respectively	99

TBP	Nitric acid (0.1 to 5.0 mol.dm ⁻³)	n-Dodecane	Fe, Cu, Ni, V, Cd	IR of the complex showing following species: $UO_2(NO_3)_2 \cdot 2TBP$ 0.5 mol.dm ⁻³ solution of $(NH_4)_2CO_3$ was used for back extraction of metal from loaded synergistic organic phase	103
2-Ethyl hexyl hydrogen 2-ethyl hexyl phosphonate (PC88A) and octyl (phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide (CMPO)	—	—	—	—	113
2-Ethylhexyl phosphonic acid-mono-2-ethylhexyl ester (PC88A in dimeric form, H_2A_2), tri-n-butyl phosphate (TBP), trioctyl phosphine oxide (TOPO), and dioctyl sulfoxide (DOSO)	Nitric acid (0.5 to 6 mol.dm ⁻³)	n-Dodecane	—	The extracted species of uranium using PC88A as extractant were identified as $UO_2(NO_3)_2(HA_2)H_2A_2$ (low acidity: 3 mol.dm ⁻³ HNO_3) and $UO_2(NO_3)_2_2(H_2A_2)$ (high acidity: 3 mol.dm ⁻³ HNO_3)	—
<i>Sulfur-based extractants</i>	Hydrochloric acid (> 8 mol.dm ⁻³)	—	—	The species extracted would appear to be $UO_2Cl_2 \cdot 2DPSO \cdot HCl$, $UO_2Cl_2 \cdot 3DOSO$, and $UO_2Cl_2 \cdot 3TBP$.	20
Di-2-ethylhexylsulfoxide Di(2-ethylhexyl) sulfoxide (DEHSO)	Nitric acid	n-Dodecane	—	1:1 (DEHSO) (HNO_3) adduct was formed	44
Sulfoxides	Nitric acid	Ketosene	Th, Zr, Nd and Ru	The extracted species was reported as $UO_2(NO_3)_2 \cdot 2DEHSO$	52
Bis-2-ethylhexylsulfoxide (BEHSO)	Nitric acid	—	—	Uranium and thorium was extracted as disolvates, whereas HNO_3 is extracted as monosolvate	56
Bis(2,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301)	Nitric acid (ionic strength 0.1 mol.dm ⁻³)	Ketosene	—	Elemental analysis and IR spectra was recorded for metal solid samples	70
Dihexyl sulfoxide (DHSO, R_2SO)	HCl (1.0 to 10 mol.dm ⁻³)	Benzene	—	Kinetic results indicated that the extraction of uranium is of first order	96
				The extraction efficiencies for U(VI) are in following order: $TOPO > DHSO > TBP$	100

(Continued)

TABLE 1 (Continued)

Name of the extractant	Aqueous medium and range	Diluent	Selectivity	Remarks	Ref.
Bis(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302)	Nitric acid (0.001 to 8.0 mol.dm ⁻³)	Xylene	Th(IV), Nd(III), Ce(IV), Yb(III), Y(III), Dy(III), Gd(III), La(III), V(IV), Cr(VI), Pb(II), Cd(II), Co(II), Zn(II), Mn(II), Ni(II), Cu(II), Mg(II), Ca(II), K(I) and Na(I) Ti(IV), Zr(IV), Hf(IV) and Th(IV)	Uranium recovery from uramicrolite tailings (leachate) was successfully tested	102
Di-n-butyl sulfoxide (DBSO)	Nitric acid (2.0 mol.dm ⁻³)	Petroleum ether	—	104	
Bi-functional carbamoyl methyl sulfoxides	Nitric acid (0.5 to 9.5 mol.dm ⁻³)	Toluene	—	Back extraction of uranium from loaded organic phase was possible with 5% sodium carbonate or 1.0 mol.dm ⁻³ HNO ₃ + 0.2 mol.dm ⁻³ ascorbic acid.	110
<i>Other extractants</i>					
Mesityl oxide	Nitric acid and ammonium nitrate	—	Ag(I), Pb(II), Ti(IV), Zn(II), Cd(II), Ni(II), Ba(II), Mo(VI), phosphate, citrate, tartrate, and EDTA	Addition of sodium or ammonium nitrate to the aqueous phase enhances the extraction and permits almost complete extraction even from 0.5 mol.dm ⁻³ nitric acid.	14
1-(4-Tolyl)-2-methyl-3-hydroxy-4-pyridone	Hydrochloric acid (pH 1 to 4)	Chloroform	Protactinium(V)	A metal complex with the formula UO ₂ Y ₂ . HY was isolated from the chloroform solution	22
Neotridecanohydroxamic acid	Phosphate	Shellsol T	Phosphate ions	The lower acidic conditions favorable for high extraction efficiencies	23
1-Phenyl-3-methyl-4-benzoylpyrazolone-5 (PMBP)	Phosphoric acid (2.9 to 6.33 mol.dm ⁻³)	—	Metal species in the aqueous phase is the neutral complex as U(H ₅ P ₂ O ₈) ₄	25	

Cis, syn, cis-dicyclohexano-18-crown-6	Hydrochloric acid —	Thorium	X-ray crystallography was used for examined of the crystal structure of the extraction complex	35
LIX-54 (a β -diketone derivative = HA)	—	Benzene	—	38
DC-18-crown-6	Hydrochloric acid (6 to 8 mol. dm^{-3})	Chloroform	Th, Zr, Sc, Y, Tl and Sn	40
3-Phenyl-4-acetyl-5-isoxazolone	—	4-Methyl-2-pentanone	La(III), Ce(III), Eu(III) and Th(IV)	41
3-Phenyl-4-benzoyl-5-isoxazolone (HPBI)	—	Chloroform	La(III), Ce(III) and Eu(III)	42
1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) and thenoyltrifluoroacetone (HTTA)	—	Nitric acid	Th(IV)	50
N-octylcaprolactam and N-(2-ethyl)hexylcaprolactam	—	Hydrochloric acid (6 to 10 mol. dm^{-3})	Alkali and alkaline earth metals, transition metals W(V), Zr(IV), V(V) and Mo(VI)	53
Dibenzo-24-crown-8 (DB24C6)	Nitrobenzene	Toluene	Pu(IV)	54
Dicyclohexano-18-crown-6 (DC18C6)	Nitric acid	Toluene	Mn, Cd, Pb, Tl and Ni	54
Cryptand-222 and Eosin	pH 5.5 to 6.5 (pH 6.0)	Chloroform	Ni(II)	67
3-Methyl-4-(p-nitrobenzoyl)-5-oxo-phenylprazole (HNP)	—	Benzene	—	75
N-alkylcaprolactams	Nitric acid	Toluene	—	76

(Continued)

TABLE 1 (Continued)

Name of the extractant	Aqueous medium and range	Diluent	Selectivity	Remarks
Tetra-carboxylated calix[4]arene (IH_4)	—	Chloroform	Th(IV)	Thorium and uranium separation factor reported about 1000 in the presence or absence of alkali ions Ref. 78
Dibenzo-24-crown-8 (DDB24C8)	Hydrobromic acid (6.0 to 8.0 mol. dm^{-3})	Nitrobenzene	Rb(I), Cs(I), Th(IV), Ce(III), La(III), Be(II) and Li(I)	The title metal was quantitatively stripped from the organic phase with 0.1 to 1.0 mol. dm^{-3} hydrochloric acid, 0.5 to 10 mol. dm^{-3} nitric acid, 2 to 10 mol. dm^{-3} perchloric acid, 3.0 to 10 mol. dm^{-3} sulfuric acid or 3.0 to 10 mol. dm^{-3} acetic acid Ref. 84
4-Acylbis(1-phenyl-3-methyl-5-pyrazolones)	Nitric acid (0.2 mol. dm^{-3})	Chloroform	Th(IV)	The results demonstrate that uranium was extracted into chloroform as $\text{UO}_2(\text{HSP})_2$ and $\text{UO}_2(\text{HDDP})_2$ with H_2SP or H_2DDP Ref. 88
$[\text{4-sebacoylbis(1-phenyl-3-methyl-5-pyrazolone)}(\text{H}_2\text{SP})$ and $4\text{-dodecanedioylbis(1-phenyl-3-methyl-5-pyrazolone)}$ (H ₂ DdP)]	Nitric acid	Carbon tetrachloride Toluene	— —	The extraction of U(VI) with DOPEZ from nitric acid media is exothermic The extraction constant ($\log k_{\text{ex}}$) for the binary species $\text{UO}_2(\text{PBD})_2\text{-nH}_2\text{O}$ was found to be 1.42 ± 0.14 , for the ternary species $\text{UO}_2(\text{PBD})_2\cdot\text{D2EHAA}$, $\text{UO}_2(\text{PBD})_2\cdot\text{D2EHPrA}$, $\text{UO}_2(\text{PBD})_2\cdot\text{D2EHAA}$, $\text{UO}_2(\text{PBD})_2\cdot\text{D2EHPrA}$ and $\text{UO}_2(\text{PBD})_2\cdot\text{D2EHPrV}$ were estimated to be 6.51, 6.21, 6.11 and 5.77 respectively Ref. 91 Ref. 92
$\text{N,N}'\text{-Diocanoylpiperazine}$ (DOPEZ)	Nitric acid	—	—	
3-Phenyl-4-benzoyl-5-isoxazolone	Nitric acid	—	—	

1-phenyl-3-methyl-4-(2-ethylhexanoyl)-5-pyrazolone (HPM2EHP)	Nitric acid	Xylene	Th(IV) and trivalent lanthanides	The results demonstrate that U(VI) was extracted into xylene as $\text{UO}_2(\text{PM2EHP})_2$ with HPM2EHP alone and as $\text{UO}_2(\text{PM2EHP})_2\cdot\text{TRPO}$ in the presence of TRPO.	93
Benzyl octadecyl dimethyl ammonium chloride (BODMAC)	HCl (1.0 to 6.0 mol. dm^{-3})	Chloroform	—	The composition of the extracted species was $\text{R}_4\text{N}\cdot\text{UO}_2\text{Cl}_3$ and $(\text{R}_4\text{N})_2\cdot\text{UO}_2\text{Cl}_4$.	108
N-phenylbenzo-18-crown-6-hydroxamic acid (PBCHA)	pH (4.0 to 6.5)	Dichloromethane	Cerium, thorium and lanthanides	Uranium was recovered in 99.95% purity from monazite sand and phosphate rocks	109

Nitrogen-based Extractants

Amides/amines (having various carbon chains) are the main class of nitrogen based compounds. The reported literature reveals a large variety of extractants based on amides (57, 60, 62–65, 68, 69, 73, 77, 80, 86, 95, 101, 106) and amines (9, 18, 28, 29, 51, 55, 59) used for uranium extraction from various sources.

Uranium extraction from carbonate solutions using 8-quinolinol (HO_x) as chelating extractant was reported in hexane (8). A $0.1 \text{ mol} \cdot \text{dm}^{-3}$ HO_x in hexane extracted $0.01 \text{ mol} \cdot \text{dm}^{-3}$ of $\text{UO}_2(\text{NO}_3)_2$ with a distribution ratio of 10.9. To examine the influence of Arquad 2 C (dialkyl-dimethyl-ammonium chloride) concentration varying from 0.08 to $0.1 \text{ mol} \cdot \text{dm}^{-3}$ on uranium extraction process, it was observed that the increase in total carbonate concentration decreased the distribution ratio. A higher pH value like 12.6 favored the transfer of $\text{U}_3\text{O}_{8\text{aq}}$ to organic phase with $0.3 \text{ mol} \cdot \text{dm}^{-3}$ extractant concentration at $1.0 \text{ mol} \cdot \text{dm}^{-3}$ Na_2CO_3 (8). However the Na_2HCO_3 solutions and a lower pH were found to be the most efficient extracting media for uranium in a multi stage loading by countercurrent method (8).

Tris (iso-octyl) amine (TOA) was used as a promising reagent for extraction of uranium and plutonium from chloride solutions (9). An initial study on time effect concluded that 1 to 2 min time was more than enough to achieve equilibrium for the metal extraction. The high acidic range such as $2\text{--}8 \text{ mol} \cdot \text{dm}^{-3}$ was more favorable for extraction of metal. Equal phase ratio of the aqueous and organic xylene or MIBK phase containing uranium counts of 4×10^4 α count per min per ml of and 5% (v/v) TOA in xylene (or MIBK), respectively was used for study. At acidity $4\text{--}6 \text{ mol} \cdot \text{dm}^{-3}$ good extraction ($\sim 99\%$) with excellent phase behavior was observed whereas at acidity higher than $9 \text{ mol} \cdot \text{dm}^{-3}$, a gel was formed in the extraction process (9). Diluents such as carbon tetrachloride, xylene, Amsco 125-82 (a purified kerosene) gave ~ 95 to 99% extraction yield but with the formation of some yellow gel at the interface, whereas di-isobutyl-carbinol was able to extract only 59% uranium but with clear phases (9).

Trioctylamine (TOA) dissolved in benzene was used for uranium(IV) extraction from sulfate solutions (18). A mixture of U(IV) and U(VI) was tested for extraction efficiency and selectivity. It indicated that U(VI) formed more stable complex with TOA as compared to U(IV) (18). High purity TOA dissolved in kerosene was used for uranium extraction from heap leach solutions (28). A distribution ratio (D_0) as high as 1388 was obtained with a $0.172 \text{ mol} \cdot \text{dm}^{-3}$ amine solution in kerosene. The McCabe-Thiele diagram confirmed that two stages were required for full uranium extraction with 5% v/v TOA, whereas $0.1 \text{ mol} \cdot \text{dm}^{-3}$ Na_2CO_3 stripped (back extraction) the metal from the loaded kerosene phase in two stages (28).

The extraction of uranium from sulfuric acid-sodium sulfate solutions by di-*n*-decylamine sulfate in benzene (12) was examined as a function of

amine, acid and sulfate ion concentration. The stoichiometry of the principal organic complex was determined to be uranium:sulfate:amine 1:4:6 (12). A new extractant 2-*n*-butyl-2-ethyl octanohydroxamic acid (HX) was diluted in chloroform, hexane and xylene for uranium extraction and equilibrium constant values (K_{ex}) 1.3×10^{-3} , 2×10^{-3} and 6.6×10^{-3} were respectively calculated for the three solvent systems (24).

A model was developed and reported for uranium extraction from sulfate solutions at pH 2.6–3.6, while maintaining the phase contact for 24 hours at $21 \pm 1^\circ\text{C}$ and ionic strength of 1.00 for Na_2SO_4 and H_2SO_4 by using tri-*n*-octylamine as an extractant in benzene (29). Uranium extraction from acetic acid (OAc) with 7-dodecetyl-8-quinolinol (HL) formed mixed ligand complexes such as $\text{UO}_2(\text{OAc})\text{L}\text{HL}$ in the toluene phase. Preliminary experimental data indicated the release of two moles of H^+ ions during the extraction following the ion-exchange process (30).

In another study reported (45) with the main objective of recovering the molybdenum, the conditions established for uranium separation and quantitative extraction were as follows: 10% (v/v) LIX 622 diluted in benzene and pH 5.9 (45). Amongst the various anions like Cl^- , SCN^- and SO_4^{2-} tested for uranium extraction, SCN^- was found to be the more favorable producing a complete extraction of the $0.15 \text{ mol} \cdot \text{dm}^{-3}$ U(VI) at pH 4 (45).

The precipitation methodology was used for uranium and technetium metal separation followed by extraction process (51). The extraction and separation of uranium and molybdenum was carried out using Alamine 310, TBP or DPSO as extractants. The efficiency followed the order: TBP > DPSO > Alamine 310 (55). Based on the slope analysis data (1 ± 0.3), it was concluded that one mole of extractant was involved in the extraction process with the three reagents (55).

An extractant N,N,N',N'-tetraalkyl –2 alkyl propane –1,3 diamides was used as an extractant for uranium extraction and separation of plutonium (57). Two isomeric monoamides, dihexylbutyramide (DHBA) and dihexylisobutyramide (DHIBA), and three N,N-dihexyl substituted amides, di(2-ethyl hexyl) butyramide, di(2-ethyl hexyl)isobutyramide and N,N-dihexyloctanamide (DHOA) were proposed as promising extractants for uranium and plutonium from nitric acid media (60, 62, 65, 77, 86).

The equilibrium data clearly demonstrate that separation of U(IV) and U(VI) as well as better extraction of U(VI) with TOA takes place with very acidic 4 and 6 $\text{mol} \cdot \text{dm}^{-3}$ HCl. Various diluents such as kerosene, cyclohexane, xylene, toluene and mesitylene were tested for uranium extraction from $4 \text{ mol} \cdot \text{dm}^{-3}$ hydrochloric acid solutions containing $300 \text{ g} \cdot \text{L}^{-1}$ of uranyl ions. Kerosene and cyclohexane as the diluents exhibited the formation of a third phase. The aromatic diluents except benzene formed a cloudy organic upper phase followed by precipitation (59). N,N'-Dimethyl-N,N'-dibutylmalonamide (DMDBMA) was used for extraction of lanthanide(III) and uranyl(VI) ions from nitric acid solution. At $3 \text{ mol} \cdot \text{dm}^{-3}$

nitrate concentration, the calculated slope for uranium extraction was 2.3 indicating that two moles of extractant molecules were associated to one mole of uranium metalion. The reaction was reported to be exothermic in nature with the value of enthalpy close to -20 kJ mol^{-1} (63). Different alkyl groups in N-alkyl carboxylic acid amides were tested for uranium and thorium extraction with little influence (64).

At 20°C good extraction of UO_2^{2+} ($5 \times 10^{-3}\text{ mol.dm}^{-3}$) at 5 to 7 mol.dm^{-3} nitric acid concentration with 0.5 mol.dm^{-3} N,N,N,N-tetrabutyl succinylamide (TBSA) in toluene was reported with formation of 1:1 complex (68). Further, the variation of temperature concluded that the TBSA- UO_2^{2+} extraction process (68) was exothermic, based on a calculated enthalpy value of $-18.63\text{ kJ mol}^{-1}$. The study finally suggested that a 1:2:1 complex with UO_2^{2+} , NO_3^- and TBSA, respectively, was actually formed (68).

Uranium extraction from nitric acid solutions (69) by N,N,N,N-tetrabutyl dipicamide (TBAA) in toluene show that up to $\sim 5\text{ mol.dm}^{-3}$ acid the U(VI) extraction ($5 \times 10^{-3}\text{ mol.dm}^{-3}$) increased with increasing nitric acid concentration and thereafter decreased in hyper acid media. The lower acidic conditions like 1 mol.dm^{-3} HNO_3 gave good separation possibility between uranium and thorium with a separation factor close to 360 (69). The reaction was exothermic as confirmed by temperature experiments and the calculated enthalpy value ($-14.18\text{ kJ mol}^{-1}$). A 0.01 mol.dm^{-3} HNO_3 (pH 2) stripped about 48% uranium from the loaded toluene phase (69). The study confirms the complex structure 1:2:1 U(VI), NO_3^- and TBAA, respectively (69).

Binary mixture of 5% (v/v) Aliquat 336 and PC88A diluted in chloroform, kerosene, benzene or xylene was used for U(VI) extraction from H_3PO_4 aqueous solutions (71). The experimental results found uranium extraction ratios of 5.3% in CHCl_3 , 62.7% in xylene, 55.5% in kerosene, and 45% in benzene from the aqueous feed of $\sim 1\text{ mmol.dm}^{-3}$ uranium whereas no metal was extracted with polar hexanol and octanol organic phase (71). The synergistic effect for uranium extraction decreased from 1.89 to 0.06 with increasing the acid concentration from 0.4 to 1.4 mol.dm^{-3} (71).

Extraction of uranyl(VI) ion from nitric acid solutions by using N,N-diethyloctadecanamide as an extractant was temperature dependant. The calculated ΔH was found to be $-34.25\text{ kJ mol}^{-1}$ (73). N,N-dibutyldecanamide (DBDEA) in TBP was used for U(VI) extraction from nitric acid media at a constant temperature of 25°C and varying the HNO_3 concentration from 2 to 7 mol.dm^{-3} (80). A positive influence on UO_2^{2+} ($5 \times 10^{-3}\text{ mol.dm}^{-3}$) extraction was found increasing the temperature with 0.2 mol.dm^{-3} DBDEA. The synergistic distribution ratio, D_{DT} , was reported as 0.96–3.01 for DBDEA ($0.3\text{--}0.6\text{ mol.dm}^{-3}$) + TBP ($0.02\text{--}0.4\text{ mol.dm}^{-3}$). The highest D_{DT} (0.96) was observed with 0.3 mol.dm^{-3} DBDEA + 0.14 mol.dm^{-3} TBP at 3.0 mol.dm^{-3} HNO_3 and 25°C temperature (80).

Extraction of U(VI) from nitric acid solutions by N-octanoylpyrrolidine (OPOD) diluted in toluene was investigated varying extractant and acid concentrations, salting-out reagent and temperature. Homo-ion shifting of the uranyl(VI) extraction equilibrium was influenced by lithium nitrate. The enthalpy was calculated to be 27.73 kJ mol⁻¹ (83).

N,N'-Dioctanoylpiperazine (DOPEZ) diluted in the highly toxic carbon tetrachloride solvent was proposed as a novel extractant for U(VI) extraction from nitric acid solutions (91). Based on the slope analysis data for extractant as well as acid concentrations on metal extraction the 1:2:2 stoichiometry of the extracted species with a possible formula: $\text{UO}_2(\text{NO}_3)_2(\text{DOPEZ})_2$ (91). From high level nuclear waste, uranium extraction and recovery was carried out by di(2-ethylhexyl) pivalamide (D2EHPVA) and separation of U(VI) associated with other elements like Pu, Np and Am was reported (95).

High distribution values were observed for uranium(VI) ($D > 10$) when 75 elements were also extracted with N,N,N',N'-tetraoctyl-3-oxapentanediamide (TODGA) (97). Another amide used for extraction of U(VI) from nitric acid solutions was N,N'-dioctylsuccinylamide diluted in toluene (101). Three structural isomers of diamides of dipicolinic acid (N,N'-diethyl-N,N'-ditolyl-dipicolinamide, EtTDPA) were also reported for U(VI) extraction from nitric acid solutions (106).

Pyrrolidone derivatives such as N-cyclohexyl-2-pyrrolidone (NCP), N-octyl-2-pyrrolidone (NOP) and N-dodecyl-2-pyrrolidone (NDP) were also reported as possible extractants for U(VI) (10 mmol dm⁻³) from nitric acid solutions (107). The kinetics of extraction was fairly rapid with equilibrium achieved in 5 min showing $91 \pm 2\%$ extraction (107). At more than 3 mol dm⁻³ nitric acid concentration, NOP and NDP were effective U(VI) extractants; good stripping was possible by diluted nitric acid (107).

Collect et al. (111) investigated the U(VI) extraction (5 g L⁻¹) from sulfate solutions using 0.146 mol dm⁻³ Alamine 336 diluted in kerosene containing 5% 1-tridecanol and applied computer simulation for optimizing the flow sheets. A computer simulation was similarly applied for U(VI) extraction (737 mg L⁻¹) from sulfate media (5 mol dm⁻³) by tri-n-octylamine (TOA) and di-n-octylamine (DOA) in toluene (112). The stripping of the uranium was done at high pH using a 200 g L⁻¹ sodium carbonate solution recovering 7.95 g L⁻¹ U(VI) loaded in the toluene phase (112). N,N,N',N'-tetraoctyl diglycolamide (TODGA) was also used (114).

Recently, the study of solvent extraction of U(VI) and its separation of vanadium(V) from sulfate solutions was reported by our group (115). In this study Alamine 336 in kerosene was used for the extraction from sulfate solutions, followed by an ion-exchange mechanism for stripping with 0.1–1 mol dm⁻³ acid solution. The highest separation factor (S.F = 45) was observed at 0.1 mol dm⁻³ H₂SO₄ concentration with 0.005 mol dm⁻³ Alamine 336. Back extraction (~100%) of the metal from loaded kerosene phase, a key step in the process, was achieved with 0.5 mol dm⁻³ of NH₄Cl

in five stages. The recycling and reusing capacity of Alamine 336 was possible for 10 cycles of extraction and stripping successively. This study demonstrates the possible separation of uranium and vanadium from leach solutions by processing of yellow cake (115).

Full evaluation of the results seems to show that, amongst all nitrogen based extractants for uranium, TOA is the more promising. Its extraction efficiency is found clearly better than all other N-based extractants.

Phosphorous-based Extractants

The phosphorous-based extractants namely tri-butyl-phosphate (TBP), di(2-ethylhexyl) phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl (PC88A), Tri-*n*-octyl-phosphine oxide (TOPO or Cyanex 923) and bis(2,4,4-trimethyl pentyl) phosphinic acid (Cyanex 272) were used for uranium extraction from various acidic solutions. The reported literature reveals that D2EHPA (10, 13, 17, 31–34, 37, 39, 46, 72, 79) was predominantly used for uranium extraction when compared with other phosphorous extractants like TBP (27, 34, 47, 48, 66, 74, 89, 99, 103), PC88A (61, 71, 89, 105), TOPO or Cyanex 923 (19, 34, 49, 72, 81, 87, 89, 98) and Cyanex 272 (90).

U(VI) extraction from aqueous $\text{HCLO}_4\text{-NaClO}_4$ solutions (ionic strength = 2 mol. dm^{-3}) by di-(2-ethylhexyl)-phosphoric acid (D2EHPA) diluted in hexane was carried out (11) at 25°C (10). Tri-octyl-phosphine oxide (TOPO) diluted in cyclohexane extracted uranium from nitric acid solutions at lower acidity (0.5 mol. dm^{-3}). TOPO diluted in kerosene was used for uranium recovery from chloride solutions (19). Sato (13) reported U(VI) extraction from sulfate solutions using D2EHPA dissolved in kerosene.

The extraction mechanism for U(VI) by tetrabutylpyrophosphate (TBPP) dissolved in carbon tetrachloride followed a zero order reaction (15). Mono-2,6,8-trimethylnonyl-4- and mono-*n*-butylphosphoric acids were proposed for uranium extraction from sulfate media by varying the two different diluents such as benzene and carbon tetrachloride (16). D2EHPA formed complexes with uranium in perchloric solutions such as $\text{U}(\text{D2EHPA})_2(\text{H(D2EHPA})_2)_2$ at moderate concentrations and $\text{U}(\text{ClO}_4)_4(\text{D2EHPA})_n \cdot 2\text{HClO}_4$ at strong concentrations; it also shows that an ion-exchange process is replaced by a solvation process (17).

Octaethyltetraamidopyrophosphate (OETAPP) diluted in chloroform was proposed as a extractant for uranyl ions from nitrate and chloride solutions (21). The time-effect study showed that a 30 min time was sufficient to achieve equilibrium for chloride media whereas only 10 min were needed for nitrate media. In both cases higher acidic conditions are much favorable for extraction process and the distribution ratio increased from $1.0\text{--}4.0 \times 10^{-3}$ for chloride media and $2.0\text{--}9.3 \times 10^{-3}$ for nitrate media in the acid range 0.1 to 10 mol. dm^{-3} . In this study, a distribution potentials and surface tension of the extraction system was measured. At 1 mol. dm^{-3} chloride

concentration and UO_2Cl_2 , the measured $\Delta\Psi$ potential was -0.080V . With 1 mol.dm^{-3} sodium hydroxide at pH 13 it was only $\Delta\Psi = -0.020\text{V}$ (21).

Compounds based on bis-(di-n-butylphosphosphate) were prepared and used as promising extractants for U(VI) from nitrate solutions (26). Then, 50 mg of naphthalene added in the toluene phase enhanced the uranium extraction (4 mg.L^{-1}) from 75% to 95% with 150 mg of tributylphosphine oxide (TBPO) within 2 min shaking time at 2 mol.dm^{-3} nitric acid concentration (27). Nitrate solutions were found more favorable for uranium extraction when compared with chloride solutions in the entire acid region up to 4 mol.dm^{-3} . The method was successfully applied for uranium separation from metal ions such as magnesium, iron, lanthanum and aluminum (27).

U(VI) was extracted from a diluted aqueous solutions ($0.0005\text{ mol.dm}^{-3}$) at pH = 1.0 with 0.04 mol.dm^{-3} di-2-ethylhexyl-dithiophosphoric acid (HEhdtp) with the following diluents: cyclohexane ($D = 0.08$), chloroform ($D = 0.04$) and carbon tetrachloride ($D = 0.02$); the extraction process followed the ion-exchange mechanism (31). Uranium extraction from various mineral acids such as nitrate, chloride, sulfate and phosphate with HEhdtp in toluene was reported following the order: $\text{ClO}_4^- \sim \text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{PO}_4^{3-}$ (33). Organophosphorus esters such as acidic D2EHPA and two neutral extractants, TBP and TOPO, were employed for uranium extraction from phosphoric and nitric acid solutions (34). TBP was not sufficiently effective.

Based on this, an extraction methodology was developed with H_3PO_4 (3.5 mol.dm^{-3}) concentration while varying the nitric acid concentrations from 0.1 to 3 mol.dm^{-3} . The lower ($< 1\text{ mol.dm}^{-3}$) and higher ($> 1.5\text{ mol.dm}^{-3}$) nitric acid media were not favorable for uranium extraction (34). OPAP (0.6%) in kerosene extracted more than 90% of U(VI) ($10^{-3}\text{ mol.dm}^{-3}$) from 0.5 mol.dm^{-3} nitric acid solutions, whereas good extractions of other metal ions such as $\sim 80\%$ Tb(III), $\sim 70\%$ Gd(III), $\sim 68\%$ Ce(III) and $\sim 65\%$ of Nd(III) were noticed under this experimental condition. These metals were tested for their binary mixture separation at 1:1 and 1:10 ratios from 2 mol.dm^{-3} nitric acid concentration. The back extraction of the uranium form loaded kerosene phase was achieved by 6 mol.dm^{-3} HCl (36). The extraction of U(VI) complex from the nitrate solutions by D2EHPA was confirmed by NMR spectra (37). Kinetic extraction and stripping studies were also made (39).

At pH 3.0 to 4.7 uranium was extracted quantitatively by 4% of tris-2-ethyl-hexyl phosphate diluted in xylene from 0.025 mol.dm^{-3} sodium salicylate solution (43). For quantitative stripping from loaded organic xylene, mineral acids and NaOH in the concentration range $0.1\text{--}3.0\text{ mol.dm}^{-3}$ were effective (43). Uranium separation from its binary mixture with other metals such as thorium, cerium, titanium, zirconium, hafnium, copper, vanadium and chromium was tested using tris-2-ethyl hexyl phosphate (43). Octyl(phenyl)-*n,n*-diisobutylcarbamoylmethylphosphine

oxide (CMPO) diluted in dodecane was reported to be a promising extractant (47) for U(VI) with other fission products such as promethium(III), plutonium(IV), americium(III), zirconium(IV), ruthenium(III), iron(III) and palladium(II) from nitrate solutions.

Extraction of uranium (40 mg dm^{-3}) process was investigated with a mixed extractant consisting of 0.4 mol dm^{-3} D2EHPA + Cyanex 921 diluted in kerosene at $25 \pm 1^\circ\text{C}$, 5 mol dm^{-3} phosphoric acid and 15 minutes' shaking time (72). The U(VI) species extracted with TOPO was found to be $(\text{TOPOH}_2\text{UO}_2(\text{SO}_4)_2(\text{TOPO})$ with the equilibrium constant value of $10^{7.61 \pm 0.15}$ (81). U(VI) extraction from various mineral acids such as HNO_3 , HCl and HClO_4 by Cyanex 272 (bis[2,4,4 trimethyl pentyl] phosphinic acid) diluted in n-dodecane was reported and compared with other organophosphorus extractants such as PC88A, D2EHPA and TBP. At 0.01 mol dm^{-3} acid concentration and a feed of 0.5 mg mL^{-1} uranium, $0.005 \text{ mol dm}^{-3}$ Cyanex 272 extracted metal with a distribution ratio, D , of 136 for HNO_3 , 158 for HCl and 169 for HClO_4 . At 2 mol dm^{-3} HNO_3 , the maximum extraction (78.65%) of uranium by 2.0 mol dm^{-3} Cyanex 272 was observed (90). Stripping from loaded dodecane was easy using a 0.5 mol dm^{-3} Na_2CO_3 solution with two contacts to recover 2.34 mg mL^{-1} of uranium (90).

The influence of the TBP loaded diluent such as chloroform ($D = 3.21$), carbon tetrachloride ($D = 7.22$), dodecane ($D = 12.89$), n-hexane ($D = 11.93$) on U(VI) extraction (15 g dm^{-3}) from nitrate solutions was studied (103). Nitric acid in the range $0.1\text{--}3.0 \text{ mol dm}^{-3}$ showed positive influence on uranium extraction with TBP diluted in dodecane; the highest extraction efficiency ($D = 12.89$) was observed at 3.0 mol dm^{-3} acidity (103). Synergistic extraction of uranium (0.1 mol dm^{-3}) from nitrate solutions was also studied (113) using PC88A in the presence of neutral oxodonors such as TOPO, TBP and DOSO (dioctyl sulfoxide) (113). Uranium extraction from a 0.1 mol dm^{-3} aqueous feed was tested in various diluents such as xylene, carbon tetrachloride, n-dodecane and methyl iso-butyl ketone; all giving a 99% + extraction. The highest synergistic coefficient was 1.06 with 0.03 DOSO associated to the same concentration 0.03 mol dm^{-3} PC88A in 2 mol dm^{-3} HNO_3 concentration and $0.002 \text{ mol dm}^{-3}$ uranium feed (113).

A careful analysis of all reported literature for phosphorus-based extractants shows that TBP is clearly the best extractant with respect to extraction efficiency as well as its cost and availability.

Sulfur-based Extractants

Sulfoxides and petroleum sulfoxides are one of the most important classes of reagents for uranium extraction and recovery from various mineral acids like chloride, sulfate, nitrate, etc. (20, 44, 52, 56, 70, 104).

Various sulfoxides such as di-n-pentyl sulfoxide (DPSO), di-n-octyl sulfoxide (DOSO) and diphenyl sulfoxide (DPhSO) associated to tri-n-butyl phosphate (TBP) and their mixtures in different diluents, over a wide range

of conditions were investigated (19) for uranium extraction from hydrochloric acid solutions. Solvent extraction equilibrium analysis by slope analysis was established (44) by studying various factors for the extraction of uranyl nitrate from nitric acid by di-2-ethylhexylsulfoxide (DEHSO). The extracting abilities of five sulfoxides for thorium, uranium and some fission products were reported (56). DEHSO is not only completely miscible with kerosene, but also superior to TBP in some aspects (56).

At lower acidity ($1 \text{ mol} \cdot \text{dm}^{-3} \text{ HNO}_3$) uranium extraction ($0.2 \text{ mol} \cdot \text{dm}^{-3}$) DEHSO at $1.0 \text{ mol} \cdot \text{dm}^{-3}$ is more favorable ($D_U = 2.65$) than TBP whereas at higher acidity ($4.0 \text{ mol} \cdot \text{dm}^{-3} \text{ HNO}_3$) 2-ethyl hexyl-p-methyl-phenyl sulfoxide (EHMPSO) also at $1.0 \text{ mol} \cdot \text{dm}^{-3}$ is better ($D_U = 4.41$) (56). At this acidity ($4 \text{ mol} \cdot \text{dm}^{-3} \text{ HNO}_3$) the highest separation factor (SF= 60.2) between uranium and thorium was observed with DEHSO whereas SF is only 19.3 with TBP (56). The drawback of DEHSO is the stripping step from any organic phase that is much more difficult than with TBP. The stripping difference between DEHSO and TBP can be reduced working with higher acidity (56).

The rate of U(VI) extraction by Cyanex 301 in kerosene from nitrate medium of constant ionic strength ($0.1 \text{ mol} \cdot \text{dm}^{-3}$) was investigated using a stirred Lewis cell. The different parameters affecting the U(VI) extraction rate were optimized (96). U(VI) extraction from hydrochloric solutions followed a solvation mechanism with DEHSO and other R_2SO similar to that of TBP or TOPO, forming complexes such as $\text{UO}_2\text{Cl}_2 \cdot n\text{R}_2\text{SO}$ in organic phase (100). Formation of 2:1 complexes ($\text{R}_2\text{SO}_4 \cdot \text{UO}_2$) in organic phase was further checked by IR studies (100).

Various mineral acids such as chlorhydric, nitric, sulfuric, perchloric and acetic acids were tested for uranium extraction with Cyanex 302 in xylene (102). The metal extraction was quantitative from $1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3} \text{ HNO}_3$ using $5 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ Cyanex 302 in xylene and U(VI) was satisfactorily stripped from xylene with $5 \text{ mol} \cdot \text{dm}^{-3} \text{ HCl}$. The method was tested recovering uranium from the solutions of uranmicrolite tailings. The methodology was found to recover $51.4 \pm 0.4\% \text{ U(IV)}$ and $99.6 \pm 0.4\% \text{ U(VI)}$ (102).

Solvent extraction method has been developed for quantitative recovery of uranium from $2 \text{ mol} \cdot \text{dm}^{-3} \text{ HNO}_3$ solution using di-n-butyl sulfoxide in petroleum ether. A classical change in U(VI) partition reaction was observed with the HNO_3 concentration, the extractant nature and temperature (104). U(VI) and other metal extraction was reported by using carbamoyl methyl sulfoxide from nitric acid solutions (110). Higher acid contents such as $5\text{--}10 \text{ mol} \cdot \text{dm}^{-3}$ nitric acid were more favorable for U(VI) extraction with separation from Am(III) (110).

A full study of the selected works for uranium extraction with sulfur based extractants showed that sulfoxides are not better than the thiophosphinic extractants. From a commercial point of view, Cyanex 301 (2,2,4-trimethylpentyl) dithiophosphinic acid, and Cyanex 302, its monothio equivalent, are recommended extractants for uranium bench extraction. At a larger plant scale, no definitive reports were found.

Other Extractants

Mesetyl oxide (100%) was able to extract 900 μg of uranium(VI) quantitatively from a nitric acid ammonium nitrate mixed solution (1 mol. dm^{-3} HNO_3 + 0.5 mol. dm^{-3} NH_4NO_3) (14). A kinetic study confirmed that 10 min time was enough to reach the extraction equilibrium. The developed method showed separation possibilities for U(VI) as well as foreign ions such as Ag^+ , Pb^{2+} , Ti^+ , Zn^{2+} , Co^{2+} , Ni^{2+} , Ba^{2+} , Mo^{4+} , phosphate, citrate, tartrate and EDTA while seriously interfering metal ions were Hg^{2+} , Cu^{2+} , Fe^{3+} , Al^{3+} , Zr^{4+} , Th^{4+} and Ce^{4+} (14).

The extraction of uranium(VI) from aqueous hydrochloric or nitric acid and protactinium from hydrochloric acid by 1-(4-tolyl)-2-methyl-3-hydroxy-4-pyridone (HY) dissolved in chloroform has been studied (22). At $\text{pH} > 4$, U(VI) is quantitatively extracted while at acidic $\text{pH} < 1$ practically all uranium remains in the aqueous phase (22). Quantitative U(VI) (5–70 μg) extraction was also achieved at lower pH (<1.0–4.0) with HY (0.005 mol. dm^{-3}) diluted in chloroform. The back extraction from chloroform was possible with diluted hydrochloric or nitric acid solution (>0.1 mol. dm^{-3}). The developed method was tested for separation of uranium from protactinium (22).

Extraction of U(IV) with neotridecanohydroxamic acid (HX-70) depends primarily on the diluent used as well as on the hydrogen, phosphate and hydroxamate ion concentrations. Of the diluents tested, the low-polarity paraffinic solvent, Shellsol® T, (P_e between 170 and 190°C) gave the best results (23). The extraction coefficient (E°) was 2.2×10^{-5} mol. dm^{-3} with 0.14 mol. dm^{-3} HX-70 in butanol; the E° value was 200 times higher, 0.005 in Shellsol® T. The E° values were 0.0016 in MIBK, 0.0013 in dibutyl carbonate, 0.0011 in mesitylene or 1,3,5-trimethyl benzol, 0.0001 in diethylene glycol butyl ether and almost nil in nitrobenzene (23).

The extraction of U(IV) from phosphoric acid solutions with 1-phenyl-3-methyl-4-benzoylpyrazolone-5 and TOPO mixtures has been studied (25). The most probable U(IV) species in the aqueous phase (2.9–6.33 mol. dm^{-3} H_3PO_4) is suggested to be the neutral complex $\text{U}(\text{H}_5\text{P}_2\text{O}_8)_4$ (25).

Comparative UO_2^{2+} extraction studies were reported (38) between hydrochloric acid solutions containing different mixture of LIX 54 (HA) and TBP diluted in benzene. The quantitative extraction of U(VI) (5×10^{-3} mol. dm^{-3}) with the mixture of 5% LIX 54 + 5% TBP was achieved at pH 4.2, whereas the 5 % LIX 54 alone showed a maximum extraction (30%) at pH 5.3. At pH 4.0, the maximum synergistic behavior was observed with 10% and 20% of TBP mixed with 5% LIX 54. This system follows the ion exchange mechanism: $\text{UO}_2(\text{OH})^+ + 2\text{HA} + \text{TBP} = [\text{UO}_2(\text{OH})(\text{A})(\text{HA})(\text{TBP})] + \text{H}^+$ (38).

The mechanism of U(VI) extraction from aqueous solutions into MIBK containing 3-phenyl-4-acetyl-5-isoxazolone (HPAI) was investigated and the extracted species have been identified. Solid 2:1 complexes found with HPAI were also isolated and characterized by using elemental analysis, IR and

NMR spectroscopy (41). Similarly extraction mechanism and 2:1 species extracted U(VI) with 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) in chloroform have been identified (42). Distribution coefficients of U(VI) extraction from nitric acid with N-octylcaprolactam and N-(2-ethyl)hexylcaprolactam were calculated as a function of aqueous NO_3^- concentration, extractant concentration and temperature (50).

U(VI) was quantitatively extracted from 6 to 8 $\text{mol} \cdot \text{dm}^{-3}$ hydrochloric acid with 0.02 $\text{mol} \cdot \text{dm}^{-3}$ di-cyclo-18-crown-6 (DC18C6) in chloroform and was stripped from the organic phase with 0.5 $\text{mol} \cdot \text{dm}^{-3}$ hydrochloric acid (40). U(VI) was similarly quantitatively extracted with 0.01 $\text{mol} \cdot \text{dm}^{-3}$ DB24C8 (di-benzo-24-crown-6)/0.01 $\text{mol} \cdot \text{dm}^{-3}$ DC18C6 in nitrobenzene from 6–10 $\text{mol} \cdot \text{dm}^{-3}$ hydrochloric acid (53–54). The quantitative extraction of 5 $\mu\text{g mL}^{-1}$ U(VI) with 0.01 $\text{mol} \cdot \text{dm}^{-3}$ cryptand-222 diluted in chloroform at pH 6.0 (0.005 $\text{mol} \cdot \text{dm}^{-3}$ Eosin used as a counter ion) was reported (67).

The extraction efficiencies in percentage of different diluents was as follows: xylene (78%), benzene (82%), toluene (86%), 1,2-dichloroethane (88%), chloroform (88.8%), 1,2-dichloromethane (97.1%) and nitrobenzene (98%). Various mineral acids such as HCl , H_2SO_4 , HNO_3 and HClO_4 used as stripping agents and 0.1 $\text{mol} \cdot \text{dm}^{-3}$ HClO_4 quantitatively stripped the uranium from all loaded organic phases. Separation of multicomponent tertiary and quaternary mixtures of Mn, Pb, Tl, Cd, Ni each metal 5 $\mu\text{g mL}^{-1}$ was successfully applied the developed method for uranium extraction (67). Lower pH conditions 1.0–1.2 favorable for uranium(VI) ($1.0 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$) whereas pH 4.0–4.1 favorable for nickel(II) ($1.7 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$) with 0.025 $\text{mol} \cdot \text{dm}^{-3}$ 3-methyl-4-(pnitrobenzoyl)-5-oxo-phenylprazole (HNP) diluted in benzene was reported (75). The influence of complexing reagents follows the extraction efficiency for uranium: tartrate > fluoride > citrate > ascorbate > oxalate > EDTA at pH 2.8 with 0.025 $\text{mol} \cdot \text{dm}^{-3}$ HNP and 0.035 $\text{mol} \cdot \text{dm}^{-3}$ TBP in benzene (75).

Various other crown ethers (CE's) such as 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), di-benzo-18-crown-6 (DB18C6), di-cyclohexano-18-crown-6 (DC18C6), di-benzo-24-crown-8 (DB24C8) and di-cyclohexano-24-crown-8 (DC24C8) were used for uranium extraction from hydrobromic acid (84). Among the all CE's, DC18C6, DC24C6 and DB24C8 were the ones able to quantitatively extract all uranium (100 μg).

Stripping of the uranium from loaded 0.005 $\text{mol} \cdot \text{dm}^{-3}$ DB24C6 was quantitatively back extracted by 0.1–1.0 $\text{mol} \cdot \text{dm}^{-3}$ HCl , 0.5–10 $\text{mol} \cdot \text{dm}^{-3}$ HNO_3 , 2.0–10 $\text{mol} \cdot \text{dm}^{-3}$ HClO_4 and 3.0–10 $\text{mol} \cdot \text{dm}^{-3}$ H_2SO_4 (84). Finally, the method was successfully applied to separate the alkali, alkaline and other transition metals (tolerance limits: 1.5–30 mg) (84).

Solvent extraction of U(VI) was investigated from nitrate solutions using 3-methyl-4-(p-nitrobenzoyl)-5-oxo-phenylprazole (HNP) dissolved in benzene, 4-sebacoylbis(1-phenyl-3-methyl-5-pyrazolone) (H₂SP) and 4-dodecandioylbis(1-phenyl-3-methyl-5-pyrazolone) (H₂DdP) in chloroform. The extracted metal complexes were identified as $\text{UO}_2(\text{HSP})_2$, $\text{UO}_2(\text{HdDp})_2$.

The equilibrium constants of the above species were deduced by non-linear regression analysis (88). The factors affecting the distribution ratio of uranium(VI) with N,N'-dioctanoylpiperazine (DOPEZ) diluted in carbon tetrachloride including concentration of aqueous nitric acid, extractant and salting-out agent were investigated (91).

Maximum extraction of uranium (VI) ($D = \sim 10$ for 5.0×10^{-3} mol. dm^{-3} metal) was reached at $6.0 \text{ mol} \cdot \text{dm}^{-3}$ HNO_3 using $0.5 \text{ mol} \cdot \text{dm}^{-3}$ DOPEZ in CCl_4 at $25 \pm 1^\circ\text{C}$, 40 min shaking time (91). The uranium extraction process obeyed an exothermic reaction and was influenced by the lithium nitrate concentration range $1\text{--}5 \text{ mol} \cdot \text{dm}^{-3}$ as salting out reagent (91).

The extraction behavior of U(VI) from aqueous nitric acid medium employing 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) has been studied in the presence of various amides, such as di-2-ethylhexylacetamide (D2EHAA), di-2-ethylhexylpropanamide (D2EHPrA), di-2-ethylhexylisobutylamide (D2EH*i*BA) and di-2-ethylhexylpivalamide (D2EHP*v*A) in toluene. Calculation of enthalpy and entropy variations indicated that the extraction was thermodynamically favored with maximum extraction exhibited through the adduct formation: $\text{UO}_2(\text{PBI})_2 \cdot \text{D2EHAA}$ (92).

The 1-Phenyl-3-methyl-4-(2-ethylhexanoyl)-5-pyrazolone (HPM2EHP) was synthesized and utilized for the extraction of U(VI) from dilute nitric acid solutions. The addition of an adduct-forming reagent such as trialkylphosphine oxide (Cyanex 923 or TOPO) to the metal chelate system significantly enhanced the extraction efficiency of these metal ions (93). A method for extraction, separation and recovery of uranium was developed using a new reagent, N-phenylbenzo-18-crown-6-hydroxamic acid (PB18C6HA) in the presence of cerium, thorium and lanthanides (109).

Observations on Uranium Extraction

As per the reported extraction methodologies on uranium, it is known that nitric acid media is one of the most used systems. Many compounds with different functional groups were utilized as extractants. Among these, nitrogen based extractants like amides/amines have been observed to be the best class of functional group in these extractants. Various diluents such as xylene, n-hexane, cyclohexane, benzene, methyl isobutyl ketone, carbon tetrachloride, chloroform, toluene, nitrobenzene, and kerosene were used in uranium extraction. The choice of the optimum diluent depends on the nature of functional group of the extractant. For industrial applications and to meet the environmental regulation, kerosene appears to be an excellent diluent. It is a proven industrial diluent cost-wise and is less toxic when compared with other diluents.

Based on the reported extractive technologies on uranium extraction from various mineral acids, the summary of the extraction efficiencies with the concerned extractants is presented in Table 2. It may be observed from

the reported literature that nitrogen and phosphorus based extractants are employed predominantly for uranium extraction and separation from other associated metals.

- Among all nitrogen extractants amine-based reagents perform better and tri-octyl amine (TOA) is proved to be one of the best extractants. 40% TOA in kerosene will be able to extract 100 g.L^{-1} uranium, whereas 100% TOA in kerosene could extract 262 g.L^{-1} from chloride media (59).
- Many phosphorus-based extractants are employed for uranium extraction; TBP is proved as the best extractant for uranium. 20% of TBP were found able to extract 78 g.L^{-1} uranium from nitric acid solutions (103).
- As regards the sulfur-based extractants, sulfoxides are mainly used for the extraction of uranium from various acidic solutions. EHMPSO is proved to be a good extracting reagent from nitric acid solutions when compared with other sulfur-based reagents (56).
- N-octylcaprolactam (1 mol.dm^{-3}) in kerosene has extracted 95.7% uranium from a 0.05 mol.dm^{-3} uranium solution in nitric acid (50). It can also be considered in some cases.

Any commercial process requires a cost-effective extractant. As per the available data, TBP is cheaper than TOA and HCl is cheaper than HNO_3 . Taking in account environmental problems, HCl may be more useful than HNO_3 , although, the two well established processes TBP- HNO_3 and TOA-HCl are equally in vogue for recovery of the uranium. With respect to cost and extraction efficiency, TBP is the best extractant. When environmental concerns are raised, TOA is the best extractant for uranium recovery from various sources.

CONCLUSIONS

The reported extraction methodologies for uranium(VI) show that the nitric acid media is one of the most studied system the recovery of uranium when different class of extractants are considered. Among all possible extractants, the nitrogen based extractants such as amides and amines are proved to be the best class of functional group. As regards the overall extraction efficiency and the cost TBP is proved the best extractant for uranium extraction. From the environmental point of view, the TOA-HCl process appears to be the best route to extract uranium. Various diluents such as xylene, n-hexane, cyclohexane, benzene, MIBK, carbonate tetrachloride, chloroform, toluene, nitrobenzene and kerosene can be used as solvents with similar efficiency in uranium SX technology. A solubility consideration renders the choice of the best diluent depending on the functional group of the extractant. For industrial applications, cost, environmental and toxicity concerns make kerosene as the best diluent.

TABLE 2 Summary of the Extraction Efficiencies on Uranium Extraction Process

Name of the extractant	Uranium concentration	Experimental conditions			% Extraction	Ref.
		Acid concentration	Extractant concentration	% Extraction		
Nitrogen-based extractants						
8-Quinolinol	0.01 mol.dm ⁻³	0.92 mol.dm ⁻³ Na ₂ CO ₃ + 0.04 mol.dm ⁻³ NaOH	0.1 mol.dm ⁻³	91.59	8	
Tri (iso-octyl) amine	16.8 mg.mL ⁻¹	6.0–9.0 mol.dm ⁻³ HCl	5%	82.7	9	
TOA	0.01 mol.dm ⁻³	H ₂ SO ₄	0.1 mol.dm ⁻³	92.7	18	
TOA	4.8 g	Heap leach liquor	0.172 mol.dm ⁻³	99.92	28	
TOA	105.2 g.L ⁻¹	4.0 mol.dm ⁻³ HCl	40%	100	59	
TBSA	5 × 10 ⁻³ mol.dm ⁻³	3.5 mol.dm ⁻³ HNO ₃	0.8 mol.dm ⁻³	90.9	68	
TBAA	5 × 10 ⁻³ mol.dm ⁻³	3.0 mol.dm ⁻³ HNO ₃	0.5 mol.dm ⁻³	90.9	69	
Aliquat 336	1 mmol.dm ⁻³	0.4 mol.dm ⁻³ H ₃ PO ₄	5%	79.8	71	
DEODA	5 × 10 ⁻³ mol.dm ⁻³	2.5 mol.dm ⁻³ HNO ₃	0.2 mol.dm ⁻³	66.62	73	
DBDEA	5 × 10 ⁻³ mol.dm ⁻³	7.0 mol.dm ⁻³ HNO ₃	0.2 mol.dm ⁻³	47.37	80	
N-octanoyl pyrrolidine	5 × 10 ⁻³ mol.dm ⁻³	3.0 mol.dm ⁻³ HNO ₃	3.0 mol.dm ⁻³	76.01	83	
N,N-di-octanoyl piperazine	5 × 10 ⁻³ mol.dm ⁻³	3.0 mol.dm ⁻³ HNO ₃	0.01 mol.dm ⁻³	79.94	91	
N,N-methyl-N,N, di-octyl succinyl amide	5 × 10 ⁻³ mol.dm ⁻³	0.01 mol.dm ⁻³ HNO ₃	0.00001 mol.dm ⁻³		101	
Alamine 336	0.1 mmol.dm ⁻³	0.1 mol.dm ⁻³ H ₂ SO ₄	0.2 mol.dm ⁻³	98.93	115	
Phosphorus-based extractants						
Octa-ethyl-tetra-amidopyrophosphate	1.6 × 10 ⁻³ mol.dm ⁻³	5.0 mol.dm ⁻³ HNO ₃	0.1 mol.dm ⁻³	99.06	21	
TBPO + Naphthalene	1 × 10 ⁻⁵ mol.dm ⁻³	1.0 mol.dm ⁻³ HNO ₃	150 mg + 350 mg	98.00	27	
Di-2-ethylhexylthiophosphoric acid in cyclohexane	0.5 × 10 ⁻³ mol.dm ⁻³	pH = 2.4	0.168 mol.dm ⁻³	99.00	31	

Di-2-ethylhexyl dithiophosphoric acid in benzene	0.5×10^{-3} mol.dm $^{-3}$	pH = 2.1	0.2 mol.dm $^{-3}$	98.76	33
D2EHPA + TOPO	0.1 g.L $^{-1}$	0.15 mol.dm $^{-3}$ HNO $_3$ + 3.5 mol.dm $^{-3}$ H ₃ PO $_4$	0.6 mol.dm $^{-3}$ + 0.3 mol.dm $^{-3}$	98.9	34
OPAP Tris-2-ethyl hexyl-phosphate Cyanex 921 + HDEHP	1×10^{-3} mol.dm $^{-3}$ 10-180 μ g 40 mg.L $^{-1}$	0.5 mol.dm $^{-3}$ HNO $_3$ pH 3.0 to 4.7 5.0 mol.dm $^{-3}$ H ₃ PO $_4$	0.6% 4% 0.5 mol.dm $^{-3}$ + 2.0 mol.dm $^{-3}$	95.00 100 88.00	36 43 72
TOPO	9.55×10^{-4} mol.dm $^{-3}$ 0.5 mg.mL $^{-1}$ 133 g.L $^{-1}$ 2.0×10^{-3} mol.dm $^{-3}$	1.746 mol.dm $^{-3}$ H ₂ SO $_4$ 0.01 mol.dm $^{-3}$ H ₃ PO $_4$ 5.0 mol.dm $^{-3}$ HNO $_3$ 0.05 mol.dm $^{-3}$ HNO $_3$	0.005 mol.dm $^{-3}$ 20% 0.03 mol.dm $^{-3}$ each extractant	79.94	81
Cyanex 272 TBP TOPO + PC 88A				99.41 58.84 99.89	90 103 113
Sulfur-based extractants					
Di(2-ethylhexyl) sulfoxide (DEHSO)	0.2 mol.dm $^{-3}$	4.0 mol.dm $^{-3}$ HNO $_3$	1.0 mol.dm $^{-3}$	75.96	56
Di(1-methylheptyl) sulfoxide (DMHPSO)	0.2 mol.dm $^{-3}$	4.0 mol.dm $^{-3}$ HNO $_3$	1.0 mol.dm $^{-3}$	16.67	56
2-Ethyl hexyl-p-methyl-phenyl sulfoxide (EHMPSO)	0.2 mol.dm $^{-3}$	4.0 mol.dm $^{-3}$ HNO $_3$	1.0 mol.dm $^{-3}$	81.52	56
n-Dodecyl p-methyl phenyl sulfoxide (DpEPSO)	0.2 mol.dm $^{-3}$	4.0 mol.dm $^{-3}$ HNO $_3$	1.0 mol.dm $^{-3}$	70.24	56
Di(p-ethylphenyl) sulfoxide (DEPSO)	0.2 mol.dm $^{-3}$	4.0 mol.dm $^{-3}$ HNO $_3$	1.0 mol.dm $^{-3}$	54.75	56
DHSO	0.01 mol.dm $^{-3}$ 30 μ g 10^{-10} mol.dm $^{-3}$	6.0 mol.dm $^{-3}$ [Cl] $^-$ 0.001 mol.dm $^{-3}$ HNO $_3$ 9.5 mol.dm $^{-3}$ HNO $_3$ tracer	0.1 mol.dm $^{-3}$ 0.005 mol.dm $^{-3}$ 0.5 mol.dm $^{-3}$	90.9 99.30 88.89	100 102 110

(Continued)

TABLE 2 (Continued)

Name of the extractant	Uranium concentration	Experimental conditions			% Extraction	Ref.
		Extractant concentration	Acid concentration	Extraction		
Other extractants					100	14
Mesityl oxide	900 μg	0.5 mol. dm^{-3}	1.0 mol. dm^{-3} HNO_3 + NH ₄ NO ₃	100%	100	
PMBP	40 μg	0.98 mol. dm^{-3} H ₃ PO ₄	0.05 mol. dm^{-3} 5% + 5%	99.94	25	
LIX 54 + TBP	5 $\times 10^{-3}$ mol. dm^{-3}	pH 5.0	0.02 mol. dm^{-3}	98.00	38	
DC18C6	50 μg	6.0 mol. dm^{-3} HCl	1.0 mol. dm^{-3}	100	40	
N-octylcaprolactam	0.05 mol. dm^{-3}	3.0 mol. dm^{-3} HNO ₃	0.01 mol. dm^{-3}	95.70	50	
DB24C6	50–90 μg	6.0–10.0 mol. dm^{-3} HCl	0.01 mol. dm^{-3}	100	53	
DC18C6 + Acetonitrile	10 ⁻⁶ to 10 ⁻⁴ tracer	6.0 mol. dm^{-3} HNO ₃	0.2 mol. dm^{-3} + 20%	78.72	54	
Gryptand-222	5 μg	pH 6.0	0.01 mol. dm^{-3}	100	67	
HNP	8.4 $\times 10^{-5}$ mol. dm^{-3}	pH 2.8	0.1 mol. dm^{-3}	98.06	75	
DB24C8	100 μg	7.0 0.1 mol. dm^{-3} HBr	0.0008 mol. dm^{-3}	100	84	
BODMAC	4.75 $\times 10^{-5}$ mol. dm^{-3}	4.0 mol. dm^{-3} HCl	0.002 mol. dm^{-3}	62.96	108	
PBCHA	1.48 $\times 10^{-4}$ mol. dm^{-3}	pH 6.0	10 ml of 0.0045 mol. dm^{-3}	100	109	

ACKNOWLEDGEMENTS

This work is supported by Basic Research Project of the Korea Institute of Geoscience and Mineral Resources (KIGAM) funded by the Ministry of Knowledge Economy of Korea (MKE). Sincere thanks to Dr. B. D. Pandey, Sr. Dy. Director of the National Metallurgical Laboratory (CSIR), Jamshedpur 831 007, India for his precious advices and guidance to present this review paper.

NOMENCLATURE

Aliquat 336	methyl-trialkyl (C6-C8) ammonium chloride
Arquad 2C	dialkyl (C12-C14)-dimethyl ammonium chloride
B15C5	benzo-15-crown-5
CMPO	octyl(phenyl)- <i>n</i> , <i>n</i> -diisobutylcarbamoylmethylphosphine oxide
cryptand-222	4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-8,8,8-hexacosane
Cyanex 272	bis(2,4,4-trimethyl pentyl) phosphinic acid
Cyanex 301	bis(2,4,4-trimethylpentyl) dithiophosphinic acid
Cyanex 302	bis(2,4,4-trimethylpentyl) monothiophosphinic acid
Cyanex 923	see TOPO, tri- <i>n</i> -octyl-phosphine oxide
D2EHAA	di-2-ethylhexyl-acetamide
D2EHiBA	di-2-ethylhexyl-isobutylamide
D2EHPA	di-2-ethylhexyl-phosphoric acid
D2EHPrA	di-2-ethylhexyl-propanamide
D2EHPVA	di-2-ethylhexyl-pivalamide
D2EHPvA	di-2-ethylhexyl-pivylamide
DB24C6	di-benzo-24-crown-6
DB24C8	di-benzo-24-crown-8
DBDEA	N,N-di-butyl-decanamide
DC18C6	di-cyclohexano-18-crown-6
DC24C8	di-cyclohexano-24-crown-8
DDQ	7-dodecynyl-8-quinolinol
DEHBA	di-2-ethyl hexyl isobutyramide
DEHSO	di-2-ethyl hexyl sulfoxide
DEODA	N,N-di-ethyl-octadecanamide
DHBA	dihexyl butyramide
DHIBA	dihexyl isobutyramide
DHOA	N,N-dihexyloctanamide
DHSO	dihexyl sulfoxide
DMDBMA	N,N'-dimethyl-N,N'-dibutylmalonamide
DMDOSA	N,N ¹ -dimethyl- N,N ¹ -dioctylsuccinylamide
DMSO	dimethyl sulfoxide

DOPEZ	N,N ¹ -dioctanoyl-piperazine
DOSO	dioctyl sulfoxide
DPhSO	diphenyl sulfoxide
DPSO	di-n-pentyl sulfoxide
EDTA	ethylene diamine tetracetic acid
EHMPSO	2-ethyl hexyl-p-methyl-phenyl sulfoxide
EtTDPA	N,N'-diethyl-N,N'-ditolyl-dipicolinamide
H ₂ DdP	4-dodecandioylbis(1-phenyl-3-methyl-5-pyrazolone
H ₂ SP	4-sebacylbis(1-phenyl-3-methyl-5-pyrazolone
HEhdtp	di-2-ethylhexyl-dithiophosphoric acid
HNP	3-methyl-4-(<i>p</i> -nitrobenzyl)-5-orophenylpyrazole
HPAI	3-phenyl-4-acetyl-5-isoxazolone
HPBI	3-phenyl-4- benzoyl-5-isoxazolone
HPM2EHP	1-phenyl-3-methyl-4-(2-ethylhexanoyl)-5-pyrazolone
HX-70	neotridecanohydroxamic acid
LIX 54	phenyl-alkyl- β -diketone
LIX 622	apolar substituted salicylaldoxime
LLE	liquid-liquid extraction
MIBK	methyl isobutyl ketone
NCP	N-cyclohexyl-2-pyrrolidone
NDP	N-dodecyl-2-pyrrolidone
NOP	N-octyl-2-pyrrolidone
OETAPP	octaethyltetraamidopyrophosphate
OPOD	N-octanoyl-pyrrolidine
PB18C6HA	N-phenylbenzo-18-crown-6-hydroxamic acid
PC88A	2-ethylhexyl phosphonic acid mono-2-ethylhexyl
PMBP	1-phenyl-3-methyl-4-benzoyl-5-pyrazolone
SX	solvent extraction
TBAA	N,N,N,N-tetrabutyl dipicamide
TBP	tri-butyl-phosphate
TBPO	tributylphosphine oxide
TBPP	tetrabutylpyrophosphate
TBSA	N,N,N,N-tetrabutyl succinylamide
TOA	tris (iso-octyl) amine
TODGA	N,N,N',N'-tetraoctyl-3-oxapentanediamide
TOPO	tri-n-octyl-phosphine oxide

REFERENCES

1. a. *Uranium 2007: Resources, Production and Demand* (2008) OECD, International Atomic Energy Agency. Published by: OECD Publishing and <http://www.world-nuclear.org/info/reactors.html> consulted Nov, 29, 2010. b. Merritt, R.C. (1971) *The extractive metallurgy of uranium*, Library of Congress Catalog Card No. 71-157076, Colorado School of Mines Research Institute, USA.

2. Lee, J.Y. and Kumar, J.R. (2009) Liquid-liquid extraction general principles-a review, *J Kor. Inst. Res. Recycl.*, 18: 3–9.
3. Ritcy, G.M. and Ashbrook, A.W. (1984) *Solvent extraction principles and applications to process metallurgy Part I*, Elsevier, Amsterdam, The Netherlands.
4. Berthelot, M. and Jungfleisch, J. (1872) Sur les lois qui president ou partage d'un corps entre deux dissolvants (experiences), *Ann. Chim. Phys. [París]*, 26: 396–396.
5. Nernst, W. (1891) Nernst distribution law. *Z. Phys. Chem.*, 8: 110–139.
6. Blake, C.A., Baes, C.F., Brown, K.B., Coleman, C.F., and White, J.C. (1958) Proceedings of the Second International Conference on Peaceful Uses of Atomic Energy, Geneva, 28: 289.
7. Kumar, J.R. (2010) *Studies on liquid-liquid extraction of tetravalent zirconium and hafnium*, Verlag Dr. Muller Publishers, Germany (ISBN No = 978-3-639-24635-3).
8. Clifford, W.E., Bullwinkel, E.P., McClaine, L.A., and Noble Jr., P. (1958) The solvent extraction of uranium(vi) from carbonate solutions. *J. Am. Chem. Soc.*, 80: 2959–2961.
9. Moore, F.L. (1958) Liquid-liquid extraction of uranium and plutonium from hydrochloric acid solution with tri(iso-octyl)amine: Separation from thorium and fission products. *Anal. Chem.*, 30: 908–911.
10. Baes Jr. C.F., Zingaro, R.A., and Coleman, C.F. (1958) The extraction of uranium(VI) from acid perchlorate solutions by di-(2-ethylhexyl)-phosphoric acid in n-hexane. *J. Phys. Chem.*, 62: 129–136.
11. Horton, C.A. and White, J.C. (1958) Separation of uranium by solvent extraction with tri-n- octylphosphine oxide: Direct colorimetric determination with dibenzoylmethane. *Anal. Chem.*, 30: 1779–1784.
12. Medowell, W.J. and Baes Jr., C.F. (1958) Uranium extraction by di-n-decylamine sulfate. *J. Phys. Chem.*, 62: 777–783.
13. Sato, T. (1962) The extraction of uranium (VI) from sulfuric acid solutions by di-(2-ethylhexyl)-phosphoric acid. *J. Inorg. Nucl. Chem.*, 24: 699–706.
14. Dhara, S.C. and Khopkar, S.M. (1965) Solvent extraction of uranium (VI) with mesityloxide. *Mikrochim. Acta*, 53: 931–935.
15. Mikulski, J. and Vetusani, J. (1967) The extraction of hexavalent uranium from nitric acid solutions by tetrabutylpyrophosphate (TBPP). *J. Inorg. Nucl. Chem.*, 29: 209–220.
16. Deptuła, C. and Minc, S. (1967) Uranium (VI) extraction from sulfuric acid solutions with mono-2,6,8-trimethylonyl-4- and mono-n-butylphosphoric acids solutions in benzene and carbon tetrachloride. *J. Inorg. Nucl. Chem.*, 29: 229–240.
17. Kiwan, A.M. and Amin, R.S. (1971) Extraction of uranium(IV) by di-2-ethylhexyl-phosphoric acid from perchloric acid solutions. *J. Inorg. Nucl. Chem.*, 33: 2221–2228.
18. Južnič, K. and Fedina, S. (1974) The extraction of uranium (IV) from sulfuric acid by tri-octylamine in benzene. *Mikrochim. Acta*, 62: 39–44.
19. Sato, T. and Nishida, T. (1974) The extraction of uranium(VI) from hydrochloric acid solutions by tri-n-octyl phosphine oxide. *J. Inorg. Nucl. Chem.*, 36: 2087–2089.

20. Mohanty, S.R. and Reddy, A.S. (1975) Solvent extraction of uranium from hydrochloric acid solutions by sulfoxides and their mixtures. *J. Inorg. Nucl. Chem.*, 37: 1791–1795.
21. Jankowska, M., Kulawik, J., and Mikulski, J. (1976) Extraction properties of octaethyltetraamidopyrophosphate (OETAPP) –I. The extraction of uranyl nitrate and chloride. *J. Radioanal. Chem.*, 31: 9–29.
22. Tamhina, B., Gojmerac, A., and Herak, M.J. (1976) Extraction and separation of uranium(VI) and protactinium(V) with 1-(4-tolyl)-2-methyl-3-hydroxy-4-pyridone. *Mikrochim. Acta*, 66: 569–578.
23. Kamal, S. (1980) Extraction of uranium(VI) from dilute phosphate solutions with neotridecanohydroxamic acid and amines. *Hydrometallurgy*, 5: 191–206.
24. Al-Jarrah, R.H., Al-Karaghoubi, A.R., Al-Assaf, S.A., and Shamon, N.H. (1981) Solvent extraction of uranium and some other metal ions with 2-N-butyl-2-ethyl octanohydroxamic acid. *J. Inorg. Nucl. Chem.*, 43: 2971–2973.
25. Coronel, F.T., Mareva, St., and Yordanov, N. (1982) Extraction of uranium(IV) from Phosphoric acid solutions with 1-phenyl-3-methyl-4-benzoylpyrazolone-5 (PMBP). *Talanta*, 29: 119–123.
26. Archelas, E., Buono, G., and Waegell, B. (1982) Study of the extraction of uranium (VI) by bis-(di-n-butylphosphate) compounds including a polyheteroatomic chain from nitrate solutions. *Polyhedron*, 1: 683–688.
27. Shigetomi, Y., Takehiro, K., and Hideaki, K. (1983) Fundamental study on separation of uranium from other metals by solvent extraction with tributylphosphate or tributylphosphine oxide in molten naphthalene. *J. Nucl. Sci. Tech.*, 20: 140–144.
28. Goldenberg, J.F. and Abbruzzese, C. (1983) Extraction of uranium from heap leach liquor with tri-n-octylamine: Equilibrium data and flow-sheet calculations. *Int. J. Min. Pro.*, 10: 241–254.
29. Lyle, S.J. and Tamizi, M. (1983) A study of equilibria in the extraction of uranium (VI) from aqueous sulfate solution by tri-n-octylamine in benzene or petroleum spirit. *Hydrometallurgy*, 11: 1–11.
30. Lin, Z. and Freiser, H. (1983) Solvent extraction equilibria of uranium with 7-dodecenyl-8-quinolinol. *Anal. Chim. Acta*, 146: 237–241.
31. Curtui, M. and Haiduc, I. (1984) Extraction of uranium(VI) with di-2-ethylhexylthiophosphoric acid in different organic solvents. *J. Radioanal. Nucl. Chem. Lett.*, 86: 281–290.
32. Wang, W.-J., Sun, Q., and Chen, B. (1986) Extraction equilibrium of uranium(VI) with dicyclohexano-18-crown-6 and its application for separating uranium and thorium. *J. Radioanal. Nucl. Chem. Arti.*, 98: 11–16.
33. Haiduc, I., Curtui, M., and Haiduc, I. (1986) Solvent extraction of uranium(VI) with Di-2-ethylhexylthiophosphoric acid from aqueous nitrate, chloride, sulfate and phosphate media. *J. Radioanal. Nucl. Chem. Arti.*, 99: 257–263.
34. Bunus, F. and Dumitrescu, P. (1986) Uranium(VI) extraction from acid mixtures with organophosphorus esters. *Hydrometallurgy*, 16: 167–175.
35. Wang, W.-J., Chen, B., Zheng, P., Wang, B., and Wang, M. (1986) Solvent-extraction complex of uranium(VI) with cis, syn, cis-dicyclohexano-18-crown-6. *Inorg. Chim. Acta*, 117: 81–82.

36. Ramakumar, S.S.V., Singh, O.V., and Tandon, S.N. (1987) Extraction of uranium(VI) with octylphenyl acid phosphate from nitric acid solutions and its separation from some trivalent lanthanides. *J. Radioanal. Nucl. Chem. Lett.*, 118: 283–289.
37. Huang, C.-T. and Huang, T.-C. (1987) Equilibrium reaction of the extraction of uranium(VI) with di-(2-ethylhexyl) phosphoric acid from nitric acid solutions. *Sol. Extr. Ion Exch.*, 5: 611–631.
38. Singh, S., Chakravortty, V., and Dash, K.C. (1988) Solvent extraction of uranium(VI) by LIX-54 and its mixtures. *J. Radioanal. Nucl. Chem. Arti.*, 122: 137–142.
39. Huang, T.-C. and Huang, C.-T. (1988) Kinetics of the extraction of uranium(VI) from nitric acid solutions with bis(2-ethylhexyl)phosphoric acid. *Ind. Eng. Chem. Res.*, 27: 1675–1680.
40. Deorkar, N.V. and Khopkar, S.M. (1989) Separation of uranium(VI) as chloride complex by solvent extraction with dicyclohexyl-18-crown-6. *J. Radioanal. Nucl. Chem. Arti.*, 130: 433–441.
41. Jyothi, A. and Rao, G.N. (1989) Studies on extraction of lanthanum(III), cerium(III), europium(III), thorium(IV) and uranium(VI) with 3-phenyl-4-acetyl-5-isoxazolone (HPAI). *Polyhedron*, 8: 1111–1116.
42. Jyothi, A. and Rao, G.N. (1990) Solvent extraction behaviour of lanthanum(III), cerium(III), europium(III), thorium(IV) and uranium(VI) with 3-phenyl-4-benzoyl-5-isoxazolone. *Talanta*, 37: 431–433.
43. Sundaramurthi, N.M., Desai, G.S., and Shinde, V.M. (1990) Extraction and separation studies of uranium/vi/ with tris-/2-ethyl hexyl/ phosphate. *J. Radioanal. Nucl. Chem.*, 144: 439–445.
44. Moyer, B.A., McDowell, W.J., Baes Jr., C.F., Case, G.N., and Case, F.I. (1991) Liquid-liquid equilibrium analysis in perspective. Part 1. Slope analysis of the extraction of uranyl nitrate from nitric acid by di-2-ethylhexylsulfoxide. *Sol. Extr. Ion Exch.*, 9: 833–864.
45. Mohanty, R.N., Singh, S., Chakravortty, V., and Dash, K.C. (1991) Liquid-liquid extraction of molybdenum(VI) and uranium(VI) by LIX 622. *J. Radioanal. Nucl. Chem.*, 152: 21–29.
46. Bunuş, F. and Dumitrescu, R. (1992) Simultaneous extraction of rare earth elements and uranium from phosphoric acid. *Hydrometallurgy*, 28: 331–338.
47. Mathur, J.N., Murali, M.S., Natarajan, P.R., Badheka, L.P., and Banerji, A. (1992) Extraction of actinides and fission products by octyl(phenyl)-N,N-diisobutylcarbamoylmethyl-phosphine oxide from nitric acid media. *Talanta*, 39: 493–496.
48. Enokida, Y. and Suzuki, A. (1992) Estimation of Uranium(VI) concentrations by temperature profile in solvent extraction processes using 30% tri-n-butyl phosphate diluted with n-dodecane. *J. Nucl. Sci. Tech.*, 29: 461–471.
49. Petkovic, D.M., Kopecni, M.M., and Mitrovic, A.A. (1992) Solvent extraction of nitric, hydrochloric and sulfuric acid and their uranyl salts with tri-n-octylphosphine oxide. *Sol. Extr. Ion Exch.*, 10: 685–696.
50. Shen, C.-H., Bao, B.-R., Wang, G.-D., Qian, J., Bao, Y.-Z., and Cao, Z.-B. (1992) Extraction of uranium(VI) and thorium(IV) from nitric acid solution by N-alkylcaprolactam. *J. Radioanal. Nucl. Chem.*, 162: 207–216.

51. Ito, K. (1993) Extraction of technetium(VII) from uranium(VI) in nitric acid system by primary amine –n-heptane solution. *J. Radioanal. Nucl. Chem.*, 171: 371–382.
52. Cao, Z., Bao, Y., Shen, C., Bao, B., Wang, G., and Qian, J. (1993) Comparison of extraction of U(VI) and Th(IV) from nitric acid media by di(2-ethylhexyl) sulfoxide (DEHSO) and by TBP. *He Jishu/Nuclear Techniques*, 16: 380–384.
53. Mohite, B.S., Patil, J.M., and Zambare, D.N. (1993) Solvent extraction separation of uranium(VI) with dibenzo-24-crown-8. *J. Radioanal. Nucl. Chem.*, 170: 215–224.
54. Shukla, J.P., Kumar, A., and Singh, R.K. (1993) Solvent extraction of uranium(VI) into toluene by dicyclohexano-18-crown-6 from mixed aqueous-organic solutions. *Talanta*, 40: 1261–1266.
55. Behera, P., Mishra, R., and Chakravortty, V. (1993) Solvent extraction of uranium(VI) and molybdenum(VI) by alamine 310 and its mixtures from aqueous H_3PO_4 solution. *J. Radioanal. Nucl. Chem.*, 173: 161–169.
56. Shen, C., Bao, B., Bao, Y., Wang, G., Qian, J., and Cao, Z. (1994) Extraction of U(VI), Th(IV) and some fission products from nitric acid medium by sulfoxides and effect of γ -irradiation on the extraction. *J. Radioanal. Nucl. Chem.*, 178: 91–98.
57. Nigond, L., Musikas, C., and Cuillerdier, C. (1994) Extraction by N,N,N',N' -tetraalkyl-2 alkyl propane-1,3 diamides. II. U(VI) and Pu(IV). *Sol. Extr. Ion Exch.*, 12: 297–323.
58. Suresh, A., Srinivasan, T.G., and Rao, P.R.V. (1994) Extraction of U(VI), Pu(IV) and Th(IV) by some trialkyl phosphates. *Sol. Extr. Ion Exch.*, 12: 727–744.
59. White, D.A. and Fathurrachman. (1994) Extraction of uranium (VI) and uranium (IV) from hydrochloric acid using tri-n-octylamine in a benzene diluent. *Hydrometallurgy*, 36: 161–168.
60. Nair, G.M., Prabhu, D.R., and Mahajan, G.R. (1994) Extraction of uranium(VI) and plutonium(IV) with dihexylbutyramide and dihexylisobutyramide from nitric acid medium. *J. Radioanal. Nucl. Chem.*, 182: 393–399.
61. Godbole, A.G., Mapara, P.M., and Swarup, R. (1995) Extraction of U(VI) by phosphonic acid in the presence of neutral donors. *J. Radioanal. Nucl. Chem.*, 200: 1–8.
62. Nair, G.M., Mahajan, G.R., and Prabhu, D.R. (1995) Extraction of uranium(IV) and plutonium(IV) with some high molecular weight aliphatic monoamides from nitric acid medium. *J. Radioanal. Nucl. Chem.*, 191: 323–330.
63. Nakamura, T. and Miyake, C. (1995) Extraction of lanthanide(III) and uranyl(VI) from nitric acid solution by N,N' -dimethyl- N,N' -dibutylmalonamide. *Sol. Extr. Ion Exch.*, 13: 253–273.
64. Preston, J.S. and Du Preez, A.C. (1995) Solvent extraction of uranium(VI) and thorium(IV) from nitrate media by carboxylic acid amides. *Sol. Extr. Ion Exch.*, 13: 391–413.
65. Ruikar, P.B., Nagar, M.S., Subramanian, M.S., Gupta, K.K., Varadarajan, N., and Singh, R.K. (1995) Extraction behaviour of uranium(VI), plutonium(IV) and some fission products with gamma pre-irradiated n-dodecane solutions of N,N' -dihexyl substituted amides. *J. Radioanal. Nucl. Chem.*, 196: 171–178.

66. Zhou, Z.-M., Sun, Y.-X., Yu, S.-N., Du, H.-F. (1996) Kinetic studies on the solvent extraction of uranium(IV), thorium(IV) and uranium(VI) from nitric acid solutions with tributyl phosphate. *J. Radioanal. Nucl. Chem.*, 214: 369–391.

67. Mathew, V.J. and Khopkar, S.M. (1995) Liquid-liquid extraction of uranium(VI) with cryptand-222 and Eosin as the counter ion. *J. Radioanal. Nucl. Chem.*, 201: 281–292.

68. Wang, Y.-S., Shen, C.-H., Zhu, J.-K., and Bao, B.-R. (1996) Solvent extraction of uranyl(II) ion with N,N,N,N-tetrabutylsuccinylamide from nitric acid solution. *J. Radioanal. Nucl. Chem.*, 212: 101–106.

69. Wang, Y.-S., Sun, G.-X., Xie, D.-F., Bao, B.-R., Cao, W.-G. (1996) Extraction of uranium(VI) and thorium(IV) ions from nitric acid solutions by N,N,N',N'-tetrabutyladipicamide. *J. Radioanal. Nucl. Chem.*, 214: 67–76.

70. Mathur, J.N., Ruikar, P.B., Balarama Krishna, M.V., Murali, M.S., Nagar, M.S., and Iyer, R.H. (1996) Extraction of Np(IV), Np(VI), Pu(IV) and U(VI) with amides, BEHSO and CMPO from nitric acid medium. *Radiochim. Acta*, 73: 199.

71. Mishra, S. and Chakravortty, V. (1997) Extraction of uranium(VI) by the binary mixture of Aliquat 336 and PC88A from aqueous H_3PO_4 medium. *Hydrometallurgy*, 44: 371–376.

72. El-Reefy, S.A., Awwad, N.S., and Aly, H.F. (1997) Liquid-liquid extraction of uranium from phosphoric acid by HDEHP-CYANEX-921 mixture. *J. Chem. Technol. Biotechnol.*, 69: 271–275.

73. Sun, G., Bao, B., and Liu, Ch. (1997) Extraction of uranyl(VI) ion with N,N-diethyloctadecanamide from nitric acid solution. *J. Radioanal. Nucl. Chem.*, 218: 101–102.

74. Daoud, J.A., Rahman, N.A., and Aly, H.F. (1997) Kinetic studies on the extraction of U(IV) by TBP in kerosene from nitrate medium. *J. Radioanal. Nucl. Chem.*, 221: 41–44.

75. Ogwuegbu, M.O.C. and Orji, E. (1997) Liquid-liquid extraction separation of uranium(VI) and nickel(II) by a substituted oxo-pyrazole. *Miner. Eng.*, 10: 1269–1278.

76. Yang, L. and Takeuchi, H. (1997) N-alkylcaprolactams and their mixtures as extractants for U(VI) from nitric acid media. *Sol. Extr. Ion Exch.*, 15: 189–202.

77. Prabhu, D.R., Mahajan, G.R., and Nair, G.M. (1997) Di(2-ethyl hexyl) butyramide and di(2-ethyl hexyl)isobutyramide as extractants for uranium(VI) and plutonium(IV). *J. Radioanal. Nucl. Chem.*, 224: 113–117.

78. Montavon, G., Duplâtre, G., Asfari, Z., and Vicens, J. (1997) Solvent extraction of uranium(VI) and thorium(IV) with a tetra-carboxylated calix[4]arene and effect of alkali ions (Na^+ , K^+). *Sol. Extr. Ion Exch.*, 15: 169–188.

79. Daoud, J.A., Zeid, M.M., and Aly, H.F. (1997) Tetravalent uranium extraction by HDEHP in kerosene from phosphate medium. *Sol. Extr. Ion Exch.*, 15: 203–217.

80. Sun, G.-X., Zhu, J.-K., Wang, Y.-S., and Bao, B.-R. (1998) Influence of TBP on the extraction of uranium(VI) from nitric acid media by N,N-dibutyldecanamide. *J. Radioanal. Nucl. Chem.*, 229: 183–186.

81. Yonghui, Y., Sixiu, S., Shuyunm, X., Yanzhao, Y., and Borong, B. (1998) Extraction of uranium(VI) from sulfuric acid solution with TOPO. *J. Radioanal. Nucl. Chem.*, 237: 171–173.
82. Fedorov, Y.S., Zilberman, B.Y., Kulikov, S.M., Blazheva, I.V., Mishin, E.N., Wallwork, A.L., Deniss, I.S., May, I., and Hill, N.J. (1999) Uranium(VI) extraction by TBP in the presence of HDBP. *Sol. Extr. Ion Exch.*, 17: 243–257.
83. Han, J.-T., Sun, G.-X., Fang, J.-H., and Bao, B.-R. (1999) Solvent extraction of uranium (VI) by N-octanoylpyrrolidine in toluene. *J. Radioanal. Nucl. Chem.*, 241: 215–217.
84. Mohite, B.S. and Burungale, S.H. (1999) Liquid-liquid extraction separation of uranium(VI) from associated elements using dibenzo-24-crown-8 from hydrobromic acid medium. *J. Radioanal. Nucl. Chem.*, 241: 589–593.
85. Turanov, A.N., Karandashev, V.K., Kharitonov, A.V., Lezhnev, A.N., Safronova, Z.V., Yarkevich, A.N., and Tsvetkov, E.N. (1999) Extraction with N,N-dialkylcarbamoylmethyl(diphenyl)-phosphine oxides from hydrochloric acid solutions. *Russ. J. Gen. Chem.*, 69: 1068–1074.
86. Gupta, K.K., Manchanda, V.K., Subramanian, M.S., and Singh, R.K. (2000) Solvent extraction studies on U(VI), Pu(IV), and fission products using N,N-dihexyloctanamide. *Sol. Extr. Ion Exch.*, 18: 273–292.
87. Sahu, S.K., Reddy, M.L.P., Ramamohan, T.R., and Chakravortty, V. (2000) Solvent extraction of uranium(VI) and thorium(IV) from nitrate media by Cyanex 923. *Radiochim. Acta*, 88: 33–37.
88. Reddy, M.L.P., Sahu, S.K., and Chakravortty, V. (2000) 4-acylbis(1-phenyl-3-methyl-5- pyrazolones) as extractants for f-elements. *Sol. Extr. Ion Exch.*, 18: 1135–1153.
89. Singh, D.K., Singh, H., and Mathur, J.N. (2001) Synergistic extraction of U(VI) with mixtures of 2-ethyl hexyl phosphonic acid-mono-2-ethyl hexyl ester (PC-88A) and TBP, TOPO or Cyanex 923. *Radiochim. Acta*, 89: 573–578.
90. Dogmane, S.D., Singh, R.K., Bajpai, D.D., and Mathur, J.N. (2002) Extraction of U(VI) by cyanex-272. *J. Radioanal. Nucl. Chem.*, 253: 477–482.
91. Yang, X.-C., Bao, B.-R., Sun, G.-X., and Cao, W.-G. (2003) N,N'- Dioctanoylpiperazine as a novel extractant for U(VI). *J. Radioanal. Nucl. Chem.*, 258: 677–679.
92. Banerjee, S., Bhattacharyya, A., Mohapatra, P.K., Basu, S., and Manchanda, V.K. (2003) Extraction of the uranyl ion with 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) and neutral donors from dilute nitric acid medium. *Radiochim. Acta*, 91: 729–736.
93. Meera, R., Luxmi Varma, R., and Reddy, M.L.P. (2003) The synergistic extraction of thorium(IV) and uranium(VI) with mixtures of 1-phenyl-3-methyl-4-(2-ethylhexanoyl)-5-pyrazolone and trialkylphosphine oxide. *Sol. Extr. Res. Dev. Japan*, 10: 13–27.
94. Litvina, M.N., Chmutova, M.K., Kulyako, Yu.M., and Myasoedov, B.F. (2004) Extraction of Am(III), U(VI), and Pu(IV) from HCl solutions with diphenyl (dibutylcarbamoylmethyl) phosphine oxide. *Radiochemistry*, 46: 41–43.

95. Manchanda, V.K., Pathak, P.N., and Rao, A.K. (2004) Di(2-ethylhexyl) pivalamide (D2EHPVA): A promising extractant for selective removal of uranium from high level nuclear waste solutions. *Sol. Extr. Ion Exch.*, 22: 353–375.
96. El-Dessouky, S.I. (2004) Mechanism of U(VI) extraction by CYANEX 301 in kerosene from nitrate medium. *J. Radioanal. Nucl. Chem.*, 260: 613–617.
97. Zhu, Z.-X., Sasaki, Y., Suzuki, H., Suzuki, S., and Kimura, T. (2004) Cumulative study on solvent extraction of elements by N,N,N', N'-tetraoctyl-3-oxapentanediamide (TODGA) from nitric acid into n-dodecane. *Anal. Chim. Acta*, 527: 163–168.
98. Mishra, S.L., Vijayalakshmi, R., and Singh, H. (2005) Extraction of uranium from acidic media with a novel synergistic mixture of di-nonyl phenyl phosphoric acid and tri-n-octyl phosphine oxide. *Ind. J. Chem. Tech.*, 12: 708–712.
99. Stas, J., Dahdouh, A., and Shlewit, H. (2005) Extraction of uranium (VI) from nitric acid and nitrate solutions by tributylphosphate/kerosene. *Periodica Polytechnica: Chem. Engineering*, 49: 3–18.
100. Sato, T., Adachi, K., and Sato, K. (2006) Liquid-liquid extraction of uranium(VI) from hydrochloric acid solutions by dihexyl sulfoxide. *Sol. Extr. Res. Dev. Japan*, 13: 73–81.
101. Yu, C., Guoxin, S., Zhenwei, Z., Yufen, H., and Sixiu, S. (2007) Extraction of U(VI) with N,N'-dimethyl-N,N'- dioctylsuccinylamide in toluene. *J. Radioanal. Nucl. Chem.*, 272: 199–201.
102. Karve, M. and Gaur, C. (2007) Extraction of U(VI) with Cyanex 302. *J. Radioanal. Nucl. Chem.*, 273: 405–409.
103. Alibrahim, M. and Shlewit, H. (2007) Solvent extraction of uranium (VI) by tributyl phosphate/dodecane from nitric acid medium. *Periodica Polytechnica: Chemical Eng.*, 51: 57–60.
104. Khan, M.H., Shahida, S., and Ali, A. (2008) Liquid-liquid extraction of uranium from nitric acid solution using di-n-butylsulfoxide in petroleum ether as extractant. *Radiochim. Acta*, 96: 35–40.
105. Singh, S.K., Dhami, P.S., Dakshinamoorthy, A., and Sundersanan, M. (2009) Studies on the recovery of uranium from phosphoric acid medium using synergistic mixture of 2-ethyl hexyl hydrogen 2-ethyl hexyl phosphonate and octyl(phenyl)-N,N-diisobutyl carbamoyl methyl phosphine oxide. *Sep. Sci. Tech.*, 44: 491–505.
106. Lapka, J.L., Paulenova, A., Alyapyshev, M.Yu., Babain, V.A., Herbst, R.S., and Law, J.D. (2009) Extraction of uranium(VI) with diamides of dipicolinic acid from nitric acid solutions. *Radiochim. Acta*, 97: 291–296.
107. Takahashi, Y., Hotokezaka, H., Noda, K., Nogami, M., and Ikeda, Y. (2009) Extraction of Uranium(VI) from nitric acid solution using pyrrolidone derivatives. *J. Nucl. Sci. Tech.*, 46: 787–792.
108. Guo, J.-X., Sun, S.-X., Du, D.-L., Li, M.-X., Hua, P., and Meng, Z.-L. (2006) Uranium(VI) extraction with benzyl octadecyl dimethyl ammonium chloride (BODMAC) from chloride and sulfate solutions. *J. Radioanal. Nucl. Chem.*, 267: 675–678.

109. Agrawal, Y.K., Shah, G., and Vora, S.B. (2006) Solvent extraction, speciation, separation and recovery of uranium(VI) from nuclear fuel, phosphate rocks and monazite sand with N-phenylbenzo-18-crown-6-hydroxamic acid. *J. Radioanal. Nucl. Chem.*, 270: 453–459.
110. Gamare, J.S., Chetty, K.V., Mukerjee, S.K., and Kannan, S. (2009) Extraction studies of uranium(VI), Plutonium(IV) and americium(III) from nitric acid using the Bi-functional carbamoyl methyl sulfoxide ligands. *Anal. Sci.*, 25: 1167–1170.
111. Collet, S., Chagnes, A., Courtaud, B., Thiry, J., and Cote, G. (2009) Solvent extraction of uranium from acidic sulfate media by Alamine® 336: Computer simulation and optimization of the flow-sheets. *J. Chem. Tech. Biotech.*, 84: 1331–1337.
112. Chagnes, A., Courtaud, B., Thiry, J., and Cote, G. (2009) Computer simulation of flow-sheets for the solvent extraction of uranium: A new route to delay the effect of chemical degradation of the organic phase during uranium recovery from acidic sulfate media. *J. Chem. Tech. Biotech.*, 84: 1899–1907.
113. Biswas, S., Pathak, P.N., Singh, D.K., Roy, S.B., and Manchanda, V.K. (2010) Synergistic extraction of uranium with mixtures of PC88A and neutral oxodonors, *J. Radioanal. Nucl. Chem.*, 284: 13–19.
114. Ansari, S.A., Prabhu, D.R., Gujar, R.B., Kanekar, A.S., Rajeswari, B., Kulkarni, M.J., Murali, M.S., Babu, Y., Natarajan, V., Rajeswari, S., Suresh, A., Manivannan, R., Antony, M.P., Srinivasan, T.G., and Manchanda, V.K. (2009) Counter-current extraction of uranium and lanthanides from simulated high-level waste using N,N,N',N'-tetraoctyl diglycolamide, *Sep. Peri. Technol.*, 66: 118–124.
115. Kumar, J.R., Kim, J.S., Lee, J.Y., and Yoon, H.S. (2010) Solvent extraction of uranium(VI) and separation of vanadium(V) from sulfate solutions using Alamine 336. *J. Radioanal. Nucl. Chem.*, 285: 301–308.
116. Kraus, K.A., Nelson, F., and Johnson, G.L. (1949) Chemistry of aqueous uranium(V) solutions. I. Preparation and properties analogy between uranium(V), neptunium(V), plutonium(V). *J. Am. Chem. Soc.*, 71: 2510–2517.
117. Kraus, K.A. and Nelson, F. (1949) Chemistry of aqueous uranium(V) solutions. II. Thermodynamic stability of UO_2^{2+} . Potential of U(IV)/(V), U(IV)/(VI) and U(V)/(VI) couples. *J. Am. Chem. Soc.*, 71: 2517–2522.
118. Nelson, F. and Kraus, K.A. (1951) Chemistry of aqueous uranium(V) solutions. III. The uranium(V)(IV)-(V)-(VI) equilibrium in perchlorate and chloride solutions. *J. Am. Chem. Soc.*, 73: 2157–2161.
119. Sato, A. (1967) Studies of the behaviour of trivakent uranium in an aqueous solution. I. Its reduction and its stability in various acid solutions. *Bull. Chem. Soc. Jpn.*, 40: 2107–2110.
120. Sato, A., Suzuki, S. (1968) Studies of the behaviour of trivalent uranium in an aqueous solution. II. Absorption spectra and ion exchange behaviour in various acid solutions. *Bull. Chem. Soc. Jpn.*, 41: 2650–2656.
121. Moll, H., Reich, T., Hennig, C., Rossberg, A., Szabo, Z., and Grenthe, I. (2000) Solution coordination chemistry of uranium in the binary UO_2^{2+} - SO_4^{2-} and the ternary UO_2^{2+} - SO_4^{2-} - OH^- system. *Radiochim. Acta*, 88: 559–566.

122. Ligying, D. (1982) *The Analytical Chemistry of Uranium*. Atomic Energy Press, Beijing, China, p. 158 (In Chinese).
123. Pathak, P.N., Kumbhare, L.B., and Manchanda, V.K. (2001) Structural effects in n n-dialkyl amides on their extraction behaviour toward uranium and thorium. *Solv. Extr. Ion Exch.*, 19: 105–126.
124. Bunus, F.T., Domocoş, V.C., and Dumitrescu, P. (1978) Synergic extraction of uranium from phosphate solutions with di-(2 ethylhexyl) phosphoric acid and tri-n-octylphosphine oxide. *J. Inorg. Nucl. Chem.*, 40: 117–121.
125. Muller, K., Brendler, V., and Foerstendorf, H. (2008) Aqueous hydrolysis species characterized by attenuated total reflection Fourier-transform infrared spectroscopy. *Inorg. Chem.*, 47: 10127–10134.
126. Brown, G.E., Henrich, V.E., Casey, W.H., Clark, D.L., Eggleston, C., Felmy, A., Goodman, D.W., Gratzel, M., Maciel, G., McCarthy, M.I., Nealson, K.H., Sverjensky, D.A., Toney, M.F., and Zachara, J.M. (1999) Metal oxide surfaces and their interactions with aqueous solutions and microbial organisms. *Chem. Rev.*, 99: 77–174.
127. Rush, M.R., Johnson, S.J., and Kraus, A.K. (1961) Hydrolysis of uranium(VI): Ultracentrifugation and acidity measurements in chloride solutions. *Inorg. Chem.*, 1: 378–386.
128. Rush, M.R. and Johnson, S.J. (1963) Hydrolysis of uranium(VI): Absorption spectra of chloride and perchloride solutions. *J. Phys. Chem.*, 67: 821–825.
129. Comarmond, M.J. and Brown, P.L. (2000) The hydrolysis of uranium(VI) in sulfate media. *Radiochim. Acta*, 88: 573–577.
130. Brown, P.L. (2002) The hydrolysis of uranium(VI). *Radiochimica Acta*. 90: 589–593.
131. Zanonato, P., Bernardo, P.D., Bismundo, A., Liu, G., Chen, X., and Rao, L. (2004) *J. Am. Chem. Soc.*, 126: 5515–5522.
132. Kirishima, A., Kimura, T., Tochiyama, O., and Yoshida, Z. (2004) Speciation study on uranium(VI) hydrolysis at high temperatures and pressures. *J. Alloys Com.*, 374: 277–282.
133. Bernhard, G., Geipel, G., Brendler, V., and Nitsche, H. (1998) Uranium speciation in waters of different uranium mining areas. *J. Alloys Com.*, 271–273: 201–205.
134. Selbib, J. and Schober, M. (1966) The chemistry of uranium-I uranium-oxygen bonds in some products derived from the hydrolysis of UCl_4 . *J. Inorg. Nucl. Chem.*, 28: 817–823.