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Solvent Extraction and Isolation Strategies for Uranium, Thorium, and Radium in Rare Earth Element Recovery from Ores: A Review

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ABSTRACT
The process of recovering rare earth elements (REEs) from ores and secondary sources are often made difficult by the presence of radioactive elements such as uranium (U), thorium (Th), and their daughters, where radium (Ra) is especially troublesome. Effectively separating these radionuclides from REEs is essential for ensuring environmental safety and producing high-purity REE concentrates. This review thoroughly explores solvent extraction (SX) methods for the selective isolation of U, Th, and Ra during REE recovery, with a focus on Phosphorus, nitrogen, and sulfur-based extractants, as well as macromolecules and synergistic systems. Key extractants like TBP, the Cyanex series, and nitrogen-donor ligands are assessed for their extraction efficiency, selectivity, and environmental impact. The review also points out emerging green alternatives, such as ionic liquids and bio-based methods which offer potential for reducing the ecological footprint of traditional SX systems. Other separation techniques, including solid-phase extraction and cloud point extraction are also discussed for their role in enhancing selectivity and minimizing secondary waste. Challenges, including extractant degradation, third-phase formation, and the necessity for sustainable practices, are addressed. This work provides an overarching and practical approach to the SX processes with a special emphasis on addressing current environmental challenges and evolving regulatory frameworks, making it a valuable resource for both researchers and industry professionals.

KEYWORDS
Solvent extraction; uranium; thorium; radium; rare earth elements

Introduction

REEs are primarily extracted from different minerals such as monazite, bastnäsite, and xenotime, which are phosphate, carbonate, and silicate-based minerals.[1] Secondary resources are also processed for their REE content, including coal dust and end-of-life products.[2] Moreover, several rare earth

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deposits have been identified worldwide.[3] Europe, for instance, is home to several important REE deposits, each with unique compositions and extraction possibilities, including Kvanefjeld and Kringlerne (Greenland), and Fen (Norway).[4–6] The extraction of REEs from their primary resources has been reported as complex and lengthy due to their production as a byproduct material along the process chain and the refractory nature of the matrix.[7] Secondly, of environmental concern due to the presence of Naturally Occurring Radioactive Material (NORM), including U, Th, and Ra – a decay product of U and Th, existing in the ore mineral assemblage (Table 1) as a result of co-crystallization and similar geochemical properties[8] with regards to REEs, similar ionic radii and charge states.[8] To that end, each mining activity and operation has a specific impact on the environment and ecology.

The typical treatment of REEs, which is depicted in Figure 1 involves the production route, which requires a series of operations with the intent to liberate the mineral, generally achieved through crushing and milling.[9] The latter is followed by a concentration stage, usually conducted using various techniques, including gravity or magnetic separation and flotation. The obtained concentrate is generally dissolved in acidified media to recover the targeted metallic values. However, due to the complexity of the ore mineral matrix, other components of the ore are also entrained into the solution.[10–12] The leachate from the treatment of rare earth minerals was reported to possess U, Th, as seen in Table 1, and other gangue-related metals such as Ca, Mg, and Fe, requiring a step further with a focus on solution purification through selective separation methods[11]precipitation, ion-exchange, and SX. Precipitation is achieved through pH adjustment, while the ion exchange involves a solid resin to bind with the targeted metal.[13] In the SX process, two immiscible or partially immiscible solvents are used, which contain dissolved REEs. The two liquids are mixed, and the dissolved substances are distributed between the two phases until equilibrium is reached, after which the two liquids are separated. The concentrations of dissolved substances in the two phases depend on their relative affinity for the two solvents.[14,15] The last step is production to get critical application purity.[16,17]

Table 1. The amount of uranium and thorium present in major ree minerals.[7]

Minerals	Chemical Composition	Density (g/cm^3)	Weight Percentage		
			REO	ThO_2	UO_2
Bastnäsite	$(Ce,La)(CO_3)F$ $(La,Ce)(CO_3)F$ $(Y(CO_3)F$	3.90–5.20	70–74	0–0.3	0.09
Parisite	$Ca(Ce,La)_2(CO_3)_3F_2$ $Ca(Nd,Ce)_2(CO_3)_3F_2$	4.33–4.50	49–52	1.6	–
Monazite	$(La,Ce,Nd,Th)PO_4$ (Nd,Ce,La,Th)PO4	4.98–5.43	35–71	0–20	0–16
Xenotime (Y)	YPO_4	4.40–5.10	52–67	–	0–5

During the complete processing of REE ores, as shown in Figure 1, elements are inevitably entrained as toxic contaminants, creating difficulties in extraction, separation, and environmental management. Table 2 has been revised to list uranium and thorium concentrations reported for representative rare-earth deposits and the activity concentrations (Bq/kg) derived from these elemental values. Conversion factors used were 1 ppm U = 12.35 Bq/kg and 1 ppm Th = 4.06 Bq/kg.[23] Values were taken from project EIAs and published geochemical studies; where Th was reported as ThO_2, it was converted to elemental Th before applying the Bq conversion ($Th = ThO_2 \times 0.8788$). We note that reported values represent ores or concentrates in many cases (not background soils), and, therefore, the numbers primarily indicate process/radiological handling considerations rather than typical surface soil activity.[26] Thus, the need for a sustainable, eco-friendly, and effective separation or purification technique, such as SX, appears crucial for the isolation of either radioactive components or REEs.[27] This has initiated the need for the SX process to be widely applied on an industrial scale and reported as a simple and low-energy-consuming method.[2] To that, understanding the mechanistic process of the existing extractants used during REE extraction and radioactive component recovery/separation in different media is necessary for optimizing and designing efficient and green SX technologies for REEs. This work reviews the current trends and the latest developments of SX technologies to produce REEs. It further highlights the principle of the technique and the performance of the existing extractants based on their efficiency, selectivity, and separation. Finally, the environmental, economic, and technical imperfections of the current SX technologies were discussed, highlighting the potential future research pathways.[28]

Solvent extraction principle

Solvent, or liquid–liquid extraction, has come to be one of the most important separation processes in hydrometallurgy.[29,30] The discovery and isolation of the lanthanide and actinide elements provided impetus for the further development of SX, as the closely related properties of these f-group elements stretched the boundaries of knowledge in this young field.[29] Properties of U, Th, and Ra are listed in Table 3. This technology was later developed due to the demand and sustainable quantities of high-purity uranium and plutonium for World War II.[35] This technique is used to separate various metals, including Cu, Ni, Co, Zn, U, Mo, W, V, Zr, Hf, Nb, Ta, REEs, Ga, Ge, the platinum group metals (PGMs), and reprocessing of nuclear fuels.[9,14]

The process relies on the ability of metal ions to distribute between both phases: an aqueous solution (Leaching solution) and an immiscible organic phase (extractant). The feed solution (aqueous) contains valuable metals, free acid, and impurities. The organic phase is a homogenous mixture mainly

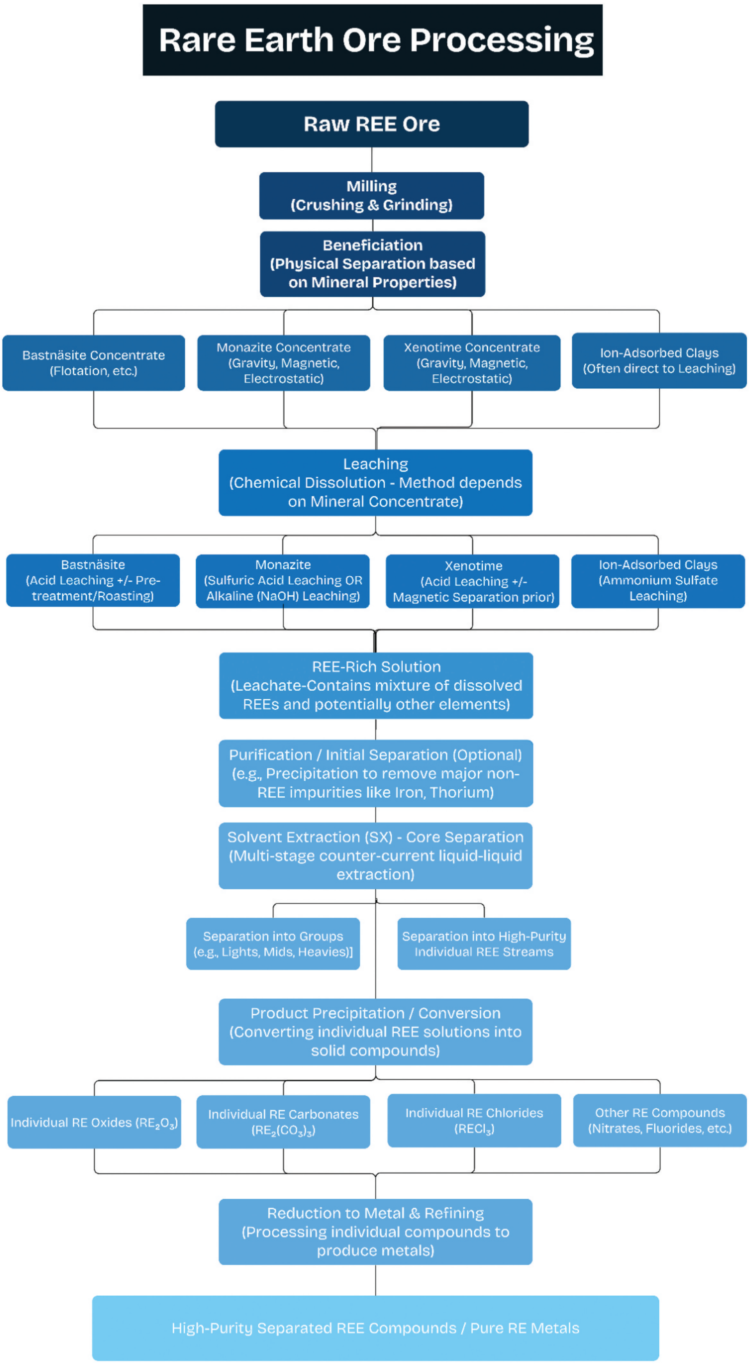


Figure 1. REE processing.

Table 2. Reported uranium and thorium concentrations in selected rare-earth element deposits worldwide and corresponding calculated activity concentrations.

Mine/deposit (country)	Host/sample	U (ppm)	Th (ppm)	U activity (Bq/kg)	Th activity (Bq/kg)	Reference
Kvanefjeld (Greenland)	Ilímaussaq intrusion (ore)	300	800	3,705.0	3,248.0	[18]
Norra Kärr (Sweden)	Peralkaline intrusive REE ore	11.4	10.9	140.79	44.25	[19]
Fen Complex (Norway)	Carbonatite/rodberg (ore average)	~10.4(avg)	~255(avg)	123.5	844.48	[20]
Bayan Obo (China) — high end	Polymetallic REE	550	~352 (from 400 ppm ThO_2 → Th)	6,792.5	1427.09	[21,22]
Browns Range concentrate (Australia)	Beneficiated concentrate	740	220	9,139.0	893.20	[23]
Steenkampskraal (South Africa) — monazite ore	High-grade monazite (ore)	600	~77,254	7,410.0	313,651.24	[24]
Mount Weld (Australia) — concentrate (Lynas)	RE concentrate	43	1630	531.05	6,617.80	[25]

*Activity concentrations calculated using conversion factors: 1 ppm U = 12.35 Bq kg^{-1} and 1 ppm Th = 4.06 Bq kg^{-1}.

composed of diluent (carrier) and an extractant. Modifier dissolved in diluent or carrier, whereby the extractant is the active component primarily responsible for the transfer via complex formation. The diluent improves the solubility of the metal–extractant complex, leaving behind impurities in aqueous solution.[36]

Extractants classification

The efficiency of the process is dependent on several factors, including the pH of the aqueous phase, affinity, A/O ratio, diluent, and contact time, which determines the chemical species present and their ability to form extractable complexes. The extractant type and concentration are regarded as the major factors dictating the overall metal transfer, affecting selectivity, transfer kinetics, and metal loading capacity.[1,14] This review organizes extractants based on their molecular structure, as it offers insight into extraction mechanisms, selectivity, and coordination chemistry. Figure 2 shows a summary of the extractants used for REE recovery.

Phosphorus-based extractants

P-containing extractants are industrially efficient compounds for REE production. This is due to the possibility of forming different types of chemical bonds between such extractants and metal ions, as presented in (Eqs. 1 and 2)

Table 3. Uranium, thorium, and radium properties.[31–34]

Property	Uranium (U)	Thorium (Th)	Radium (Ra)
Oxidation States	+4, +6 (predominantly UO_2^{2+} in aqueous systems)	+4 (dominates in all chemical environments)	+2 (stable in all conditions)
Insoluble Compounds	UO_2, UO_2SO_4, $UO_2(HPO_4)$	ThO_2, $Th(SO_4)_2$, $Th_3(PO_4)_4$	$RaSO_4$, $RaCO_3$
Adsorption Behavior	Strong binding to Fe/Al oxides and clay minerals	High affinity for oxides, hydroxides, and organic matter	Moderate binding to sulfates and mineral surfaces (e.g., barite)
Decay Chain Relation	Parent isotope in natural decay chains (e.g., U-238 → Th-234)	Intermediate daughter (e.g., Th-232 → Ra-228)	Final decay product in series (e.g., Ra-226 → Rn-222)
Chelating Agents	High affinity for EDTA, DTPA, organophosphates (e.g., TBP)	Strong chelation with EDTA, DTPA, and HDEHP	Moderate chelation with crown ethers and EDTA
Solvent Extraction	Highly extractable with TBP, HDEHP, and β-diketones	Efficiently extracted with HDEHP and organophosphates	Poorly extractable; requires crown ethers or calixarenes
Environmental Behavior	Precipitates as UO_2/UO_4 under reducing conditions; forms stable carbonate complexes in oxic environments	Precipitates as ThO_2 in oxic environments; forms insoluble phosphate complexes	Remains mobile in water unless precipitated as $RaSO_4$
Coordination Chemistry	Prefers hexagonal or linear geometry with oxygen-donor ligands	Tetrahedral to 8–10 coordination with oxygen-donor ligands	Simplest coordination due to ionic radius and +2 charge

$$M^{n+}_{(aq)} + n(HL)_{(org)} \rightleftharpoons ML_n^{(org)} + nH^+ \tag{1}$$

$$M^{n+}_{(aq)} + xNO_3^- + yS_{(org)} \rightleftharpoons M(NO_3)_x.yS_{(org)} \tag{2}$$

Where:

- $M^{n+}_{(aq)}$: UO_2^{2+} or Th^{4+}
- HL: Acidic phosphorus-based extractant
- S: Solvating phosphorus-based extractant like TBP, TOPO
- L^-: Conjugate base of HL
- *Org*: Organic phase

These extractants enable REE separation with high-purity isolation and can be applied for mining, recycling, and even coal by-products.[31] This family includes four different classes: tertiary phosphine oxides ($RR_1R_2P{=}O$), phosphinic acids ($R_2P(=O)OH$) and derivatives, phosphoric acid derivatives ($ROR_1OR_2OP(=O)$), and phosphonic acids ($RP(=O)(OH)_2$) and esters.[37] Promising separation efficiency in relatively high acidity (pH = 1–4) and can be used with varying acids such as sulfuric (H_2SO_4), nitric (HNO_3), etc. Table 4 summarizes the phosphorus extractant family's recent work on the processing of radioactive elements from aqueous environments via the SX process, experimental conditions (acidic media and range, diluent and extractant concentration, and remarks.

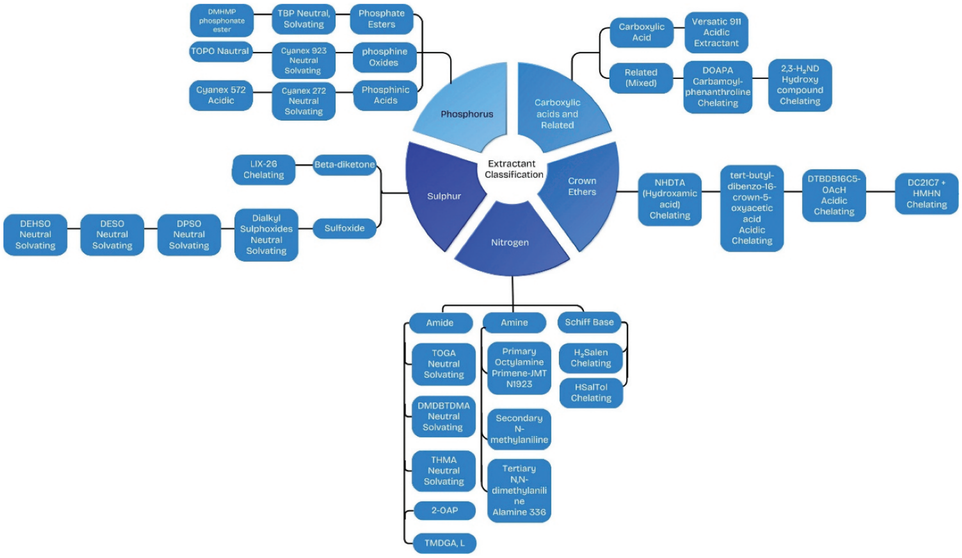


Figure 2. Extractant classification.

Solvating extractants

Phosphate ester.

(a) *TBP (tributyl phosphate)*: TBP is used conventionally for the separation of U(VI), Th(IV), and REE(III) from nitrate media. It shows a stronger affinity for U(VI) than Th(IV) and REEs. Menzies and Rigby showed that 5% (v/v) TBP in xylene extracts U, allowing its separation from Th and REEs in a nitrate leach solution. This subsequently extracts Th and separates the REEs, using an increased concentration of 40% v/v TBP in xylene.[38] However, a few processes relate to the co-extraction of U and Th, which afterward undergoes selective stripping of Th. Furthermore, TBP can extract U(VI) and Th(IV) from hydrochloric acid solutions by forming $UO_2Cl_2{\cdot}2TBP$ and $ThCl_4{\cdot}3TBP$, respectively. However, these extractions require high HCl concentrations (>5 M for U and >8 M for Th).[39]

(b) *DMHMP (Di(1-methyl-heptyl) methyl phosphonate)*: Tan *et al.* studied U (VI) and Th(IV) extraction behavior using DMHMP (Figure 3) as the extractant and kerosene as the diluent. The distribution ratio was analyzed based on contact time, acidity (0.01 to 6.0 mol/L HNO_3), extractant concentration, and temperature. Slope analysis determined that HNO_3 was extracted as a mono-solvated species, while U(VI) and Th(IV) were extracted as di-solvated and tri-solvated species, respectively. The selectivity for U(VI) was notably higher with DMHMP

Table 4. Summary of phosphorus-based extractants.

Extractant	Acid media	Extractant Concentration/ diluent	Remarks	Ref
TBP (Tributyl Phosphate)	HCl U: 5 M Th: 8 M	5%-40% v/v (Xylene)	Separation of U, Th, REEs. High HCl concentrations which is impractical.	[38,39]
DMHMP (Di(1-methyl-heptyl) methyl phosphonate)	HNO_3 0.01–6.0 M	1%-5% v/v for uranium. 30%v/v for Thorium (Kerosene)	SF U/Th = 1.4–26. Exothermic, spontaneous	[40]
Cyanex 923	HNO_3, H_3PO_4, HCl, H_2SO_4 1–5 M	0.01–0.10 M (Kerosene, ShellSol D70)	Selective way to extract U(VI) and Th(IV). Low sensitivity to temperature changes, Designed to minimize waste.	[41,42]
Cyanex 572	HCl mM – 3M	0.0064M–0.256 M (Kerosene)	Achieving a high separation factor ($\beta Th/\Sigma REEs = 4.38.10^4$)., 95–99.9% Th purity, demonstrating an efficient and scalable separation process.	[43]

($SF_aU/Th = 25–120$) compared to TBP ($SF_aU/Th = 1.4–26$). The negative ΔH confirmed that the extraction process was exothermic, and the negative ΔG suggested that the reaction was spontaneous. Additionally, the negative ΔS indicated a rise in order among the extracted species. Furthermore, under the tested conditions, DMHMP confirmed low water solubility, high thermal stability, and minimal third-phase formation, making it a better alternative to TBP.[40]

Phosphine oxide.

(a) *Cyanex 923*: Gupta *et.al.* focused on Cyanex 923 (mixture of trialkylphosphine oxides), for recovering metals from acid solutions of HNO_3, H_3PO_4, HCl, and H_2SO_4.[41] By mixing 0.01–0.10 M Cyanex 923 in toluene, nearly 99% of U(VI) and Th(IV) were extracted from 1 to 5 M HNO_3, although the extraction of lanthanides (Ce, Yb) was less than 5%, allowing for selective separation. Thorium was stripped using 2.0 M HCl, and uranium was stripped with 0.5 M H_2SO_4, leaving the lanthanides in the solution.[41] Further modified by Zhu *et. al.* (2016) to transfer uranium from 4–6 M to 0.2–0.5 M H_2SO_4, employing 10% Cyanex 923 and 10% isodecanol in ShellSol D70, which resulted in 98% extraction and 99% stripping. Equilibrium was achieved in just 0.5 min, with minimal temperature dependence observed between 30°C

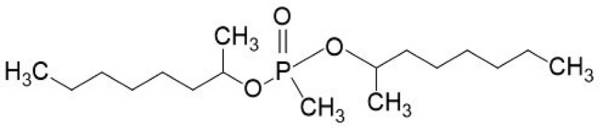
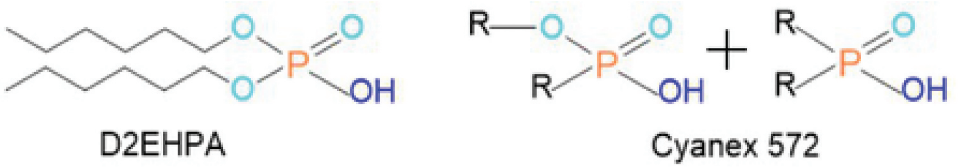


Figure 3. Structure of DMHMP.



(a) (b)

Figure 4. Molecular structure of the extractants used in this study: (a) D2EHPA, (b) Cyanex 572.[44]

and 60°C. An expected process involving four extraction stages and five stripping stages presents an efficient and sustainable approach to uranium recovery, producing minimal acid waste.[42]

Acidic extractants

Phosphinic + phosphonic acids.

(b) *Cyanex 572*: The separation and recovery of Th and REEs by Yanliang Wang *et. al*. was investigated from the radioactive waste residues of ion-absorbed type rare earth minerals by a new process using Cyanex® 572 (C572) as an extractant (shown in Figure 4). The separation factor reached a separation factor of $(\beta_{\left(Th/\Sigma REEs\right)}) = 4.38 \times 10^4$ with C572 and isooctanol in kerosene showed superior selectivity compared with conventional systems. The leaching rates of Th and REEs using 6 mol/L HCl were 69.6% and 92.1%, respectively. Recovery processes resulted in purities of 95–99.9% of Th with the least residual concentrations, hence, an efficient and scalable approach.[43]

Summary. The structural class of the extractant significantly determines its efficiency and selectivity in the separation of U(VI), Th(IV), from REEs. In the family of phosphate esters, DMHMP excels over TBP and D2EHPA (Figure 4) both in selectivity and stability and hints at its applicability as a TBP substitute. Phosphine oxides, Cyanex 923 are good sources of quick and selective U and Th extraction with low extraction of lanthanides. Cyanex 572, combining phosphinic and phosphonic acid functionalities, enables highly selective thorium recovery from complex waste streams with separation factor 4.38×10^4. Cyanex 272 demonstrates effective metal binding and excels in synergistic systems (dealt with later in part of this review). Further, Taguchi's method can be used to reinforce the value of statistical optimization[45,46] in designing efficient separation strategies.

Nitrogen-based extractants

N-containing extractants are favored because of the use of the CHNO scheme due to their environmental compatibility, tunable structures, and lower phosphorus-related secondary waste, making them increasingly attractive for REE and actinide separation.

The nitrogen donor (characteristics as hard Lewis bases) atoms facilitate metal binding via electron pair donation, primarily through amine, amide, and heterocyclic nitrogen functionalities. These extractants are capable of forming neutral or charged complexes, depending on the metal ion and solution conditions. The basicity of nitrogen allows complexation across a wider pH range (2–6), and its compatibility with both HNO_3 and HCl systems broadens their industrial applicability.[47,48]

The major classes of nitrogen-based extractants include amides, amines, Schiff bases, azoles, etc. Due to the great difference in molecular structure of all N-containing extractants, the mechanism of extraction is dealt with in subtopics. Table 5 summarizes the Nitrogen extractant family.

Neutral

Amides.

(a) *TOGA (N,N,N′,N′-tetraoctylglutaricamide)*: Hu et. al. (2014) studied U(VI) and Th(IV) extraction from nitric acid medium using TOGA (Tetra-substituted diamide). TOGA and kerosene-1,3,5-trimethylbenzene were comprising organic phase. Slope analysis showed that U(VI) and Th(IV) were controlled by $UO_2(NO_3)_2{\cdot}TOGA$ and $Th(NO_3)_4{\cdot}1.5TOGA$, respectively. The equilibrium constants for the extractions of U(VI) and Th(IV) at 298 K were estimated to be 3.35 ± 0.03 L^3/mol^3 and 1.87 ± 0.01 L^5/mol^5, respectively. A thermodynamic study suggested that the complexation was exothermic and spontaneous, as indicated by negative values of ΔG and ΔH. The negative ΔS implies a decrease in entropy, suggesting that the process is more favorable at lower temperatures. The study further analyzed how nitric acid concentration, salting-out agents ($NaNO_3$ and KNO_3), and temperature affected extraction percentage. It was found that U(VI) extraction was more effective than that of Th(IV), especially at higher nitric acid concentrations. Back-extraction studies showed that U(VI) and Th(IV) were not completely stripped from the organic phase. Additionally, U(VI)-TOGA complexes were found to be more stable than Th(IV)-TOGA complexes.[49]

(b) *N,N'-dimethyl,N,N'-dibutylteradecylmalonamide (DMDBTDMA) and N,N,N',N'-tetrahexylmalonamide (THMA)*: E. Makombe *et al.* (2022) explore the separation of U(VI) and Th(IV) from a nitrate solution using two malonamide-based extractants, DMDBTDMA and THMA (structure shown in Figure 5), both dissolved in toluene.

These isomeric compounds vary in the arrangement of their alkyl groups, which influences their selectivity. The efficiency of extraction is affected by acidity levels, with DMDBTDMA demonstrating a greater

Table 5. Summary of nitrogen-based extractants.

Extractant	Acid media	Extractant Concentration/ Diluent	Remarks	Ref
TOGA (N,N,N′,N′-tetraoctylglutaricamide)	HNO_3 1M – 8M	0.1M – 0.8M (Kerosene-1,3,5-trimethylbenzene)	TOGA was highly efficient in extraction, taking out U(VI) and Th(IV) as $UO_2(NO_3)_2$·TOGA and Th $(NO_3)_4$·1.5TOGA, respectively. Exothermic, U(VI) was superior to that of Th(IV), especially at elevated concentrations of nitric acid.	[49]
DMDBTDMA and THMA	HNO_3 1 M – 3 M	0.05 – 1 M (Toluene)	DMDBTDMA favored U(VI) at low acid levels, and THMA formed precipitates of Th(IV).	[50]
2-OAP	sodium salts of weak organic acids (pH 5.6)	1 x 10^{-3} and 1 x 10^{-1} M (Xylene, Toluene)	A green method involving the formation of a 2-$OAPH^+$ $Th(NO_3)(malonate)_2$ complex. Low extractant concentration and mild acidity	[51]
Primary Amine (N1923)	H_2SO_4 (pH dependent)	0.1M (Isoparaffin IP-2028)	Multi-stage process with N1923 (methyloctadecyl amine) Under optimized extraction, scrubbing, and back-extraction, uranium (99.3%) and thorium (99.6%) with high purity,	[52]
Amines: Octylamine, N-methylaniline, N, N-dimethylaniline	H_2SO_4 (pH dependent)	0.001 M – 0.15 M (Petroleum ether)	Possess selectivity. By the variation in amine basicity and metal complexation, they attained a sequential extraction scheme, demonstrating effective separation from monazite ore.	[53–55]
Primary and Tertiary amines (Primene-JMT and Alamine 336)	HCl, H_2SO_4 (pH dependent)	Primene-JMT – 0.025M – 0.1M Alamine 336 - 0.05M – 0.2M (dodecane + 5% of tridecanol as modifier)	A synergistic Primene JM-T/Alamine 336 system provides single-stage, efficient uranium and thorium extraction from a complex sulfuric leach liquor	[54–56]
Schiff Base (H_2Salen, HSalTol)	HCl (pH depent)	$3.1.10^{-3}$M – $2.5.10^{-2}$M (Benzene)	Extraction of Th(IV), U(VI), and Zr(IV). H_2Salen was more efficient in U(VI) extraction, where at pH 6.5, it had near quantitative extraction. Selectivity: $Zr^{4+} > UO_2^{2+} > Th^{4+}$ with H_2Salen, $Zr^{4+} > Th^{4+} > UO_2^{2+}$ with HSalTol	[57]

selectivity for U (VI) at lower acid concentrations. The Separation Factor depicted in Table 6. In contrast, Th(IV) shows a different extraction pattern: DMDBTDMA favors extraction through hydrophobic aggregation, while THMA leads to the formation of electrostatically stabilized complexes, resulting in crystalline precipitation when thorium concentrations are high. These findings underscore the importance of molecular structure in the separation of actinides.[50]

(c) *2-octylaminopyridine (2-OAP) and N,N,N′, N′-tetramethyl-diglycolamide (TMDGA, L)*: Kore *et al.* (2016) have introduced an eco-friendly and effective approach for extracting and separating Th (IV) and U(IV) using specially designed ligands (shown in Figure 6) in various solvent systems. Th(IV) is selectively extracted from sodium malonate solutions with 2-OAP in xylene under optimal conditions that are pH 5.6, 5×10^{-2} mol/L 2-OAP, and 1×10^{-2} mol/L sodium malonate.[51]

A slope analysis indicates the formation of the ion-pair complex 2-OAPH$^+$ Th(NO$_3$)(malonate)$_2$. The method shows excellent selectivity for Th(IV) over U(VI), Ln(III), and Zr(IV) with little interference. The extracted Th(IV) can be stripped well with 0.5 M HNO$_3$ and analyzed by EDTA titration with satisfactory recovery from real samples such as monazite sand and gas mantles. The mild acidity and low concentration of the extractant assist in making this process environmentally friendly for industrial and nuclear uses.[51]

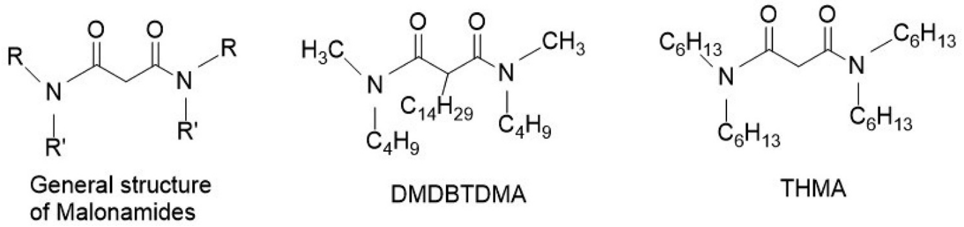


Figure 5. Structures of malonamide and its derivatives, DMDBTDMA and THMA.[50]

Table 6. Separation factors of U(VI), Th(IV), Nd(III), and Zr(IV) after extraction with 0.2 mol/L DMDBTDMA (2a) or THMA (2b) in toluene. Initial aqueous phase: 0.001 mol/L of each metal in 3 mol/L HNO$_3$.[51]

DMDBTDMA (2a)		THMA (2b)	
$S_{U/Nd}$	980 ± 136	$S_{U/Nd}$	1250 ± 173
$S_{U/Zr}$	73 ± 10	$S_{U/Zr}$	13 ± 2
$S_{Th/Nd}$	480 ± 67	$S_{Th/Nd}$	3500 ± 485
$S_{Th/Zr}$	36 ± 5	$S_{Th/Zr}$	36 ± 5

Table 7. Summary of sulphur-based extractants.

Extractant	Acid media	Extractant Concentration/ Diluent	Remarks	Ref
Dialkyl Sulphoxides	HNO_3 (0.02M)	0.04M −0.20M (Xylene)	Straight-chain alkyls provided high extraction but low Th/U separation, while branched-chain groups enhanced selectivity, with di(3-octyl) sulphoxide providing the highest separation factor. Aromatic groups inhibited extraction.	[61]
DPSO (Diphenyl sulphoxide)	HCl (3M – 10M)	0 -2M (Varied)	Forming stable coordination complexes. % Extraction increased with HCl concentration but decreased with temperature, indicating an exothermic process. Lower dielectric constant of diluents enhanced stability.	[62]
DESO (Di (2-ethylhexyl) sulphoxide)	HNO_3 (2M)	0.2 M (*n*-Dodecane)	Used for U(VI) extraction; forms $UO_2(NO_3)_2{\cdot}2DESO$	[63]
DEHSO (Di (2-ethylhexyl) sulphoxide)	Nitric acid (0.75M – 7.0M)	0.2 M (kerosene)	More efficient than TBP; high radiolytic stability; forms $UO_2(NO_3)_2{\cdot}2DEHSO$ and $Th(NO_3)_4{\cdot}2DEHSO$; better ligand than phosphoryl group	[64,65]
LIX-26	Varies (1.5 - 7.0 pH)	10% LIX-26, 10% Butanol (Benzene, MIBK + Butanol (modifier))	Complete U extraction at pH 5; SCN^- suppresses Th extraction, SO_4^{2-} enhances; anti-synergistic effect with DPSO	[66]

Table 8. Summary of macromolecules and other extractants.

Extractant	Acid media	Extractant Concentration/ Diluent	Remarks	Ref
DC21C7 + HMHN	HNO_3 (0.1 M)	Varies (Toluene)	Three species were extracted, and the extraction efficiency was controlled by reagent concentration and competitive ion exchange. Stable species formation was supported.	[70]
Hydroxamic acid-based crown ether (NHDTA)	HNO_3 (pH 3.0 - 9.0)	0.90×10^{-3} M – 4.46×10^{-3} M (Chloroform, benzene, toluene and iso-amylalcohol)	U(VI) extraction from cerium, thorium, and lanthanides using NHDTA. The process achieved fast pH 6.0–7.0 equilibration and showed good uranium selectivity, though in laboratory scale.	[71]
Sym-Di[4(5)-tert-butylbenzo]-16-crown -5-oxyacetic acid (DTBDB16C5-OAcH)	-(pH 3 - 11)	0.001 M (Benzene, Toluene, and Chloroform)	Radium separation is pH-selective separation ($\log D = -0.18\,pH + 2.71$, effective above pH 9). Extraction is prevented by high ligand concentration (log [HX] > 3.8) and high Ba^{2+} concentrations but not K^+. A favorable ligand-to-radium ratio (10^3 -10^5) must be used for selective Ra separation.	[72]
tert-butyl-dibenzo-16-crown-5-oxyacetic acid	HCl (5M + pH dependent)	0.01 M (Chloroform)	^{226}Ra extraction form a RaL_2 complex. Extraction is reversible by pH and occurs in alkaline medium, and from pH 4 to 8, efficiency is increased. Lipophilicity is increased on Ra binding, and 1:2 metal-ligand complex formation was proven.	[73]

Table 9. Summary of carboxylic acids and related extractants.

Extractant	Acid media	Extractant Concentration/ Diluent	Remarks	Ref
DOAPA (N, N-dioctylcarbamoyl-phenanthroline derivative)	HNO_3 (Up to 4 M)	1mM – 10mM (n-octanol)	Superior U(VI) extraction and selectivity, and 1:1 U(VI) and 1:1/1:2 Th(IV) complexes were obtained. 8-coordinate U(VI) and 10–12 coordinate Th(IV) complexes.	[75,76]
Versatic 911 (RCOOH)	Acetic acid, HNO_3 (0.1 M; pH 2.75–4.9)	16% (v/v) (Benzene, Xylene, Toluene, Chloroform, Butanol)	Th^{4+} recovery between pH 4.0–4.9 via cation exchange. Distribution coefficient values and graphical analysis supported a 1:4 Th^{4+} -Versatic 911 complex.	[77]
2,3-Dihydroxynaphthalene (2,3-H_2ND)	HNO_3 (pH 5–12)	2% (w/v) (Ethyl acetate)	Separation of Th, REEs, and U from geological samples by ICP-OES. Th/REEs as neutral complexes taken up in ethyl acetate, while U is anionic complex with CTA^+, extracted above higher pH.	[78]

In U(IV) complexation, "TMDGA (L)" in 1 mol/L HCl and 1 mol/L HNO_3 creates three species—UL^{4+}, UL_2^{4+}, and UL_3^{4+} with 1:1, 1:2, and 1:3 stoichiometries, respectively, as confirmed by spectroscopy. The absorption spectra demonstrate that Cl^- and NO_3^- participate in coordination, which changes the structures of the complexes.[59]

Basic

Amines. Amines represent a broad class of extractants, encompassing primary, secondary, tertiary, and quaternary amines. The extraction mechanisms

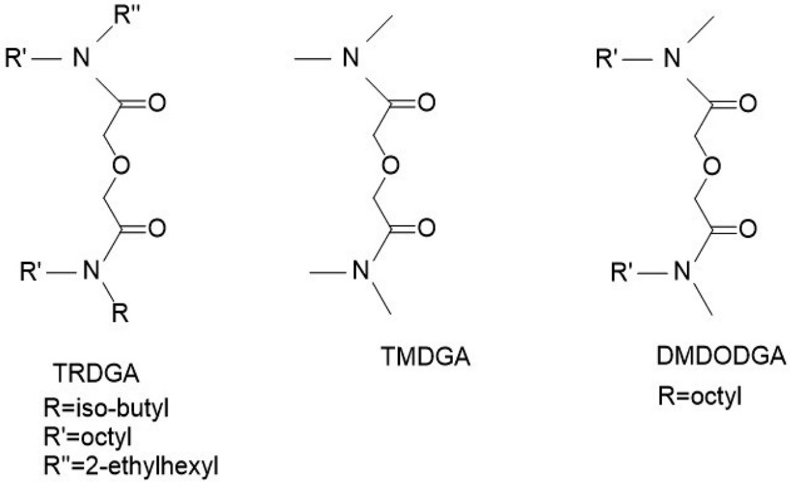


Figure 6. Structures of TRDGA (R = octyl, iso-butyl, 2-ethylhexyl), TMDGA, DMDODGA (R = octyl).[58]

of amines can generally be described as either anion exchange or Adduct formation.[47]

The reaction for Acid extraction is represented in Eq. (3), Anion Replacement in Eq. (4), Metal extraction in Eq. (5).

$$R_3N_{(org)} + H^+X^- + H_2O \rightleftharpoons R_3NHOH_{(org)} + H^+X^- \rightleftharpoons R_3NH^+X^-{}_{(org)} + H_2O \tag{3}$$

$$R_3NH^+X^-{}_{(org)} + H^+Y^- \rightleftharpoons R_3NH^+Y^-{}_{(org)} + H^+X^- \tag{4}$$

$$mR_3NH^+X^-{}_{(org)} + MX_{(m+1)}^{-m} \rightleftharpoons (R_3NH)_m MX_{(m+n)}{}_{(org)} + mX^- \tag{5}$$

(a) *N1923*: Hung *et. al.* (2022) studied a newly developed extractant and showed that an O/A ratio of 3 over six stages was adequate for effectively separating Th from U using the primary amine N1923 (methyloctadecyl amine, $(C_nH_{2n+1})2CHNH_2$, n = 9–11) at a concentration of 0.1 M in isoparaffin IP-2028. The extraction process operates on a similar ion-exchange mechanism as previously outlined in Eq. (4). The raffinate underwent further purification, resulting in U with a purity of 99.3%, which is suitable for U_3O_8 ex-AUC nuclear fuel synthesis. Scrubbing at an O/A ratio of 6 over six stages successfully eliminated impurities, raising the purity of the Th-scrubbed organic phase to 99.6%. Th recovery through back-extraction at an O/A ratio of 5 over six stages achieved a purity of 99.6%, making it appropriate for ThO_2-based nuclear applications. This study extends previous research by Trong et al. (2020) to achieve selective separation of Th from U using the assistance of N1923, aiming at a multi-stage process comprising extraction, scrubbing, and back-extraction, ultimately yielding highly pure ThO_2 and U_3O_8/UO_2 nuclear material.[52]

(b) *Primary, Secondary, and Tertiary amines*: E. H. Borai et. al. (2014) examined the selectivity and efficiency of certain amines. Primary amines (such as **octylamine**) are highly efficient for uranium (90% extraction at pH 4) and thorium (97% extraction at pH 3). Secondary amine (**N-methylaniline**) and tertiary amine (**N, N-dimethylaniline)** are selective in U and Th over REEs. In multi-element systems, tertiary amines demonstrated greater selectivity, achieving 80% extraction of thorium at pH 4 and 66% extraction of uranium at pH 7 with 0.1 M N, N-dimethylaniline. Ion-exchange and SX mechanisms, where U and Th exist as their respective sulfate complexes, extractable by amines, contribute significantly towards the separation. The author also addresses the application of petroleum ether as a diluent for extraction optimization and for avoiding the development of a third phase. Kinetic studies showed that Th reached equilibrium in 15 min, while U took up to 30 min. Sequential extraction from monazite samples resulted in 70% Th and 55% U uptake.[53] The extraction of Th with 1° amine (Eq. 6) and extraction of U with 3° amine governing the extraction reactions (Eq. 7):

$$4RNH_2H^+HSO_4^-(org) + \left[Th(SO_4)_4\right]^{4-}(aq) \rightarrow (RNH_2H^+)_4\left[Th(SO_4)_4\right]^{4-}(org) + 4HSO_4^-(aq) \tag{6}$$

$$4R_3NH^+HSO_4^-(org) + \left[UO_2(SO_4)_3\right]^{4-}(aq) \rightarrow (R_3NH^+)_4\left[UO_2(SO_4)_3\right]^{4-}(org) + 4HSO_4^-(aq) \tag{7}$$

(c) *Commercial Amines*: Alamine 336 (tri-octyl/dodecyl amine) (110), Primene-JMT [Ritcey et al.] and ALIQUAT™ 336 are utilized in industrial separation processes. Amaral *et. al.* (2018) show that a mixture of 0.05 mol/L Primene JM-T (primary amine) and 0.1 mol/L Alamine 336 (tertiary amine) allows for the complete extraction of U and Th in a single step. The leached sulfuric solution contained 0.08 g/L of Th, 0.35 g/L of U, and 9.1 g/L of REEs, along with other metals like Al, Fe, Ca, Zn, and Si. The separation factors were around $\beta^{Th}_{REE} = 145, \beta^{Th}_{Fe} = 203$, $\beta^{U}_{REE} = 292$, and $\beta^{U}_{Fe} = 410$, with extraction efficiencies of 94% for Th and 97% for U. The increased extraction of Fe with higher pH levels is due to the dominance of $FeSO_4^+$ and $Fe(SO_4)_2^-$ species in the sulfuric environment. As the ratio of extractant increases extraction of Fe increases up to 20%. U and Th were successfully stripped from the loaded organic phase using 1.7 mol/L NaCl at a pH of 1.2[54,56,57]

Schiff base. C. R. Panda *et al.* (1986) explored the liquid–liquid extraction of Th(IV), U(VI), and Zr(IV) using the quadridentate Schiff base bis-(salicylidene)ethylenediamine (H_2Salen) dissolved in benzene. The extraction efficiency of H_2Salen was compared to that of the bidentate Schiff base N-salicylidene-p-toluidine (HSalTol). Their findings show that H_2Salen has a significantly higher extraction efficiency for U(VI) compared to HSalTol.[57] The extraction process is influenced by pH, achieving nearly complete efficiency at around pH 6.5. Slope analysis determined the composition of the extracted species to be $[Zr_4(OH)_{12}(H_2Salen)_2]Cl_2$, $[UO_2(OH)(H_2Salen)]$, and $[Th(OH)_3(H_2Salen)]$. Logarithmic plots of the distribution ratio (D) versus pH for uranium and thorium show a slope of 1, indicating a single proton-dependent extraction mechanism. At the same time, zirconium displays a slope of 0.5, suggesting polymerization in solution. The extraction efficiencies follow the order $Zr^{4+} > UO_2^{2+} > Th^{4+}$ with H_2Salen, whereas with HSalTol, the order is $Zr^{4+} > Th^{4+} > UO_2^{2+}$. This suggests that HSalTol is more effective for selectively separating thorium from uranium. A single extraction at pH 6.5 can almost 99% extract U(VI), while multiple extractions are necessary when using HSalTol. The coordination chemistry of Schiff bases is vital for uranium recovery from ores, Th separation for breeder reactors and Zr purification for nuclear fuel cladding.[57]

Summary: Nitrogen-donor ligands afford considerable advantages for U and Th. Neutral amides like TOGA and malonamide derivatives exhibit high affinity for U(VI), with stability influenced by complex stoichiometry and acidity. TOGA further demonstrate coordinated species formation involving anions, enhancing the understanding of U(IV) speciation. Basic extractants such as primary and tertiary amines (e.g., N1923, Alamine 336) achieve efficient U-Th separation via ion-exchange, with performance sensitive to pH and diluents. Schiff bases highlight the effect of denticity on metal selectivity, favoring U(VI) or Th(IV) based on coordination capacity.[47]

Sulfur-based extractants

S-containing extractants (Summarised in Table 7) are commonly utilized in the industry for separating Co and Ni.[60] They function via two principal mechanisms: neutral solvation in highly acidic media and cation exchange in mild acidic conditions. The solvation pathway (shown in Eq. 8) involves coordination of neutral sulfur donors (e.g., sulfoxides) to metal ions, while the cation exchange mechanism (shown in Eq. 9) employs acidic sulfur ligands (e.g., thiophosphinic acids) that replace hydrogen ions with metal ions. The latter mechanism is generally more effective at lower acid concentrations.[30]

Despite their usefulness, they encounter difficulties in separating lanthanides from actinides due to issues like chemical and radiolytic instability, along with the formation of sulfate.[61]

$$M^{n+}_{(aq)} + nL_{(org)} \rightleftharpoons ML_n^{(org)} \tag{8}$$

$$M^{n+}_{(aq)} + nHL_{(org)} \rightleftharpoons ML_n^{(org)} + nH^{+}_{(aq)} \tag{9}$$

Neutral

Sulphoxides. Sulfoxides possess higher sensitivities towards changes in substituent extraction activity and electronegativities as compared to neutral phosphorous organic compounds (NPOC). Thus, the substitution of an aliphatic radical ($X = 2.0$) for a phenyl group ($X = 2.34$) in NPOC reduces the uranium extraction by a factor of 17, while in the case of sulphoxides, it is lowered 40 times. The extraction activity of the sulphoxides cannot be predicted by their IR spectra.[67]

(a) *Dialkyl sulphoxides*: Preston and du Preez (1997) focus on the extraction of U(VI) and Th(IV) from nitrate solutions by dialkyl sulphoxides. The molecular structure of the extractant is important in governing the efficiency and selectivity of the extraction process. Uranium forms a complex $UO_2(NO_3)_2(R_2SO)_2$, while thorium forms $Th(NO_3)_4(R_2SO)_3$. Straight-chain alkyl groups, like n-hexyl and n-octyl, provide high extraction efficiency but yield low separation factors $\beta_{Th}^{U} = 20$.[61] Conversely, branched-chain groups such as 2-ethylhexyl and 3-octyl provide lower extraction rates but better selectivity, a di (3-octyl) sulphoxide providing a separation factor of $\beta_{Th}^{U} = 70$. Cycloalkyl groups have no effect on extraction efficiency, while aromatic groups, e.g., phenyl, inhibit extraction completely due to their strong electron-withdrawing effect. Another depiction is that the extraction efficiency of nitrate concentration and log D versus log NO_3^- further supports the stoichiometry of the complexes. These results highlight the importance of steric hindrance in designing extractants for the selective recovery of U and Th.[61]

(b) *DPSO and DESO*: Mohanty *et al.* (1975) developed a process of extracting Th from hydrochloric acid solutions using diphenyl sulphoxide (DPSO) and its derivatives operate through a coordination mechanism, resulting in stable complexes like $ThCl_4\cdot 2DPSO\cdot HCl$ or $ThCl_4\cdot 3DPhSO$, which vary based on the solvent environment and the concentration of the extractant. The efficiency of extraction increases with higher concentrations of hydrochloric acid due to the formation of chloride complexes, while elevated temperatures tend to reduce extraction efficiency, suggesting that the process is exothermic. Additionally, extraction stability is enhanced in diluents that have lower dielectric constants. The presence of synergistic effects in mixed extractant systems indicates the potential for optimizing SX on an industrial scale.[62]

For U(VI) Mahajan *et al.* (1991) explore di(2-ethylhexyl)sulphoxide (DESO), a branched-chain neutral extractant, which is effective in separating U from 2 M nitric acid when using 0.2 M DESO in n-dodecane. The extraction of U with DESO is depicted in Eq. (10).[63]

$$UO_2{}^{2}+ + 2NO_3{}^{-} + 2DESO \rightarrow UO_2(NO_3)_2\cdot 2DESO \tag{10}$$

c. *DEHSO*: The extraction of U(VI) from acidic HNO_3 solutions using di(2-ethylhexyl) sulfoxide (DEHSO) is more effective than that of TBP.[64] This study was extended by Shen Chaohong et al. (1994), who claimed DEHSO is better than TBP for the extraction of U, Zr, Nb, and Ru under all conditions and is as good as TBP for Th. Gamma-ray irradiated DEHSO is also shown to have better radiolytic stability for the extraction of Zr and Nb than TBP, and therefore, enhanced U-Th discrimination.[65] The extraction processes for U(VI) and Th(IV) are exothermic, resulting in the formation of $UO_2(NO_3)_2 \cdot 2DEHSO$ and $Th(NO_3)_4 \cdot 2DEHSO$ as the extracted species. D values of U, Th, and HNO_3 as a function of aqueous HNO_3 concentration at 10°C $[U]_{aq} = [Th]_{aq} \approx 0.05$ mol/L $[DEHSO]_{org} = [TBP]_{org} = 0.2$ mol/L[65] One notable advantage of DEHSO over other dialkyl sulfoxides is its complete miscibility with non-aromatic hydrocarbon diluents, which is essential for practical applications in nuclear separation. Given these characteristics, DEHSO presents a promising alternative to TBP for the extraction processes involved in reprocessing U-Th fuels.[64] This is attributed to DEHSO containing a semi-polar sulfoxide group (–S→O), a better metal-ligand complex solvent compared to the phosphoryl group (–P→O).[65] The Separation of Th and U from their respective ores is doubtful in light of a failure to show the selectivity of these towards lanthanides.

Acidic

Beta-diketone.

(a) *LIX-26*: The study examined the extraction of Th(IV) and U(VI) using the chelating extractant LIX-26, which is an alkylated 8-hydroxyquinoline, along with its combinations with other reagents. It focused on the extraction efficiency of LIX-26 in a diluent system that included benzene and methyl isobutyl ketone (MIBK), with butanol serving as a modifier. The recovery of UO_2^{2+} by 10% LIX-26 and 10% butanol in benzene are at quantitative levels at pH 5.0, and pH 0.5 values recorded at 4.95 for Th^{4+} and 3.35 for UO_2^{2+}. The extraction of Th^{4+} is improved when using mixtures of 0.1 M oxine (8-hydroxyquinoline) and 0.1 M salicylic acid in MIBK, achieving complete extraction at pH 5.0. The study also looked into the effects of anions like Cl^-, SO_4^{2-}, and SCN^- on Th extraction and found that sulfate boosts extraction up to 1.5 M, while SCN^- has a negative impact. Additionally, the extraction of both U and Th using mixtures of LIX-26 and dipentyl sulphoxide (DPSO) revealed that U extraction is more effective with LIX-26 alone compared to LIX-26/DPSO mixtures, an indication of an anti-synergistic effect. The slopes of log D versus pH plots were found to be 1.25 for UO_2^{2+} and 0.52 for Th^{4+}.[65,66]

Summary: Sulfur-based extractants, especially sulfoxides, offer effective U(VI) and Th(IV) separation via solvation and cation exchange mechanisms. Branched dialkyl sulfoxides enhance selectivity, while DEHSO outperforms TBP in stability and efficiency. DPSO and DESO form stable complexes, and extraction is favored in low dielectric solvents. LIX-26 shows strong performance at pH 5.0 but displays anti-synergistic effects with sulfoxides. Overall, extractant structure, acidity, and ligand interactions critically influence separation efficiency.

Crown ethers

Macrocyclic compounds like crown ethers (summarized in Table 8) are highly selective extractants used for metal ion separation, particularly when conventional methods fail. These ligands coordinate metal ions through electron-donating oxygen atoms within their ring structures. Selectivity depends on both cavity size and donor basicity.[68]

In acidic media, crown ethers require aqueous anions (e.g., NO_3^-, Cl^-) to co-extract metal complexes and maintain electroneutrality. Their efficiency can be improved through structural modifications – e.g., adding anionic groups (lariat ethers) or using synergistic ligands like PMBP. Extraction trends for actinides vary with ring size: 12-crown-4 and 15-crown-5 show Th(IV) > UO_2^{2+}, while 18-crown-6 derivatives follow similar trends due to steric effects.[69] The General Extraction mechanism of crown ethers is shown in Eq. (11).

$$M^{m+}_{(aq)} + qCE_{(org)} + \frac{m}{x}X_x^- \rightleftharpoons \left[M(CE)_q X_m\right]_{(org)} \tag{11}$$

Neutral

a. *Dicyclohexano-21-crown-7 (DC21C7) and 2-methyl-2-heptylnonanoic acid (HMHN)*: The study covers radium extraction from alkaline $NaOH/NaNO_3$ solutions (pH 11–13) using DC21C7 and HMHN in toluene. Three extractable species are identified: $RaA_2{\cdot}B{\cdot}NaA$ ($\log K = 3.57$), $RaA_2{\cdot}NaA$ ($\log K = 0.99$), and $B{\cdot}2NaA$ ($\log K = -0.41$). Extraction efficiency declines at higher reagent concentrations (0.01 M) due to sodium competition and possible $Ra(OH)_2$ precipitation. Modeling confirms species stability across NaA aggregation (y = 5–25). The general extraction mechanism (Eq. 9) involves sodium carboxylate, forming a neutral complex and releasing Na^+ represented in Eq. (12). Further study is needed for acidic conditions.[70]

$$M^{2+} + \frac{n}{y}(NaA)_y + mB \rightarrow \left(\frac{1}{x}\right)[MA_2.(n-2)NaA - mB]_x + 2Na^+ \tag{12}$$

Variable definitions in Eq. (12)[70]:

- y: aggregation number of NaA
- x: aggregation number of the metal complex
- n: number of carboxylic acid units in the complex
- m: number of crown-ether (B) molecules associated with the complex

Acidic

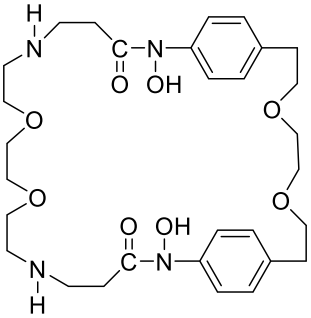
a. *Novel hydroxamic acid-based crown ether*: Agrawal et al. (2000) investigated the extraction and separation of U(VI) from Ce, Th, and REEs using a new hydroxamic acid-based crown ether, 5,14-N,N′-hydroxyphenyl-4,15-dioxo-1,5,14,18-tetraazahexacosane (NHDTA) (Figure 7). The extraction process is quick, achieving equilibrium in just 1 min within a pH range of 6.0 to 7.0. The selectivity factors, which are the ratios of the binding constant for the uranyl ion compared to those of interfering metal cations and anions, were found to be very high for uranium. This method has only been demonstrated on a laboratory scale so far.[71]

a. *Sym-Di[4(5)-tert-butylbenzo]-16-crown-5-oxyacetic acid (DTBDB16C5-OacH)*: Tieh-Chi Chu *et al.* (2001) explored the extraction of radium using DTBDB16C5-OAcH in organic diluents, specifically toluene, selected for its high distribution coefficient ($D_x = 18$ at $pH > 9$) and its compatibility with scintillation counting. The extraction process is governed by the following pH-dependent relationship: $\log D_x = -0.18\,pH + 2.71$. When the pH exceeds 9, the ionized DTBDB16C5-OAcH facilitates (Eq. 13) Ra extraction above pH 9.[72]

$$Ra^{2+} + HX \rightleftharpoons RaX + H^{+} \tag{13}$$

The efficiency of extraction improves with increasing pH but starts to decline at very high ligand concentrations (log [HX] > 3.8) due to significant aqueous complexation. Furthermore, the presence of coexisting alkaline earth ions – particularly Ba^{2+}, when present at concentrations greater than 10^4 times that of Ra – greatly hinders radium extraction, while K^+ has a negligible impact. Utilizing the Ultima Gold cocktail enhances detection sensitivity, achieving a limit of 6.46 Bq. An optimal ligand-to-radium ratio of 10^3 -10^5 is crucial for ensuring high selectivity and efficiency in the separation of Ra from radiochemical and environmental samples.[71,72]

b. *A tert-butyl-substituted dibenzo-16-crown-5-oxyacetic acid*: M. K. Beklemishev *et al.* (1994) explored the SX of ^{226} Ra using various



NHDTA

Figure 7. 5,14-N,N′-hydroxyphenyl-4,15-dioxo-1,5,14,18-tetraazahexacosane (NHDTA).[71]

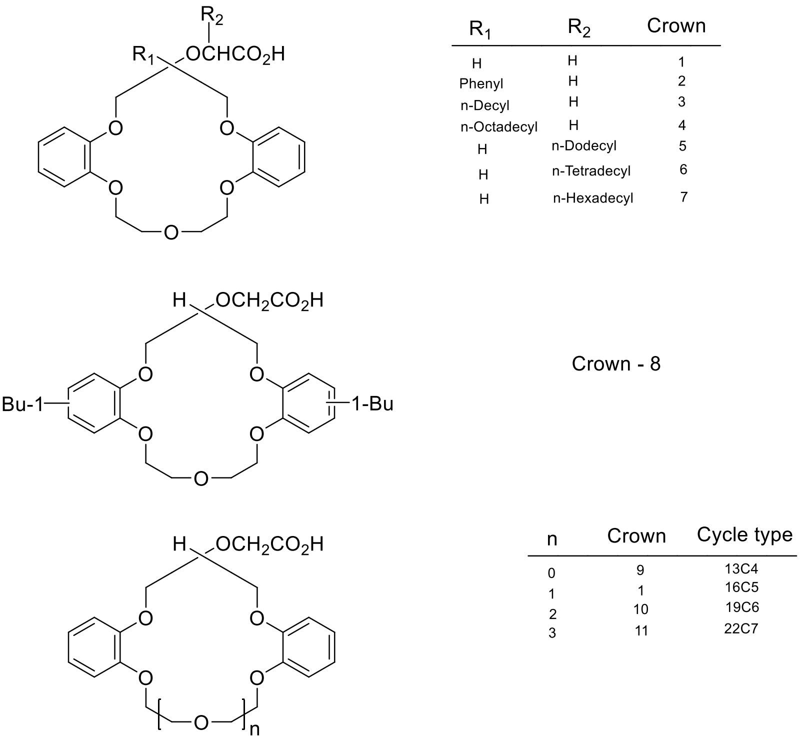
crown ether carboxylic acids (different structures in Figure 8) dissolved in chloroform. The extraction process is reversible with pH changes and takes place in alkaline conditions without requiring special counter anions. Among the compounds examined, a tert-butyl-substituted dibenzo-16-crown-5-oxyacetic acid was found to be the most effective, forming a RaL_2 complex with a stability constant of $(4.2 \pm 0.7) \times 10^8$. The research showed that the lipophilicity of the crown ether increases when radium binds to it. The extraction efficiency (D_{Ra}) was assessed over a range of pH levels, showing a significant rise between pH 4 and 7, with saturation occurring at pH 8 and higher, allowing for ligand recycling through acid stripping. Ra extraction concerning reagent concentration shows the formation of the 1:2 metal-ligand complex proved by Eq. (14).[74]

$$Ra^{2+} + 2L^{-} \rightarrow RaL_2. \tag{14}$$

L = ionized crown

In summary, the research indicates that lipophilic crown ethers are very effective for separating radium from alkaline solutions.[39]

Summary: Crown ethers are selectively ion-extractive for metals owing to their cavitation and donor atom tunability. Combinations of alkaline media like DC21C7 and HMHN efficiently extract Ra^{2+} by stable neutral



R1	R2	Crown
H	H	1
Phenyl	H	2
n-Decyl	H	3
n-Octadecyl	H	4
H	n-Dodecyl	5
H	n-Tetradecyl	6
H	n-Hexadecyl	7

n	Crown	Cycle type
0	9	13C4
1	1	16C5
2	10	19C6
3	11	22C7

Figure 8. Structures of the macrocyclic reagents tested for Ra^{+2} extraction.[74]

complexation but in the presence of high concentrations of Na^+ efficiency goes down. Functionally modified crowns under acidic conditions like U(VI)-selectively extract NHDTA, while in acidic solutions like DTBDB16C5-OAcH and tert-butyl crown derivatives show good binding of Ra^{2+}. Their reversible binding, structural flexibility, and high kinetics make crown ethers extremely appropriate for alkaline earth and selective actinide metal separation.

Carboxylic acids

Carboxylic acid-based extractants (summarised in Table 9) separating metal ions through **cation exchange mechanisms**. These acidic extractants (e.g., naphthenic acid, versatic acid) donate protons in exchange for metal cations, forming metal – carboxylate complexes in the organic phase.

They are particularly effective in mildly acidic to neutral pH ranges, where their deprotonated forms are most reactive. The extraction efficiency depends on pKa, chain length, and branching of the acid group. Due to their strong complexation with divalent and trivalent metal ions, they are useful in separating rare earth elements and base metals like copper and zinc. However, selectivity can be limited for chemically similar ions unless used with synergists or modified structures.[14]

Acidic

(a) *9-(N,N-dialkylcarbamoyl)-1,10-phenanthroline-2-carboxylic acid derivatives*: Wang *et al.* (2023) have studied selective extraction of U(VI) from Th(IV) by DEAPA and DOAPA in nitric acid medium with n-octanol as organic phase. It was found that DOAPA was a better extractant with greater distribution ratio ($D_aU = 1566$) and separation factor ($SFa^{U}_{Th} = 1582$) at 4 M HNO_3 due to increased hydrophobicity and electron donation ability. Slope study and NMR titration confirmed that DOAPA is 1:1 complex with U(VI) and 1:1 and 1:2 complexes with Th(IV), with different modes of coordination. UV–vis and X-ray diffraction also confirmed that there are 8-coordinate complexes formed by U(VI) ((Eq. 15), but 10- to 12-coordinated species by Th(IV) (Eqs. 16 and17).[75]

$$UO_2^{2+} + \mathrm{L} \rightleftharpoons \mathrm{UO_2.L}^{2+} \tag{15}$$

$$\mathrm{Th}^{4+} + \mathrm{L} \rightleftharpoons \mathrm{ThL}^{4+} \tag{16}$$

$$\mathrm{Th}^{4+} + 2\mathrm{L} \rightleftharpoons ThL_2^{4+} \tag{17}$$

(b) *Versatic 911*: Ray et al. (1981) investigated the SX of Th^{4+} using Versatic 911, a type of industrial carboxylic acid, dissolved in a benzene solvent.

Th extraction takes place within a pH range of 4.0 to 4.9 from a 0.1 M acetic acid solution, following a cation-exchange depicted in Eq. 18.

$$\mathrm{Th}^{4+} + 4\mathrm{RCOOH} \rightleftharpoons Th(RCOO)_4^{+} + 4\mathrm{H}^{+}$$

$$\mathrm{RCOOH} = \text{Versati 911 acid} \tag{18}$$

The extraction efficiency is affected by factors such as the concentration of the extractant, the concentration of metal ions, time, and the type of diluent used. The highest extraction efficiency is observed at 16% Versatic 911, with the distribution coefficient (D_{th}) rising from 0.5 at pH 2.75 to nearly 400 at pH 4.6 which is depicted in Figure 23. Additionally, the study explores the separation of thorium from elements like Mg, Ca, Sr, Ba, Mn, Co, Ni, Zn, Cd, and REEs, demonstrating excellent selectivity with minimal interference. The methodology was validated with synthetically prepared mixtures, achieving nearly 100% recovery of Th under optimal conditions. Graphs depicting thorium extraction against pH and Versatic 911 concentration against extraction confirm the 1:4 metal-to-ligand ratio.[77]

$$Th^{4+} + 2(2,3 - H_2ND) \rightarrow Th(2,3 - H_2ND)_2 \tag{19}$$

$$REE^{3+} + 3(2,3 - H_2ND) \rightarrow REE(2,3 - H_2ND)_3 \tag{20}$$

c. *2,3-dihydroxynaphthalene (2,3-H₂ND)*: Pradhan et al. (2021) have presented a systematic SX technique for obtaining Th, REEs, and U from geological samples, utilizing 2,3-H₂ND as a chelating agent, with quantification achieved through inductively coupled plasma-optical emission spectrometry (ICP-OES). Th and REEs create neutral complexes with 2,3-H₂ND, which are extracted into ethyl acetate at pH levels of 5–6 and 9–10, respectively. In contrast, however, U forms an anionic complex, (UO2 (2,3–H2ND)3CTA−), with cetyltrimethylammonium bromide (CTA+) upon contact under a pH range of 10–12, which allows it to be extracted. It separates such elements from interfering matrices with high accuracy. The chelation reaction of Th and REEs follows (Eqs. 19 and 20). In addition depicted in Figure 9.[78–81] Overall, this efficient and economical method is an appropriate approach to geochemical survey programs with large scales and an organized method of separating and measuring Th, REE, and U from silicate rocks and sediment samples.[78]

Summary: Acidic extractants show strong potential for selective metal separation in nitric and acetic acid media. DOAPA demonstrates exceptional selectivity for U(VI) over Th(IV) due to hydrophobicity and coordination geometry, forming stable 1:1 complexes. Versatic 911 effectively extracts Th^{4+} via a 1:4 metal-to-ligand ratio with excellent recovery, even in complex matrices. 2,3-H₂ND enables efficient separation of Th, REEs, and U based on pH-dependent chelation, offering a cost-effective and accurate solution for large-scale geochemical separation.

Synergic effect and synergistic extractants for norm

Synergistic effects refer to the phenomenon where the combined use of two or more extractants results in an extraction efficiency greater than the sum of their contributions.

Synergistic extraction equilibria

Metal ion extraction without a synergist follows:

$$M^{x+} + \mathrm{xHR_{org}} \rightleftharpoons \mathrm{MR}_{x(org)} + \mathrm{xH}^{+} \tag{21}$$

Adding a synergist (S) forms an adduct:

$$\mathrm{MR_{x(org)}}{+}\mathrm{yS_{(org)}} \rightleftharpoons \mathrm{MR_xS_{y\,(org)}} \tag{22}$$

Distribution ratio improves:

$$\mathrm{D} = ([\mathrm{MR_X}] + [\mathrm{MR_XS}_y])_{\mathrm{(org)}}/[M^{x+}]^{*} \tag{23}$$

This coefficient quantifies the degree of positive synergism.[82]

Synergistic extraction enhances efficiency via entropy and enthalpy effects in first-sphere coordination. Unlike chelation, mixed extractants (AA, BB, AB) increase configurational entropy, lowering free energy and boosting extraction represented by Figure 10. Key factors: additive basicity, ligand acidity, diluent nature, sterics, and kinetics.[83]

Synergistic extraction systems: Numerous synergistic extraction systems have been reported in the literature.[84] For instance, Nasab compared the

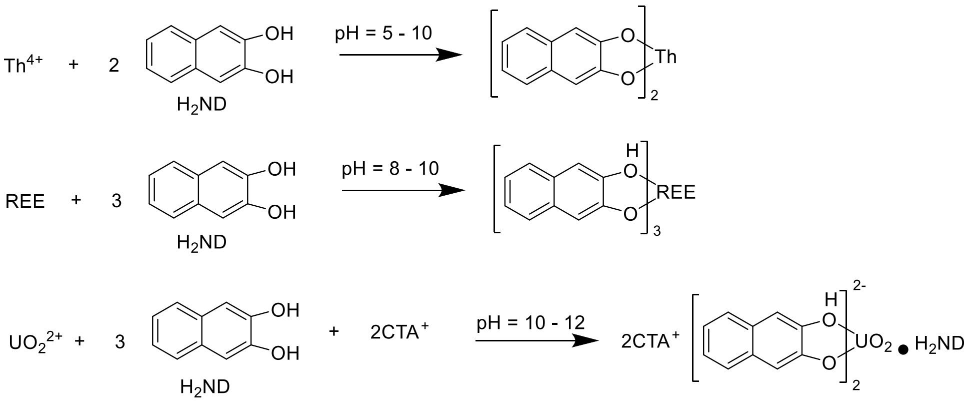


Figure 9. Reaction schemes for (a) Thorium,[79] (b) REE,[80] and (c) Uranium.[81]

synergistic effect of Cyanex 272 and the mixtures of Cyanex 272 with neutral organophosphorus extractants such as TOPO and TBP and acidic extractant Cyanex 301.[39] The author reported an enhanced recovery for both nuclides (U and Th).[85] It is believed that the observed enhancement in separation/recovery can result from the opening of chelate rings, the creation of lipophilic adducts, or increased coordination of metals.[82]

Another study conducted by Awwad et al. (2005) investigated U(VI) extraction by CYANEX 301, CYANEX 921, and their mixture in HNO_3 and H_2SO_4. The order was (301 + 921) > 921 > 301 in HNO_3, while in H_2SO_4 it was 301 > 921 ≈ (301 + 921). CYANEX 921 (oxygen donor) showed higher activity in HNO_3; CYANEX 301 (sulfur donor) performed well in H_2SO_4 due to sulfate complexation. Extraction lowered with higher concentrations of uranium and acid, diluent polarity, and temperature. n-Hexane produced the best results. Synergism occurred only in HNO_3. Uranium extracted $UO_2X_2(HX)_2$ with CYANEX 301 and $UO_2(NO_3)_2S_2$ with CYANEX 921, following HSAB rules.[86]

The proposed synergistic complex is depicted in Eqs. (24–26).

$$(\mathrm{UO2(NO3)})^{+}_{\mathrm{ap}} + 3(\mathrm{HX})_2 + 2(\mathrm{Y}) \rightleftharpoons (\mathrm{UO_2(NO_3).X.HX.2(HX)_2.2Y})_{\mathrm{org}} + \mathrm{H}^{+}_{\mathrm{aq}} \tag{24}$$

With CYANEX 301 in H_2SO_4 as in reaction 18.

$$UO_2^{2+} + 2\mathrm{X}^- + 2\mathrm{HX} \rightleftharpoons \left(\mathrm{UO_2X_2(HX)_2}\right)\mathrm{org} \tag{25}$$

where $\mathbf{X}^-$ represents the extractant anion.

With CYANEX 921 in HNO_3 as in reaction 19.

$$UO_2^{2+} + 2\left(\mathrm{NO_3}^-\right) + 2\mathrm{S} \rightleftharpoons (\mathrm{UO_2(NO_3)S_2})\mathrm{org} \tag{26}$$

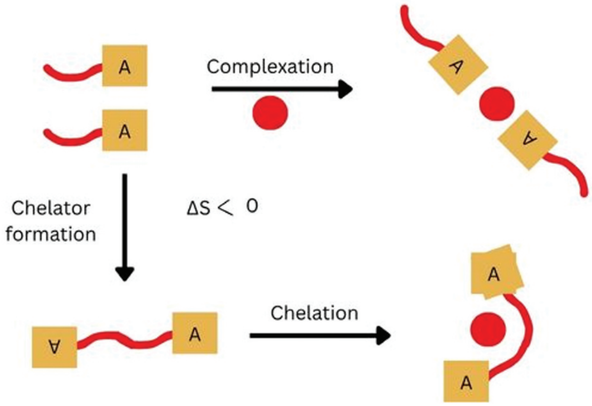


Figure 10. Entropy behind the synergy: a concept figure. (a) Difference between complexation by "loose" ligands and chelation.[83]

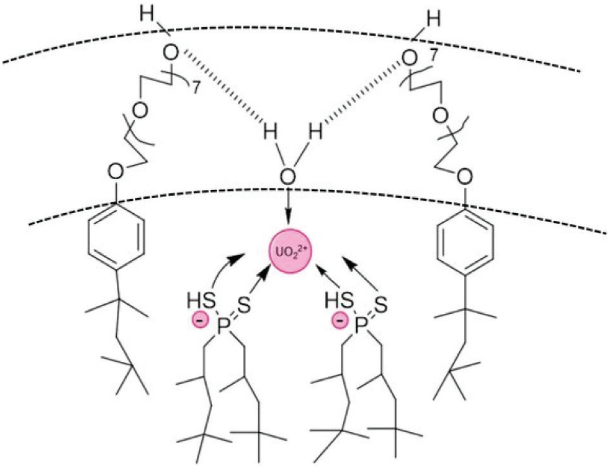


Figure 11. Schematic representation of the combination of UO_2^{2+} with Cyanex 301 in the TX-114 micelles.[102]

S is a neutral oxygen from Cyanex 921.

Another examined mixed extractant systems, especially those that pair acidic organophosphorus compounds with neutral or basic extractants, to boost extraction efficiency and selectivity. For uranium(VI), mixtures like Alamine 336 and Cyanex 272 demonstrate significant synergistic effects, facilitating better separation from iron(III) in sulfate/chloride environments. Although radium separation is less commonly explored, it also benefits from similar synergistic principles, where the coordination environment and the aggregation of extractants play a crucial role in efficiency[84].[87].[88]

Summary: Synergistic blends can be advantageous to many systems, enhance efficiency, pH range, extraction even with a lower concentration of chelating agent, stabilization of extracted species, and kinetic effects. but the mechanism is not well understood, and there is little predictive modeling. Extractive Spectrophotometry to increase the instrument's sensitivity, and the mutual separation of metal ions that can be used for pre-concentration of trace metal ions before instrumental analysis.[89]

Green alternatives for SX

The need for "green" process solvents in extraction has led to some encouraging developments. These aim to reduce ecological footprints without compromising separation effectiveness. Bio-based solvents from renewable resources offer less harmful and easily biodegradable substitutes for conventional organic solvents.[28]

There are some possible ways to make a SX system sustainable.

Ionic liquids: Such as 1-butyl-3-methylimidazolium hexafluorophosphate ($[BMIM][PF_6]$)[13,90] and functional derivatives such as betainium bis-(trifluoromethylsulfonyl)imide have intriguing features,[90] such as low volatility and thermal stability, which can be translated in terms of lowered emissions and better recyclability. Şenol Sert et al. used Cyphos® IL 101 (trihexyl(tetradecyl)phosphonium chloride) to separate Th(IV) from Ce(III) and La(III) in a nitrate solution. The anion-exchange extraction involves the co-extraction of nitrate anions, resulting in impressive separation factors of $\beta^{Th(IV)}_{Ce(III)} = 5769.32$ and $\beta^{Th(IV)}_{La(III)} = 1171.55$.[91] Possible complete reaction mechanisms are in Eqs. (27–29).

$$\mathrm{Th}^{4+}+3\mathrm{H_2O} \rightleftharpoons \mathrm{Th(OH)^+}_3+3\mathrm{H}^+ \tag{27}$$

$$[\mathrm{R_4P^+}][\mathrm{Cl^-}]+\mathrm{NO_3}^- \rightleftharpoons [\mathrm{R_4P^+}][\mathrm{NO_3}^-]+\mathrm{Cl}^- \tag{28}$$

$$\mathrm{Th(OH)^+}_3+\mathrm{Cl}^-+\mathrm{x}[\mathrm{R_4P^+}][\mathrm{NO_3}^-] \rightleftharpoons [\mathrm{R_4P^+}]_{(\mathrm{x}-1)}\left(\left[\mathrm{Th(OH)_3}\right][\mathrm{NO_3}]_\mathrm{x}\right)^{(1-\mathrm{x})} + [\mathrm{R_4P^+}][\mathrm{Cl^-}] \tag{29}$$

Deep eutectic solvents: In blends of solvents of choline chloride and oxalic acid, offer tuneable solvents through simple mixing, normally with lowered toxicity.[92]

Supercritical fluids: Based upon solvents such as carbon dioxide in critical conditions, offer minimal residual solvents and better selectivities in extractions.[93]

Water-based separation systems and membrane-based separations: Reduce organic solvent use and, consequently, waste production. With optimized process parameters and using renewable materials, such green alternatives have extensive potential for cleaner and greener separation technologies.[28]

Innovative extraction strategies beyond conventional solvent systems

In addition to classical SX methods, some new emerging techniques are potent methods for the purification and separation of radionuclides and rare earth elements. This subsection covers three of such methods and discusses their principles, advantages, and selective extracting abilities.

Solid phase extraction

Solid phase extraction is a separation technique where analytes are adsorbed onto a solid material and then eluted using a suitable solvent. SPE has been particularly useful in preconcentration and selective separation of trace radionuclides from complex matrices.[94]

SBA-15: Iryna Protsak et al. (2024) introduced a ligand-functionalized mesoporous silica (SiO₂/PMDA) designed for the selective extraction of Sc^{3+}, Th^{4+}, and UO_2^{2+} from multi-element aqueous solutions. The SBA-15 silica was functionalized with pyromellitic dianhydride (PMDA), introducing carbonyl (C = O) and carboxyl (–COOH) groups, which significantly enhanced metal ion adsorption. The modified silica structure was confirmed using XRD, TEM, NMR, and IR techniques. Results showed that the material exhibited high selectivity for Sc^{3+} at pH 4 via -COO^- chelation, preferential adsorption of Th^{4+} at pH 2 through C = O coordination, and enhanced uptake of UO_2^{2+} at pH 4 due to hydroxyl complexation. Langmuir isotherm and pseudo-second-order kinetics modeling showed monolayer chemisorption.[95]

TVEX: In recent years, solid polymeric extractants – TVEX – have emerged as a promising class of materials for the extraction and separation of actinides and REEs.[96] Unlike conventional solvent extraction systems that rely on immiscible organic and aqueous phases, TVEX systems immobilize extractant molecules within a polymeric matrix, allowing selective sorption of metal ions through ion-exchange or coordination processes while minimizing solvent losses and secondary waste generation.[96]

Korovin et al. demonstrated that TVEX materials synthesized by copolymerizing styrene and divinylbenzene with phosphoric acid and phosphine oxide extractants exhibit high distribution coefficients ($D > 10^3$) for U(VI) and Th(IV) in nitric acid media (pH 1–2). Importantly, the sorption efficiency remained above 90% after multiple adsorption – desorption cycles, indicating superior chemical stability compared to conventional liquid – liquid systems.[96] Similarly, Elatontsev et al. developed a TVEX-based sorption process for recovering uranium and light rare earth elements from leach solutions, reporting extraction efficiencies exceeding 90% for U(VI) and confirming the feasibility of large-scale hydrometallurgical application.[97]

Korovin et al. and Elatontsev et al. demonstrated that solid polymeric extractants (TVEX) functionalized with organophosphorus ligands preferentially bind U(VI) and Th(IV) over trivalent REEs because of stronger complexation and electrostatic interactions in acidic media.[96,97] Conversely, Madbouly et al. achieved selective REE recovery (Tb^{3+}, Gd^{3+}) using D2EHPA-impregnated TVEX systems under controlled nitrate conditions, emphasizing that extraction efficiency can be tuned by ligand type and matrix polarity.[98] Studies on rare-earth and radionuclide separations further support the versatility of TVEX materials.[97] Others indicate that while REEs and actinides share coordination characteristics, their separation can be effectively optimized in TVEX systems by adjusting extractant functionality and acidity to exploit charge-dependent selectivity.[99,100]

Cloud point extraction (CPE)

Cloud point extraction exploits the temperature-induced phase separation of non-ionic surfactants to partition analytes into a surfactant-rich phase. This method is eco-friendly and effective for low-level analyte separation.[101]

Liang et al. (2019) in their article mentioned reported CPE methods and their studies. In their application of TX-114 (nonionic surfactant) and Cyanex 301 (a sulfur-based extractant) used for the selective separation of UO_2^{2+} from Th^{4+} and lanthanides. Cyanex 301 exhibits a strong affinity for soft metal ions like uranium, facilitating the formation of the neutral complex shown in Eq. (30) and graphical representation shown in Figure 11.

$$UO_2^{2+} + +2(Cyanex301)^- \rightleftharpoons [UO_2(Cyanex301)_2] \tag{30}$$

Due to complex partitions into the micellar phase, the highest extraction percentage was seen at pH 3, where Cyanex 301 is deprotonated, while the addition of 0.1 M NaCl stabilized micelles and lowered the cloud point, and thermodynamic and spectroscopic analyses confirmed strong coordination with favorable enthalpic and entropic contributions, resulting in highly selective uranium extraction (~90%) with minimal interference from lanthanides and thorium.[102]

Conclusion

SX processes for selective uranium, thorium, and radium separation from rare earth elements (REEs) have been critically evaluated. Use of extractants based on phosphorus, i.e., from the REE containing solutions TBP and Cyanex series, indicated good selectivity in the separation of U(VI) and Th(IV), especially in synergistic mixtures. Use of extractants based on nitrogen, i.e., amine and Schiff bases, indicated tuneable selectivity through ion-pair as well as chelation modes. Sulfur extractants, although being underdeveloped, indicated good performance, especially in uranium separation.

The innovation of greener options, such as bio-based extractants, solid-phase systems, membrane technologies, and ionic liquids, is reflective of the industry's transition to more responsible, lower-impact processes. Areas where outstanding challenges remain include extractant stability, third-phase formation, and process scalability.

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Author contributions

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