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Recovery of minor actinides from high-level wastes: modern trends

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One of the major problems of nuclear power industry is associated with large amounts of radioactive wastes. Contemporary reprocessing technologies of spent nuclear fuel generate significant volumes of liquid high-level wastes, containing a great number of various nuclides. At present, fractionation is agreed to be the most promising and environmentally safe strategy of treating such wastes; however, this raises the problem of partitioning of minor actinides and lanthanides. Counter-current extraction in two-phase aqueous solution – organic phase systems is considered as the most efficient approach. Analysis of the extractant systems proposed to date, including systems with non-selective extractants (phosphine oxides, phosphoric acids, diamides of dicarboxylic acids, *etc*.) for joint recovery of lanthaniedes and actinides and systems with selective extractants (sulfur-containing compounds, N-heterocyclic compounds, diamides of N-heterocyclic dicarboxylic acids, *etc*.) for partitioning of actinides and lanthanides is presented. Modification methods for the known extractant systems, particularly the role of diluents, is discussed. The application of water-soluble complexing agents selective to actinides, including the possibility of combining extractants with complexants with opposite affinities, is considered.
The bibliography includes 232 references.

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I. Introduction

A major social concern over negative environmental impact brought about by steadily increasing amounts of carbon dioxide emission into the atmosphere makes the development of novel, environmentally safe, reliable and economicly efficient energy production methods a primary strategic task, solution to which eventually determines the pace of development of our civilization. Solutions to this task are extensively discussed at various levels. Despite the well-known technological risks [disasters in the Three Mile Island NPP (1979), in Chernobyl (1986) and in Fukushima (2011, Fukushima Daiichi)], nuclear power industry holds its position as an important constituent of energy production. The main limitations to its use now are problems associated with creation of large amounts of radioactive waste (RW). Therefore, the development of novel environmetally friendly processes for its reprocessing, disposal and long-term storage has become one of the key challenges of the contemporary nuclear power industry.

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The basic reprocessing technology of spent nuclear fuel (SNF) is now the PUREX process (Plutonium Uranium Recovery by Extraction) in which the SNF is diluted in nitric acid after a storage peroid needed for short-lived radionuclides to decay. Uranium and plutonium are extracted from the aqueous solutions in nitric acid with tributyl phosphate (TBP) in a hydrocarbon-based diluent and then back-extracted into an aqueous solution. This gives considerable amounts of PUREX raffinate — liquid high-level wastes (HLW) that contains large quantities of fission product nuclides with atomic masses from 75 (As) to 160 (Tb), including such radionuclides as ^{79}Se, ^{90}Sr, ^{93}Zr, ^{99}Tc, ^{126}Sn, ^{129}I, ^{137}Cs, ^{144}Ce and ^{147}Nd. Among them, the major γ-activity and heat generation (>95%) of HLW after a few years of storage are determined by caesium-137 and strontium-90. Yet after more than a 100-year storage the largest threat is constituted by the transuranium elements (TUE) formed in nuclear reactions, namely, neptunium, americium and curium (minor actinides), since they pocess long half-lives (for example, ^{243}Am, 7370 years).

There are two strategies of treating the PUREX raffinate. The first one, which is applied at present, involves conversion of the total metal salts present in the raffinate to oxides and joint vitrification of the oxides. A benefit of this method is the low amount of resulting secondary RW. However, glasses cannot serve as an optimal host for joint localization of all radionuclides. The search for new matrix materials for the final disposal of HLW is in progress.[1]

An alternative strategy[2–5] is based on fractionation of HLW in which the most long-term radioactive and radiotoxic nuclides (caesium and strontium radioisotopes, TUE) are recovered and separated into individual fractions according to their half-lives and chemical behaviour. Then particularly durable matrices are designed for each fraction enabling their safe disposal in specifically selected deep geological formations. Obviously, the creation of a matrix with equally efficient immobilization ability for all nuclides present in HLW is a dramatically bigger challenge than the design of a highly stable matrix for one nuclide or a group of nuclides with similar chemical nature. It is generally recognized today that the fractionation strategy meets the requirements of environmental safety to the fullest extent possible. The strategy makes it possible to sharply drop the economic expenses on the long-term supervised storage of HLW containing long-lived radionuclides. Contemporary reactors can use not only uranium fuel, but also mixed oxide fuels, containing uranium and plutonium, as well as uranium, plutonium and americium. In this light, americium, if separated, could be used to prepare such fuels. All minor actinides can also be subjected to transmutation in fast neutron reactors. As a result, they are transformed into stable nuclides, thus completely solving the problem of their treatment. Therefore, minor actinide partitioning and further transmutation in fast neutron reactors is to date considered the crucial stage in the engineering of advanced closed nuclear fuel cycle (NFC).

However, the presence of lanthanides, which possess excessively high capture cross-sections of thermal neutrons, hinders the transmutation of minor actinides. Lanthanide content in the PUREX raffinate exceeds that of minor actinides by a factor of 20–50, depending on the fuel burnup level. Hence, the partitioning of minor actinides from HLW and their separation appear to date the key problem, a solution to which is being looked for by numerous large research teams worldwide.

The fractionation strategy has yet another important advantage. It allows the recovery and use of not only fissile products, but also a wide range of stable fission products. Of particular value are platinum group metals. As follows from the calculations, a SNF reprocessing plant with production capacity of 1000 tonnes per year can yield around 4.5 tonnes of Ru, 3.5 tonnes of Pd, 775 kg of Rh, 175 kg of Ag, as well as ~6.0 tonnes of Mo. The total cost of the mentioned amounts of these metals is estimated as ~70 million dollars. After a long-term storage of SNF, most noble metals (Ru, Rh, Ag) are not radioactive. Fissile palladium contains the ^{107}Pd radioisotope with a half-life of millions of years; therefore, it has a low activity, which enables the use of this isotope within the nuclear industry under controlled conditions (for example, for immobilization of ^{129}I and/or TUE). SNF also contains 0.7% of stable xenon. According to estimates, recovery and utilization of stable components from SNF would make up for ~20% of the reprocessing cost. More than 20 radionuclides occurring in HLW (^{137}Cs, ^{90}Sr, ^{99}Tc, ^{85}Kr, ^{3}H, *etc.*), are in demand on the isotope production market. The economic feasibility of partitioning of these products is under discussion.

There are various HLW reprocessing methods (precipitation, sorption, chromatographic methods, *etc.*), yet of particular importance are extraction processes. A substantial experience of their industrial implementation has already been accumulated. Numerous brilliant reviews present comparative analysis of various HLW reprocessing extraction methods,[6–10] covering the literature up to 2010. However, this field of radiochemistry is rapidly developing, and in the last 4–5 years, a great number of papers, not included in the mentioned reviews, have been published. The present review attempts to highlight the most exciting new trends, which have recently appeared in the field of extractive reprocessing of HLW. Having no intention of covering the whole matter, we rather focused our attention on the most attractive and challenging task, that is, separation of minor actinides and lanthanides.

Counter-current extraction in two-phase aqueous solution–organic phase systems, where organic neutral or anionic donor ligands capable of forming stable complexes with lanthanides (Ln) and actinides (An) soluble in the organic phase are used as extractants, is currently considered to be the main separation method of minor actinides and lanthanides. This ensures most easily the process continuity and high mass transfer rates. The Ln^{3+} and An^{3+} cations can form a wide variety of complexes of different stoichiometry with donor ligands, where coordination numbers (C.N.) range from 6 to 12. On moving along the lanthanide and actinide rows from La to Lu and from Th to Lr, the inner 4f and 5f levels, respectively, are gradually occupied by electrons. Both levels are highly shielded by the occupied outer shells ($5s^25p^6$ for lanthanides and $6s^26p^6$ for actinides). The unchanged structure of the outer electron shells of these ions results in highly similar chemical properties of their compounds; hence, separation of lanthanides from actinides and separation of lanthanides from one another are exceptionally difficult tasks. The search for and design of new types of donor ligands that would be selective towards the extractive partitioning of minor actinides and lanthanides form a major line of research in this field.

Solving the considered task is actually markedly complicated by the fact that the mentioned ligands should possess a number of properties that are often poorly compatible with one another. The most important properties are the following:

— the capability of selective binding to Ln^{3+} and An^{3+} cations in the presence of transition metal ions, the concentrations of which in highly active PUREX raffinates can exceed the concentrations of the desired cations by an order of magnitude or more;

— high distribution constants (D) of the desired cations Ln^{3+} and An^{3+} between the organic and aqueous phases, which determine the extraction efficacy;

— high selectivity for the Ln^{3+}/An^{3+} pair in a wide pH range (it is commonly evaluated by the separation factor $SF_{Am/Eu}$ for the Am^{3+}/Eu^{3+} pair, usually determined as the distribution ratio $D_{Am}:D_{Eu}$; of practical interest are extractants that can provide $SF_{Am/Eu} \geqslant 5$).

— donor ligands capable of forming strong complexes with metal cations should possess high Lewis basicity, while their Brønsted basicity (protonation capacity) should remain low; otherwise protonation, being a competitive process, is likely to supress the complexation during extraction from highly acidic media;

— high rates of extraction and establishing the extraction equilibria in a wide pH range;

— high hydrolytic stability of complexes and extractant ligands in a broad pH range;

— high radiation stability of complexes and extractant ligands; together with the previous requirement, this allows for repeated recycling of the extractant during the process;

— the absence of toxicity;

— ligands containing only C, O, H and N atoms are favoured, since incineration of the isolated complexes results in pure oxides; the presence of phosphorous and sulfur atoms leads to the formation of pyrolitically non-degradable sulfates and phosphates, thus complicating the vitrification process;

— possibility of extractant synthesis and accumulation in large quantities from easily accessible precursors (economic factor).

A wide-scale research on the creation of highly efficient and selective extractants for actinide and lanthanide recovery from HLW and separation has been in progress for more than 70 years. As for today, compounds of the following classes are regarded as most promising:

— neutral organophosphorus compounds: phosphine oxides,[11,12] carbamoylphosphine oxides,[13] as well as substituted calixarenes[14] with phosphorus-containing groups on the lower rim;

— organophosphorus acids,[15,16] zirconium salts of dialkyl phosphoric acids;[17]

— macrocyclic compounds (crown ethers,[18,19] calix-crown ethers[20]);

— malonamides,[21] diglycolamides[10,22] and amides of heterocyclic dicarboxylic acids;[23]

— heterocyclic polydentate N-donor compounds;[24–26]

— synergistic solvent mixtures.[27–30]

Alongside the extractant itself, the extractant system includes a diluent (solvent), which is subject to the same high requirements on stability and accessibility. The whole system must be fire-proof and explosion-proof; it should ensure a substantially high partitioning capacity of the separated component. The diluent nature plays an important role; hence, replacement of the diluent, as well as altering the extraction conditions (pH of the solution, presence and concentration of extraneous salts, temperature, extractant concentration, promoting additives) can dramatically affect the result. In view of this, the development of an extractant system is always a multi-stage iterational process.

Large-scale investigation programmes in this field are ongoing in the United States, Europe, Japan, South Korea and India. Despite a great amount of research that has already been conducted, no perfect extractant system that meets all the set requirements still exists.

Extractant systems for the recovery of minor actinides from HLW can be divided into two types. The first type systems are those based on non-selective extractants, which usually belong to the first two of the above-mentioned compound classes. They extract actinides together with lanthanides into the organic phase. The process flow diagrams for the use of such extractants often involve separation of actinides and lanthanides during the back-extraction stage. Polyaminocarboxylic chelating agents [ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), *etc.*] are generally used for the back-extraction.

Second type systems are based on extractants that selectively recover only actinides into the organic phase, in contrast to lanthanides and other fission products. Studies of such extractant type started not long ago; nevertheless, a huge amount of experimental data has already been accumulated. Both types of systems are systematically discussed below.

II. Extractant systems based on non-selective extractants for joint recovery of lanthanides and actinides

As these extractants, organophosphorus ligands, malonamides and diglycolamides are utilized. These compounds coordinate metal cations with donor oxygen atoms of phosphoryl or amide groups. According to the Pearson classification, lanthanides and actinides are hard Lewis acids, which are bound most efficiently by these O-donor ligands, which are hard Lewis bases. Industrial processes for actinide–lanthanide fraction recovery based on these ligands have already been developed.

II.1. Organophosphorus extractants

II.1.a. Neutral organophosphorus extractants

These extractants are represented by monodentate trialkylphosphine oxides, bidentate carbamoylphosphine oxides, which bind a metal cation *via* one phosphoryl and one amide oxygen atoms, and polydentate phosphorylated calixarens. Full esters of orthophosphoric acid (alkyl phosphates) and aryl- or alkylphosphonic acids (alkyl phosphonates) have too low extraction capacity for americium and curium; therefore, they are unsuitable. In contrast, diphosphine dioxides possess very high extraction capacity for americium and curium, yet most of them have very poor solubility in almost all possible diluents.

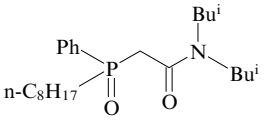
Phosphine oxides. Efficient neutral organophosphorus extractants are trialkylphosphine oxides (TRPO), which are usually mixtures of phosphine oxides containing C_6-C_8 n-alkyl groups at the phosphorus atom. Cyanex-923, a commonly used phosphine oxide, is a mixture of four

compounds $R^1_2R^2P{=}O$ ($R^1 = R^2 = n\text{-}C_6H_{13}$, $n\text{-}C_7H_{15}$; $R^1 = n\text{-}C_6H_{13}$, $R^2 = n\text{-}C_7H_{15}$; $R^1 = n\text{-}C_7H_{15}$, $R^2 = n\text{-}C_6H_{13}$).[31,32] A benefit of such extractants is their comparatively high extraction capacity for actinides (III, IV, VI), lanthanides and technetium.[33] Trialkylphosphine oxides are obtained as side products of the manufacture of phosphorus fertilizers and, hence, they are commercially available. Lanthanides and actinides are extracted from nitric acid soultions as $[M(TRPO)_n(NO_3)_3]$ (n = 3, 4) complexes. TRPO-based systems with hydrocarbon diluents can be exploited only at comparatively low concentrations of nitric acid (0.3–0.6 mol litre^{-1}),[34] while the regular content of HNO_3 in HLW is 3–4 mol litre^{-1}. The need to lower the acidity is a serious drawback of such systems.

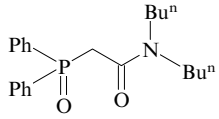
For the recovery of actinides using the TRPO–n-dodecane system, a TRPO process was developed[35–38] and tested on model solutions.[39,40] The addition of TBP into the reaction mixture contributes to an increase of uranium extraction capacity of the system.[41] The extractant system of 30% TRPO–n-dodecane is fairly resistant to γ-radiation.[42,43]

Carbamoylphosphine oxides. Out of these bidentate ligands for actinide and lanthanide binding, octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (**1**, CMPO)[44–46] and diphenyl-[*N,N*-dibutylcarbamoylmethyl]-phosphine oxide (**2**, Ph_2Bu_2-CMPO)[47,48] have been studied in greatest detail.

Structures 1, 2



1 (CMPO)



2

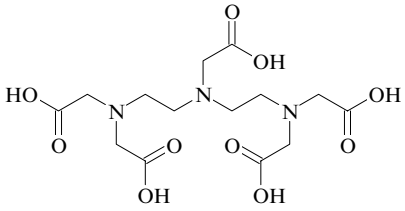
The CMPO–TBP–hydrocarbon diluent system tends to form trisolvates; utilization of polar diluents reduces the solvation number to 2.2–2.3.

The use of these compounds underlies the TRUEX (TRansUranic EXtraction) process, which provides partitioning of actinides and lanthanides from moderately acidic solutions. In the versions of the process developed in the US, Japan and Italy, actinide extraction is performed with solutions containing 0.20–0.25 mol itre^{-1} CMPO and 1.0–1.4 mol litre^{-1} TBP in a hydrocarbon diluent (dodecane or xylene);[49,50] TBP is used as a modifier preventing formation of a third phase and suppressing hydrolysis and radiolysis of CMPO. Efficient actinide partitioning (>99.95%) is achieved from HLW with HNO_3 content of >1.5 mol litre^{-1}.

In the version of TRUEX process developed in Russia, extraction is performed into a 0.06–0.12 M solution of phosphine oxide **2** in a heavy nitroaromatic diluent — *m*-nitrobenzotriflouride (*m*-trifluoromethylnitrobenzene, fluoropol-732, F-3).[51,52] Utilization of this solvent makes it possible not only to use a cheaper extractant (Ph_2Bu_2-CMPO), but also to avoid the addition of a solubilizer (TBP) into the extraction mixture. This extraction system is suitable for actinide and zirconium extraction from HLW containing from 2 to 6 mol litre^{-1} nitric acid.

Evolution of the TRUEX process brought about the SETFICS process, capable of separating actinides(III) from most lanthanides. Actinides and lanthanides are co-extracted into the system used in the TRUEX process (CMPO–TBP–n-dodecane)[53,54] and then separated by back-extraction with a solution of DTPA (**3**) and $NaNO_3$. A version of the process in which F-3 serves as the diluent, while back-extraction is performed with DTPA and ammonium nitrate has been tested.[55,56] In this procedure, actinides are separated from light lanthanides; however, samarium, europium and gadolinium remain in the actinide fraction.

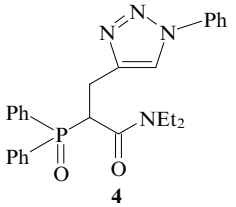
Structure 3



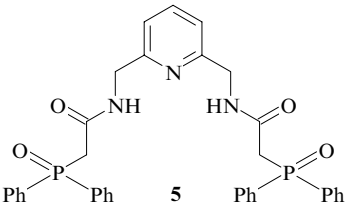
3 (DTPA)

Over the last 5 years, ligands that contain a carbamoylmethylphosphine oxide moiety bound to a more complex structure (core) have been studied most vigorously. The main goal of these studies was to improve the extraction characteristics, as well as to increase the selectivity of separation of actinides and lanthanides. Synthetic works in this area up to 2013 inclusively have been thoroughly reviewed by Russian chemists actively working in this field.[57] In particular, cobalt dicarbollide anions covalently bound to a carbamoylphosphine oxide moiety,[58] carbamoylphosphine oxides containing an additional phosphoryl group[59] or a 1,2,3-triazole moiety (structure **4**)[60] were synthesized and studied. A number of papers have been devoted to pyridines and pyridine oxides with similar moieties (*e.g.*, structures **5** and **6**)[61–63] and calixarenes having a carbamoylphosphine oxide moiety on the lower rim.[64–68] In almost all cases, the addition of several carbamoylphosphine oxide groups to a spatially pre-organized structural core makes it possible to obtain a ligand with enhanced extraction capacity compared with the initial CMPO. However, the selectivity of actinide extraction remains virtually the same, the Am/Eu separation factors being less than 3.

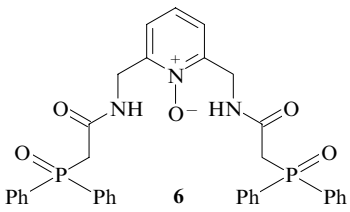
Structures 4–6



4



5



6

The composition of the diluent substantially influences the extraction process. Addition of isodecanol to dodecane results in lowering of metal distribution ratios; however, the solubility of the solvates in the organic phase increases.[69]

Over the last five years, a number of works have been reported where ionic liquids were used as diluents in extraction with carbamoylphosphine oxides.[70–75] It has been also suggested to replace hydrocarbon diluents with a fluorinated alcohol formal.[76] Extraction mixture with such compositon is non-flammable, low-toxic and extracts less nitirc acid, which makes the process flow diagram of fractionation more compact.

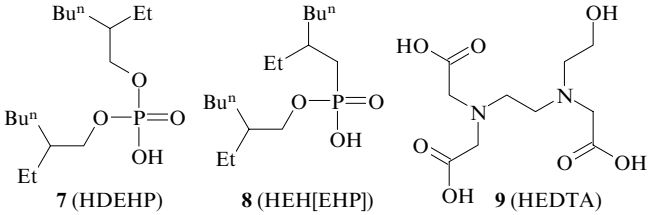
Experiments on radiolysis of a CMPO solution in dodecane proved[77–80] that nitric acid slightly enhances the CMPO stability to γ-radiolysis. Depending on the exposure conditions, different degradation products are formed, this being attributed to different mechanisms of bond rupture in the extractant molecule. The contribution of α-radiolysis to the total extractant degradation is much lower than that of γ-radiolysis. The major radiolysis products are amides and amines, which do not have a considerable impact on the extraction and back-extraction of americium. Similar results have been reported elsewhere.[81]

In summary, neutral organophosphorus mono- and polydentate ligands have a number of advantages when used as extractants. They are chemically stable. Additionally, ligands containing carbamoylphosphine oxide groups are suitable for extraction from highly acidic solutions. The main limitation of such extractants is the presence of phosphorus atoms, as mentioned above.

II.1.b. Organophosphoric acids

Acidic esters of phosphoric acid are among the first extractants to be used for actinide and lanthanide partitioning and separation. In the 1960s, the TALSPEAK process (Trivalent Actinide–Lanthanide Separation by Phosphorus reagent Extraction from Aqueous Complexes)[82] was developed, in which di(2-ethylhexyl) phosphoric acid (**7**, HDEHP) is used to extract lanthanides from a mildly acidic solution (pH ~ 3) with lactic acid as a buffer and DTPA as a complexing component into diisopropylbenzene (isomer mixture). Compositions of the forming complexes were thoroughly considered previously.[15] DTPA inhibits the extraction of minor actinides to a greater extent compared to lanthanides, the latter being predominantly transferred to the organic phase. Upon extraction of lanthanides and actinides with a HDEHP solution (0.3 mol litre^{-1}) in diisopropylbenzene from a solution containing lactic acid (1 mol litre^{-1}) and DTPA (0.05 mol litre^{-1}) at pH 3, separation factors of ~100 were achieved for Am, Cm/Ln. The lowest separation factor was obtained for the neodymium–californium pair ($SF_{Nd/Cf}$ = 10).

Structures 7–9



7 (HDEHP) **8** (HEH[EHP]) **9** (HEDTA)

In the version of TALSPEAK known as the reverse TALSPEAK process, actinides and lanthanides are simutaneously extracted from a HNO_3 solution (0.1 mol litre^{-1}) with a HDEHP solution (1 mol litre^{-1}). Then americium and curium are selectively extracted back with a solution containing 0.05 mol litre^{-1} DTPA (**3**) and 1.5 mol litre^{-1} lactic acid.[83] Process modifications have also been made recently. In particular, amino acids were used as buffering agents instead of lactic acid.[84] Successful separation of americium from lanthanides at pH 2 was demonstrated. A TALSQuEAK version of the process has been suggested.[85] It employs 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (**8**, HEH[EHP]) in dodecane as the extractant and *N*-(2-hydroxyethyl)ethylenediaminetriacetic acid (**9**, HEDTA) as a selective back-extractant in the presence of lactic or citric acid. The applicability of buffering agents based on malonic acid has also been investigated.[86] The key distinctive features of the TALSQuEAK process are better metal extraction kinetics into the organic phase and lesser dependence of Am/Ln separation factor on pH of the medium.[87] Nevertheless, during dynamic experiments in centrifugal contactors,[88] it was noted that Sm, Eu and Gd extraction was not complete. Equilibration time for the extraction of mentioned lanthanides is ~5 min, while the phase contact time in a centrifugal contactor is < 30 s. Hence, the separation factors necessary for efficient partitioning of the metals cannot be achieved. Several reviews devoted to TALSPEAK process chemistry have been published (for example, see Ref. 15); note an excellent recent review.[16]

Hydrogen alkyl phosphates and alkylphosphonates are the first extractants that facilitated efficient separaiton of americium and lanthanides. Their common drawback is inhibition of the extraction upon increase in the solution acidity.

II.2. Extractant systems based on diamides of dicarboxylic acids

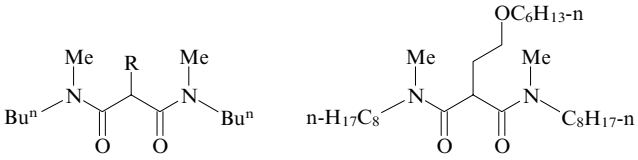
II.2.a. Malonamides

Malonamides, which were proposed for minor actinide partitioning from PUREX raffinates by French scientists in 1980, are bidentate chelating ligands (L); they coordinate lanthanide and actinide ions by oxygen atoms of the amide groups and form complexes $[ML_3(NO_3)_3]$.[89] They have a series of advantages over organophosphorus extractants: first, they make it possible to perform extraction from highly acidic solutions; second, they are free of phosphorus atoms, hence phosphorus oxide is not formed during combustion, which significantly simplifes the disposal of spent solvents. In addition, these ligands are resistant to hydrolysis in highly acidic media and comparatively cheap. For extraction of actinides and lanthanides from 3–4 M HNO_3 solutions, *N*,*N*′-dimethyl-*N*,*N*′-di-n-butyl(tetradecyl)malonamide (**10**, DMDBTDMA) exhibits the best characteristics (solubility in the hydrocarbon diluent, actinide extraction capacity).[89]

The use of malonamides underlies the DIAMEX-process.[90] Its flow diagrm comprises the extraction of actinides and lanthanides from 3–5 M nitric acid solutions into solutions of DMDBTDMA (**10**) or other alkylmalonamides in dodecane. Later, *N*,*N*′-dimethyl-*N*,*N*′-dioctyl(2-hexyloxyethyl)malonamide (**11**, DMDOHEMA) was proposed as an alternative to DMDBTDMA, as the former has a greater solvation capacity and high affinity for trivalent actinides.[91]

At present, research into the properties of both DMDBTDMA[92–94] and DMDOHEMA,[95–97] as well as other malonamides is ongoing. Actinide extraction with *N*,*N*′-dimethyl-*N*,*N*′-dicyclohexyl-malonamide

Structures 10, 11



10 (DMDBTDMA) **11** (DMDOHEMA)

R = n-$C_{14}H_{29}$

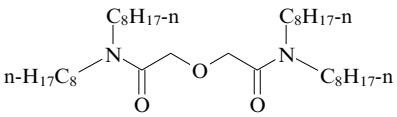
(DMDCMA) in a polar fluorinated diluent, phenyl trifluoromethyl sulfone (FS-13) has been reported.[98] High extraction capacity of the new compound was demonstrated. The benefits of DMDCMA are simplicity of synthesis and purification. The possibility of utilizing ionic liquids as diluents for malonamides is also investigated: the extraction of actinides and fission products has been studied[99] and uranium and plutonium separation from americium has been demonstrated.

II.2.b. Diglycolamides

Diglycolamides (DGA), being tridentate ligands, bind to lanthanide and actinide ions through coordination with two amide oxygen atoms and the ether oxygen atom, coordination bond with the latter being substantially weaker than the other two bonds. Diglycolamides form complexes $[ML_3(NO_3)_3]$ and belong to one of the most promising extractant classes for partitioning of minor actinides from HLW. These amides were originally proposed by Stephan *et al.*[100, 101] for strontium extraction. It was found later that they can partition actinides from nitric acid solutions more efficiently than malonamides.[102, 103]

It is generally agreed that *N*,*N*,*N*′,*N*′-tetraoctyldiglycolamide (**12**, TODGA) possesses the superior extraction properties of all tetraalkyldiglycolamides. This compound has been studied rather comprehensively: its extraction capacity toward actinides, lanthanides, strontium and other metals,[104] radiation stability,[105, 106] aggregation[107] and other properties were reported. A few extractant systems employing TODGA as the extractant for actinide partitioning from nitric acid solutions were developed and tested.[108, 109] High actinide(III) and actinide(IV) extraction capacity of TODGA was demonstrated. The risk of the third phase formation upon saturation of the organic phase with metal was highlighted for the TODGA–dodecane system.

Structure 12



12 (TODGA)

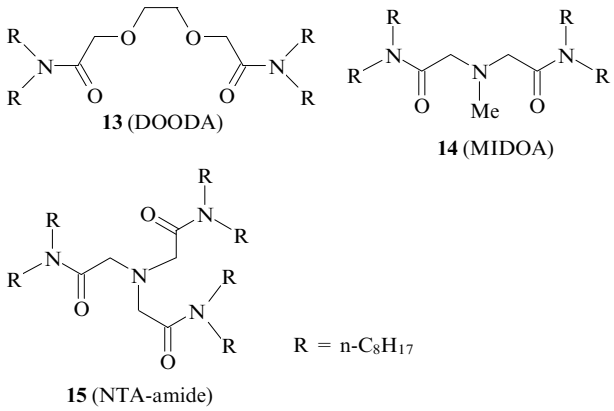
A thorough review devoted to TODGA and other diglycolamides has been published.[22] Research into both the known and new diglycolamides,[110, 111] their derivatives such as calixarenes[112–116] and tripodal ligands,[117, 118] as well as bis(diglycolamides)[119] is now in progress. Unsymmetrical diglycolamides incorporating octyl and other alkyl groups (2-ethylhexyl, heptyl, decyl, dodecyl) were synthesized and studied.[120–122] It was demonstrated that for some of the compounds, distribution constants of actinides and limiting concentrations in the organic phase can be higher than those for TODGA.

An investigation of the influence of addition of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) and nonanoic acid to the organic phase for lanthanide extraction with TODGA has been carried out.[123] These modifying agents were found to improve hydrodynamic characteristics of the system. TODGA analogues with enhanced extraction performance, such as compounds **13**–**15**, have been synthesized and tested in extraction experiments.[124–127]

A change in the extractant structure leads to significant changes in extraction selectivity within the lanthanide row [namely, while for TODGA, the exctraction capacity increases from lanthanum to lutetium, the lanthanide extraction capacity of *N*,*N*,*N*′,*N*′-tetraoctyl-3,6-dioxaoctane diamide **13** (DOODA) varies to a much lesser extent].

The insertion of an additional nitrogen atom into the extractant structure [methylimino-bis-*N*,*N*-dioctylacetamide **14** (MIDOA), (hexaoctyl-nitrilotriacetamide **15** (NTA-amide)] results in a dramatic increase in the extraction capacity of soft ions such as palladium and in enhancement of pertechnetate ion extraction.[128]

Structures 13–15



13 (DOODA) **14** (MIDOA)

15 (NTA-amide)

Diglycolamides are the most promicing compounds for HLW reprocessing. Their undoubted advantages, namely high actinide extraction capacity in acidic media, as well as outstanding chemical stability and radiation resistance aroused lively interest in these compounds and their analogues. The prime drawback of this class of compounds, associated with sparing solubility of metal solvates in hydrocarbon diluents, is generally overcome by utilizing either modifying agents (TBP, acid monoamides, *etc.*) or polar diluents.

II.3. Combinations of acidic and neutral organophosphorus extractants

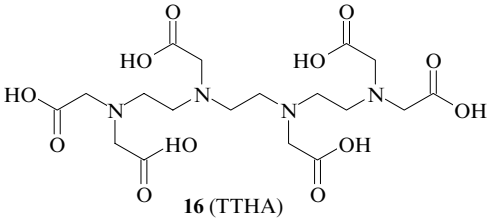
Recently, the use of combined acidic and neutral extractants has become one of the primary trends in the development of novel extractant systems. Such systems were considered in a review.[29] Over the six years since the publication of that review, a few other papers have been published.

Various modifications of the TALSPEAK process extractant (HDEHP in dodecane) have been studied;[129] CMPO, octanol, TBP and xylene were used as modifying agents. The addition of these compounds made it possible to sharply reduce the phase separation time. A new variant of the reverse TALSPEAK process based on HDEHP and TBP has been suggested and physicochemical properties of

a 0.3 mol litre^{-1} HDEHP + 0.2 mol litre^{-1} TBP mixture in dodecane were studied.[130] Americium back-extraction was performed with a solution containing 0.05 mol litre^{-1} DTPA and 0.1 mol litre^{-1} citric acid (pH 3).

The influence of nitric acid concentration on americium and lanthanide extraction capacity of a HEH[EHP] (**8**) and Cyanex-923 mixture in dodecane has been investigated.[131] The extraction capacity proved to drop upon increasing the nitric acid concentration. In order to provide high distribution constants of metal ions in the extraction from solutions with HNO_3 concentration of >1 mol litre^{-1}, high ligand concentrations are required such as 0.6 mol litre^{-1} HEH[EHP] + 0.6 mol litre^{-1} Cyanex-923 in dodecane. Actinide and lanthanide separation occurs upon the selective actinide back-extraction stage. Two alternative solutions for back-extraction have been proposed: 0.1 mol litre^{-1} glycine + 0.02 mol litre^{-1} HEDTA or 0.1 mol litre^{-1} glycine + 0.01 mol litre^{-1} TTHA (triethylenetetraamine-*N*,*N*,*N*′,*N*″,*N*‴,*N*⁗-hexaacetic acid, **16**). The back-extraction is carried out at pH 2–3. Both complexants ensure efficient separation of americium and lanthanides. When using TTHA, higher separation factors are achieved. For identical conditions and pH 2.5, the Am/Eu separation factors are ~20 for HEDTA and ~40 for TTHA.

Structure 16



16 (TTHA)

American scientists proposed a TRUESPEAK extractant system, in which a mixture of TALSPEAK- and TRUEX-process extractants [HDEHP (**7**) and CMPO (**1**) in dodecane] is utilized.[132] The presence of CMPO in the extractant system facilitates better recovery of actinides and lanthanides from acidic solutions, compared to the conventional TALSPEAK system; however, in this case, the distribution constants of metals decrease with increasing acid concentration[133] due to a complex nature of interactions between the two mixed extractants. The decrease in metal distribution constants when a ligand mixture is used compared with the TRUEX-process extractant can be explained by lowering of the free CMPO concentration upon the formation of an acidic adduct between CMPO and HDEHP in the organic phase. Under the conditions when HDEHP is in excess relative to CMPO, the acidic proton of HDEHP is hydrogen-bonded to the oxygen atom of CMPO phosphoryl group. The metal complex formation follows a combined mechanism: the metal ion substitutes for the HDEHP acidic proton *via* cation exchange mechanism and the resulting complex is additionally solvated by one or more CMPO molecules. The composition of the complex varies, depending on the ligand ratio and aqueous phase acidity.[134] Actinides are selectively separated from all of the lanthanides *via* back-extraction from dilute acidic solutions containing complexing agents; Ln^{III}/An^{III} separation factors are, nonetheless, lower than thiose in a conventional TALSPEAK process.

An extractant system based on HDEHP (**7**) and tetrabis(2-ethylhexyl)diglycolamide (T2EHDGA) in dodecane has been proposed by Indian scientists[135] for HLW resulting from high burnup fuel processing. The extractant mixture was chosen as follows: 0.1 mol litre^{-1} T2EHDGA + 0.25 mol litre^{-1} HDEHP in dodecane. A strong synergistic effect was observed in Am^{III} extraction. Regardless of aqueous phase acidity (from 0.1 to 3 mol litre^{-1} HNO_3), the distribution constants of >10 are achieved for americium. At such component ratio, the third phase is not formed. A solution containing 0.5 mol litre^{-1} citric acid and 0.05 mol litre^{-1} DTPA (**3**) was used for americium back-extraction at pH 3. A dynamic experiment on americium stripping from a model HLW solution produced from high burnup fuels[136] revealed good hydrodynamic performance of the system. Actinides and lanthanides were extracted together. Americium was quantitively back-extracted from the organic phase; however, ~20% of light actinides were back-extracted along with americium. The radiation resistance of the proposed extractant has been studied (up to 500 kGy absorbed dose).[137] After irradiation of the extractant mixture, the distribution constants of Am^{III} and Eu^{III} significantly decreased. The Am^{III}/Eu^{III} separation factor for the back-extraction stage was also reduced as a result of increased Eu back-extraction from the irradiated extractant. The extraction capacity of a system based on tetraoctyldiglycolamide (TODGA, **12**) and HDEHP (**7**) in dodecane has been investigated.[138] The extraction capacity of a TODGA–HDEHP mixture towards Am^{III} and Eu^{III} is roughly equal to that of TODGA at high acidity.

A process of actinide and lanthanide separation (Actinide Lanthanide SEparation Process, ALSEP) involving a diglycolamide (T2EHDGA or TODGA) and HEH[EHP] (or HDEHP) mixture in dodecane has been developed.[139] Depending on the diamide used, one can achieve full or partial stripping of lanthanides from the nitric acid solution. When T2EHDGA is utilized, some of the light lanthanides remain in the raffinate. Stripping of Am^{III} is carried out in the back-extraction stage with DTPA and ammoium citrate solution at pH 4. High separation factors are achieved ($D_{Ln}/D_{Am} > 30$).[140, 141]

The properties of an extractant system based on HEH[EHP] and CMPO in dodecane have been studied.[142] The HEH[EHP]–CMPO mixed system provides joint recovery of actinides and lanthanides from 0.1–5 M HNO_3 solutions; the separation is achieved *via* americium selective back-extraction with HEDTA (**9**) in citrate buffer solution. When the pH of the back-extraction solution is 2.5–3.7, the mentioned system makes it possible to selectively separate americium from the saturated organic phase with an Am/Eu separation factor of >14. The main advantages of the proposed system over TALSPEAK- and TRUESPEAK-process extractants are the improved kinetics of metal transfer into the organic phase and minor dependence of the An/Ln separation factor on the pH of the medium.

For convenience of comparison, all of the discussed systems based on acidic organophosphorus extractants are summarized in Table 1.

An attractive idea of combining the benefits of acidic and neutral extractants by utilizing synergistic mixtures has such a drawback that not only the benefits but also the shortcomings of the extractants would be summed up. The

Table 1. Extractant systems for americium recovery with HDEHP or HEH[EHP] and their mixtures with mono- and bidentate ligands.

Process name	An/Ln extractant	An back-extractant	Ref.
	Systems based on HDEHP or HEH[EHP]		
TALSPEAK	0.3 M HDEHP in diisopropylbenzene (0.05 M DTPA + 1 M lactic acid are added to the aqueous phase at pH 3)	–	15, 16
Reverse TALSPEAK	HDEHP in dodecane	DTPA + lactic acid	15, 16
TALSQuEAK	1 M HEH[EHP] in dodecane (HEDTA + lactic or citric acid are added to the aqueous phase)	–	85, 88
	HDEHP or HEH[EHP] mixtures with monodentate ligands		
–	HDEHP + TBP in dodecane	0.05 M DTPA + 0.1 M citric acid at pH 3	129, 130
–	0.2 M HEH[EHP] + 0.2 M Cyanex-923 in dodecane	0.02 M HEDTA + 0.1 M glycine or 0.01 M TTHA + 0.1 M glycine	131
	HDEHP or HEH[EHP] mixtures with bidentate ligands		
TRUESPEAK	1 M HDEHP + 0.1 M CMPO in dodecane	0.05 M DTPA + 1.5 M ammonium citrate at pH 3.5	132–134
–	1 M HEH[EHP] + 0.2 M CMPO in dodecane	HEDTA + citrate buffer at pH 2.5–3.7	142
–	0.25 M HDEHP + 0.1 M TEHDGA or TODGA in dodecane	0.05 M DTPA + 0.5 M citric acid at pH 3	135–138
ALSEP	HDEHP or HEH[EHP] + T2EHDGA or TODGA in dodecane (HEDTA is added to the aqueous phase)	DTPA + ammoium citrate at pH 4	139–141

highly promising results obtained for model solutions require verification on real HLW.

III. Selective extractants for separation of actinides(III) and lanthanides

The extractants considered in the previous section contain hard donor O-centres. Upon interaction with hard Lewis acids such as lanthanide and actinide cations, they from stable coordination bonds, but they possess omly moderate selectivity. Taking into consideration the more covalent nature of actinide coordination bonds, it seemed highly promising to switch to ligands that are coordinated *via* softer donor centres, like sulfur and nitrogen atoms. This intuitively formulated hypothesis proved to be exceptionally useful. The synthesis and investigation of ligands containing soft donor centres or both hard oxygen and soft nitrogen centres have become a major trend in this field. The obtained dithiophosphinic acids and polydentate nitrogen-containing compounds showed very high selectivity towards actinide(III) and lanthanide separation. Similar performance is demonstrated by amides of heterocyclic carboxylic acids, which have hard carbonyl oxygen atoms along with soft N-donor centres.

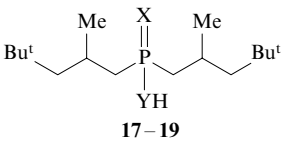
III.1. Organosulfur compounds

Among the organosulfur compounds, the most commonly used selective extractants for actinides(III) are dithiophosphinic acids [$R^1R^2P(S)SH$; R^1, R^2 = Alk, Ar] and dithiophosphoric acids [$R^1O(R^2O)P(S)SH$; R^1, R^2 = Alk, Ar]. The structures of complexes of these compounds with actinides in comparison with the lanthanide complexes have been discussed elsewhere.[143]

The first compound of the class found to exhibit selectivity towards actinide(III) extraction was bis(2-ethylhexyl) dithiophosphoric acid (HDEHDTP). For a HDEHDTP–TBP mixture, an Am/Eu separation factor of ~50 was achieved.[144, 145]

A number of phosphinic acids have also been studied, namely, bis(2,4,4-trimethylpentyl)phosphinic acid (**17**, Cyanex-272), bis(2,4,4-trimethylpentyl)monothiophosphinic acid (**18**, Cyanex-302) and bis(2,4,4-trimethylpentyl)dithiophosphinic acid (**19**, Cyanex-301).[146] Cyanex-302 and Cyanex-301, containing soft sulfur donor atoms, were shown to selectively extract americium. Cyanex-301 exhibited the highest selectivity. For a specimen purified by recrystallization from benzene, the Am/Eu separation factor of > 5000 was obtained.[147]

Structures 17–19



17–19

X = Y = O (**17**, Cyanex-272),
S (**19**, Cyanex-301);
X = S, Y = O (**18**, Cyanex-302)

A research team from the United States[148] has shown that a mixture of dicyclohexyldithiophosphinic acid and TBP exhibits high extraction selectivity toward actinides(III) ($D_{Am}/D_{Eu} \approx 1000$).

Cyanex-301 possesses exceptional selectivity toward actinides(III), although effective extraction is possible only from solutions with pH > 3. In order to extend the working pH range for the extraction, the alkyl subtituents in the Cyanex-301 molecule were replaced by more electron-withdrawing aromatic groups, particularly, bis(4-chloro-

phenyl)dithiophosphinic acid and bis(4-fluorophenyl)dithiophosphinic acid have been synthesized.[149,150] These compounds selectively recover americium from nitric acid solutions (up to 1 mol litre^{-1} HNO_3) in the presence of synergistic additives — TBP, trioctylphosphine oxide or tributylphosphine oxide. Extraction capacity towards Am^{III} and Eu^{III} increases in the sequance $Ph_2P(S)SH$ < $(4\text{-}FC_6H_4)_2P(S)SH$ < $(4\text{-}ClC_6H_4)_2P(S)SH$. Meanwhile, the Am/Eu separation factors diminish in the very same sequence, reaching values of 230–280, 41–57 and 28–31 respectively. Toluene was used as a diluent for aromatic dithiophosphinic acids, since they are insoluble in dodecane, which is used for aliphatic compounds.

A more oxidation resistant, compared to its analogues, bis(*o*-trifluoromethylphenyl)dithiophosphinic acid has been synthesized. Investigation of actinide extraction with this compound,[151] as well as with a mixture of bis(*o*-trifluoromethylphenyl)dithiophosphinic acid and trialkylphosphine oxide,[152] showed high selectivity of actinide and lanthanide separation (D_{Am}/D_{Eu} > 200). It was demonstrated in a chemical stability study of diarylphosphinic acids[153] that even the most stable of them are oxidized on contact with 2 M nitric acid. Hydrazine retards the oxidation.

Consequently, despite the exceptionally high selectivity, dithiophosphinic acids cannot be utilized for americium separation from lanthanides during HLW reprocessing, since they work only at low acidity and are also poorly resistant to hydrolysis, radiolysis or oxidation.[154–156] The acid and oxidative stability can be slightly improved through replacement of alkyl sustituents with electron-withdrawing aromatic groups containing halogen atoms, but this advesely affects extraction efficacy and selectivity.[157]

It is also worth mentioning that the use of sulfur-contaning compounds is unfavourable due to waste reprocessing issues; sulfates formed during incineration are poorly incorporated into the borosilicate glass.

III.2. Donor N-heterocyclic ligands

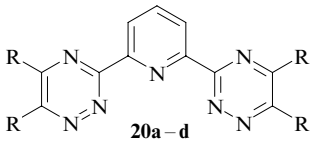
The extractants with S-donor centres have demonstrated excellent selectivity towards actinide and lanthanide separation; nevertheless, the mentioned drawbacks strongly limit their engineering applications. As a result, the major effort made in the development of soft donor ligands has been lately devoted to creation of new extractants based on nitrogen-containing aromatic heterocycles. Fascinating results have been achieved in this field; Am^{III}/Eu^{III} selectivity factors ranging from 100 to several thousands have been achieved along this line.

A widely known class of nitrogen-containg compounds is 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines (BTP). They act as tridentate ligands to form complexes $[M(BTP)_3(NO_3)_3]$. The first discovered BTP capable of selective stripping of americium from nitric acid solutions was 2,6-bis(5,6-di-n-propyl-1,2,4-triazin-3-yl)-pyridine (**20a**, Pr^n-BTP).[158] For the extraction of americium from an aqueous solution containing 0.9 mol litre^{-1} HNO_3 and 1 mol litre^{-1} NH_4NO_3 with an extractant based on Pr^n-BTP in a kerosene–octanol mixture, the Am/Eu separation factor is >130. Still, Pr^n-BTP has serious disadvantages as regards both low stability to nitric acid and extraction rate.[159]

With the goal to improve the BTP stability, 2,6-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazol-3-yl)pyridine (**20b**, $CyMe_4$-BTP), which can endure heating with nitric acid, was synthesized.[160] $CyMe_4$-BTP demonstrated outstanding selectivity towards actinides(III) (D_{Am}/D_{Eu} > 1000). Yet, the distribution constants of americium in the extraction with the considered BTP are too high, resulting in problematic back-extraction. Yet another drawback is the low extraction rate.[161]

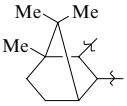
To overcome the limitations of $CyMe_4$-BTP, a new BTP, bis-2,6(5,9,9-trimethyl-5,6,7,8-tetrahydro-5,8-methano-1,2,-4-benzotriazin-3-yl)pyridine (**20c**, CA-BTP), has been synthesized.[162] This derivative has certain benefits over other BTPs such as higher solubility in octanol, higher americium extraction rate, as well as greater stability to HNO_3. Other than that, CA-BTP properties are similar to those of Pr^n-BTP.

Structures 20



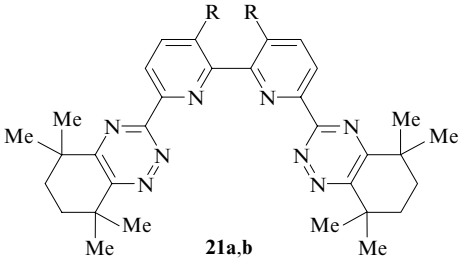
20a–d

R = Pr^n (**a**, Pr^n-BTP), $C_6H_4SO_3Na$-3 (**d**);

R–R = $CMe_2(CH_2)_2CMe_2$ (**b**, $CyMe_4$-BTP),  (**c**, CA-BTP)

The next step in investigation of this type of extractants was the synthesis of 6,6′-bis(1,2,4-triazin-3-yl)-2,2′-bipyridines (BTBP).[163] These tridentate ligands extract actinides(III) by forming metal–ligand complexes with 1 : 2 components ratio.[164] Among the studied BTBP, note 6,6′-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-2,2′-bipyridine (**21a**, $CyMe_4$-BTBP) similar to **20b** ($CyMe_4$-BTP).

Structures 21



21a,b

R = H (**a**, $CyMe_4$-BTBP); R–R = CH=CH (**b**, $CyMe_4$-BTPhen)

In the extraction with $CyMe_4$-BTBP solutions in a kerosene–octan-1-ol mixture or in octan-1-ol from 1 M nitric acid, the Am/Eu separation factors reached 150, yet the extraction rate was too low, hindering the practical application of the system. To accelerate the extraction, malonamides and diglycolamides are added to the organic phase.[165,166] The main disadvantage of Me_4-BTBP is low (0.01 mol litre^{-1}) solubility in octanol-based diluents. This concentration of $CyMe_4$-BTBP is insufficient for the recovery of substantial amounts of actinides(III).

Attempts to improve the $CyMe_4$-BTBP performance led to the creation of its phenanthroline analogue $CyMe_4$-BTPhen (**21b**) in which the system of two pyridine rings was replaced by a more rigid 1,10-phenanthroline moiety.[167,168] Americium distribution constants in the

extraction with $CyMe_4$-BTPhen increase by several orders of magnitude compared with $CyMe_4$-BTBP, reaching $\sim$1000 for extraction from 1–4 M HNO_3 solutions. Also, $CyMe_4$-BTPhen has a slightly higher americium extraction selectivity ($SF_{Am/Eu} \approx 250$). In addition, $CyMe_4$-BTPhen possesses superior kinetic performance and does not require additives to facilitate the phase transfer.

Several reviews have been published lately, dealing with chemistry and possible commercial applications of heterocyclic poly-N-donor ligands[24, 25, 169] and giving comparison of various compounds. Heterocyclic phenanthroline derivatives are considered to be the most promising. The insufficient solubility of the ligands in hydrocarbon diluents is outlined and possible approaches to diluent modification are proposed.

Despite the plenty of good results obtained with polydentate-N-heterocyclic extractants, these ligands have not yet withstood the scrutiny of testing under industrial conditions. Therefore, practical extractant systems based on these compounds are still under development.

III.3. N-heterocyclic carboxylic acid amides

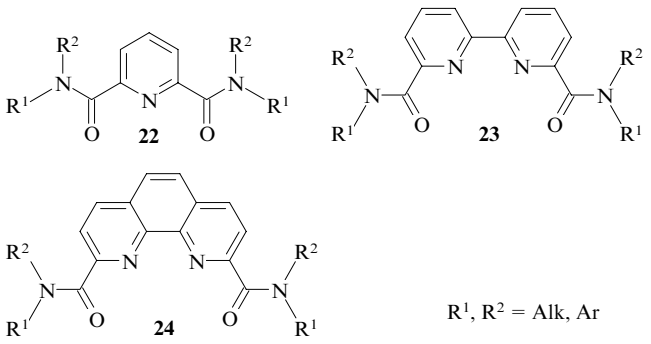
Amides of N-heterocyclic carboxylic acids comprise both hard donor centres (oxygen atoms) and soft donor pyridine nitrogen atoms. Such a combination facilitates the creation of extractants that efficiently recover metals from acidic solutions, exhibiting increased selectivity towards actinides.

A review published in 2014[23] is dedicated to comparison of the exctraction performance of heterocyclic carboxylic and dicarboxylic acid amides and diamides. The extraction properties of amides and diamides of picolinic, dipicolinic, bipyridinedicarboxylic, phenanthrolinecarboxylic, phenanthrolinedicarboxylic and other acids were considered. It was demonstrated that with decreasing the ligand basicity, the extraction capacity maximum shifts to higher nitric acid concentration. Two main factors determine the extraction properties of heterocyclic dicarboxylic acid diamides: the diamide structure and the utilized diluent type. The most promising extractants of this type for actinide and lanthanide separation are tri- and tetradentate ligands, dipicolinic (**22**) and bipyridinedicarboxylic (**23**) diamides. Amides of 1,10-phenanthroline-2-carboxylic acid and diamides of 1,10-phenanthroline-2,9-dicarboxylic acid **24** are also characterized by high selectivity with regard to transplutonium and rare earth metals; these compounds, though, are not adequately studied yet.

Over recent years, several interesting papers considering phenanthrolinedicarboxylic acid diamides have appeared. Actinide (Th^{IV}, U^{VI}, Am^{III}) and lanthanide (La^{III}, Eu^{III}, Yb^{III}) extraction[170, 171] with a 0.01 M solution of *N*,*N*′-diethyl-*N*,*N*′-di-*p*-tolyl-2,9-diamide-1,10-phenanthroline in cyclohexanone was investigated. The mentioned ligand selectively recovers actinides from nitric acid solutions. The Am/Eu separation factor for extraction from 1 M HNO_3 reaches 67. The extraction capacity toward La^{III} is approximately an order of magnitude lower than that for americium. The extraction of transition and post-transition metals (Ni^{II}, Co^{II}, Cu^{II}, Zn^{II}, Pb^{II}) was also investigated; high extraction capacity toward copper was found.

Lanthanide extraction with *N*,*N*′-diethyl-*N*,*N*′-di(4-n-hexylphenyl)-4,7-dichloro-1,10-phenanthroline-2,9-dicarboxamide in a polar fluorinated diluent [*m*-nitro(trifluoromethyl)benzene] has been studied, along with quantum

Structures 22–24



chemical simulation of lanthanide phenanthrolinedicarboxamide complexes.[172] It was demonstrated that the extraction capacity toward lanthanides decreases monotonically from La to Lu. Concurrently, the composition of the extracted metal–ligand complexes alters from 1 : 2 for La to 1 : 1 for Lu.

Quantum chemical simulations of tetra-, penta- and hexavalent actinide complexes with structurally different phenanthrolinedicarboxamides have been conducted.[173] As follows from the results of the simulations, the extraction capacity of diamides toward actinides changes in the series $Pu^{IV} > U^{VI} > Pu^{VI} > Np^{V}$, which is in good agreement with experimental data reported previously.[170, 171] So-called anomalous aryl strengthening effect was observed.[173] It consists in enhancement of the stability of complexes upon replacement of one of the alkyl groups at the amide nitrogens by an aryl group. This effect was previously observed for carbamoylphosphine oxides,[174] dipicolinamides[175] and bipyridinedicarboxamides.[176] The effect has also been studied for phenanthrolinediamides.[177] A comparative study of the extraction performance of structurally different ligands toward americium and lanthanides and toward d elements was reported.[177] The results of americium and lanthanide extraction from nitric acid are presented in Fig. 1 (the extractant used is diamide **24**; R^1 = Et, R^2 = 4-EtC_6H_4).

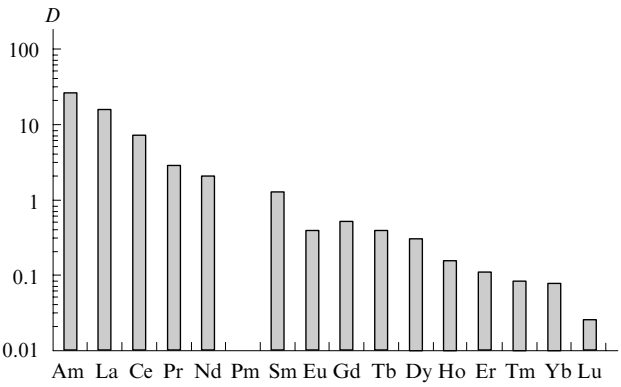


Figure 1. Distribution constants of metals.[177]
Extractant is a 0.01 M solution of *N*,*N*′-diethyl-*N*,*N*′-bis(4-ethylphenyl)-1,10-phenanthroline-2,9-dicarboxamide (**24**; R^1 = Et, R^2 = 4-EtC_6H_4) in F-3; aqueous phase contains 1×10^{-4} mol litre^{-1} of every metal, trace quantities of Am.

A quantum chemical simulation of Am^{III} and Eu^{III} complexes with tetraalkyl-1,10-phenanthrolinedicarboxamides was performed and the extraction properties of two diamides for Am^{III} and Eu^{III} recovery from perchloric acid solutions were studied.[178] For the *N*,*N*,*N*′,*N*′-tetradecyl-1,10-phenanthroline-2,9-dicarboxamide (**24**; $R^1 = R^2 =$ n-$C_{10}H_{21}$) in a dodecane–octanol mixture, the Am/Eu separation factor reached 51.

IV. Concepts of actinide partitioning

A great amount of experimental material obtained during investigation of new extractant systems has served as a basis for development of novel concepts of SNF and HLW reprocessing. Currently, there are two basic approaches to minor actinide partitioning from irradiated nuclear fuel applied around the world. The first one involves heterogenous partitioning of minor actinides from PUREX raffinates that are already stripped of uranium and plutonium. To achieve the selective recovery of americium and curium, several approaches have been developed.

The DIAMEX-SANEX concept involves a number of sequential processes. At the first stage, joint partitioning of actinides and lanthanides from HLW is performed by the DIAMEX-process.[90, 179] The name is derived from the phrase DIAMide EXtraction and is used to designate a few processes that employ dicarboxylic acid amides as extractants. At first, the *N*,*N*′-dimethyl-*N*,*N*′-dibutyl-2-tetradecylmalondiamide (**10**, DMDBTDMA) in an aliphatic solvent was used as the extractant. Later on, it was replaced by *N*,*N*′-dimethyl-*N*,*N*′-dioctyl-2-(2-hexyloxyethyl)malondiamide (**11**, DMDOHEMA).[180, 181] The process recovers >99% of actinides (along with lanthanides) and provides high degree of purification of fission products. In another version of the DIAMEX process, a *N*,*N*,*N*′,*N*′-tetraoctyldiglycolamide (**12**, TODGA) solution in dodecane is used as the extractant.[109, 182, 183] In the latest version of the process, a mixture of 0.2 mol litre^{-1} TODGA in kerosene containing 5 vol.% octanol serves as the extractant,[184] making possible the efficient partitioning of >99.9% of actinides and lanthanides without the risk of third phase formation.

The next stage of the DIAMEX-SANEX concept consists in separation of actinides and lanthanides through a selective r-SANEX-process.[185] The r-SANEX name originates from the phrase regular Separation of ActiNide(III) elements by Extraction. For the separation of actinides and lanthanides, a solution of bis(triazinyl)bipyridine $CyMe_4$-BTBP (**21a**) in octanol is used. To enhance the extraction kinetics, diamides of dicarboxylic acids, such as DMDOHEMA (**11**) or TODGA (**12**), are added to the extraction mixture.[186] Reprocessing of the solutions is performed in 1–2 M nitric acid. This kind of process allows for partitioning of >99% of americium and curium with residual lanthanide content of <0.1%.

The last stage is separation of Am and Cm, employing the LUCA process (Lanthaniden Und Curium Americium separation). A solution of bis(4-chlorophenyl)dithiophosphinic acid [(4-$ClC_6H_4)_2P(S)SH$] and tris(2-ethylhexyl) phosphate (TEHP) in a *tert*-butylbenzene and isooctane mixture is used as an extractant in this method. For this extraction mixture, high Am^{III}/Eu^{III} separation factors of > 3000 and Am^{III}/Cm^{III} separation factors of ~6–10 are achieved. Reprocessing is conducted for the solution containing 0.08 mol litre^{-1} HNO_3 and 0.5 mol litre^{-1} $NaNO_3$.[187] The process can be implemented both for Am and Cm separation and for selective recovery of Am after the DIAMEX-process. In the latter case, all lanthanides and curium remain in the raffinate.

Another modification of the DIAMEX-SANEX concept is the i-SANEX (innovative SANEX) concept. In this case, actinides and lanthanides are extracted from PUREX raffinate with a TODGA solution in kerosene containing 5% octanol. The actinides and lanthanides are separated *via* selective back-extraction with water-soluble sulfonated bis(triazinyl)pyridine **20d** (R = $C_6H_4SO_3Na$-3).[188]

In order to selectively partition actinides directly from PUREX raffinates without the the stage of joint actinide/lanthanide stripping, 1-cycle-SANEX concept was developed.[189] In this case, selective partioning of trivalent actinides from 3 M HNO_3 is achieved with a modified r-SANEX extractant containing 0.015 mol litre^{-1} bis(triazinyl)bipyridine $CyMe_4$-BTBP (**21a**) and 0.005 mol litre^{-1} TODGA (**12**) in a kerosene–octanol mixture (40 : 60). Palladium is also transferred into the extract; its back-extraction is performed with L-cysteine. Americium and curium back-extraction is accomplished with a glycolic acid solution at pH 4.[190, 191]

On the basis of the DIAMEX-SANEX process, the EXAm process concept has been developed for selective recovery of americium.[192] At the first stage, americium is extracted from the PUREX raffinate together with light lanthanides (La–Nd). A mixture of malonamide DMDOHEMA (**11**) and HDEHP (**7**) in a hydrogenated tetrapropylene (THP) serves as the extractant. Utilization of a water-soluble complexant, *N*,*N*,*N*′,*N*′-tetraethyldiglycolamide (TEDGA), in this stage provides the required Am/Cm and Am/Ln separation factors. Total curium, as well as europiun, samarium and gadolinium remain in the raffinate. The separation of Am from the co-extracted lanthanides is accomplished *via* back-extraction stage with a mixture of EDTA and citric acid at pH 3.

There is yet another approach that implements the homogeneous recovery of all actinides. In France, GANEX-concept (Grouped ActiNide EXtraction) has been proposed for selective partitioning of all actinides directly from spent fuel solutions.[193, 194] It involves preliminary separation of the bulk uranium during the first cycle (with TBP or a carboxylic acid monoamide) followed by extraction of the remaining uranium, plutonium, neptunium, americium and curium during the second cycle (being, in fact, the GANEX process itself). According to the authors, the main benefit of this concept is its full accordance with the terms of the Non-Proliferation Treaty, since none of the process stages involves isolation of pure plutonium. In addition, the authors believe that isolation of uranium in a separate process flow and subsequent co-extraction of all actinides in one cycle should make it possible to design a more compact process flow diagram, thus lowering both the reprocessing cost and the amount of waste.

Since 2010, several versions of the GANEX process, differing basically in the composition of extractant mixture, have been intensely studied. For one, a mixture of CyMe4-BTBP (**21a**) and TBP in cyclohexanone can recover U, Np, Pu and Am from solutions containing 4 mol litre^{-1} HNO_3 and high amounts of metals (>9 g litre^{-1}).[195, 196] Afterwards, TBP was replaced by *N*,*N*-di(2-ethylhexyl)-n-butyramide (DEHBA).[197] This component is free of phos-

phorus, hence, it does not produce solid phosphates upon incineration, *i.e.*, this is in accordance with the so-called CHON concept, postulating that the extractant should contain only the title atoms. Compared to TBP, minor differences regarding the extraction of some fission products were observed; however, this should not be a significant drawback of DEHBA. In order to inhibit the Pd^{II} extraction, a water-soluble complexing agent, (2*S*,2′*S*)-4,4′-ethane-1,2-diylbis(sulfanediyl)bis(2-aminobutanoic acid) (bimet) has been proposed [198] and to inhibit molybdenum and zirconium extraction, 1,2,3,4,5,6-hexahydroxyhexane (mannitol) has been chosen.[199] The search for diluents for the GANEX extractant is ongoing. The feasibility of utilizing caproic acid as an alternative to cyclohexanone has been evaluated;[200] however, its application within the GANEX process framework proved impossible, due to exceptionally low distribution constants of americium and lanthanides. Trifluoromethyl phenyl sulfone possessing high chemical stability and radiation resistance and providing superior extraction and capacity characteristics for lanthanide and actinide recovery, was shown to be a good diluent for the GANEX process.[201]

A process called Euro-GANEX, in which a mixture of dicarboxylic acid diamides [0.2 mol litre^{-1} TODGA (**12**) and 0.5 mol litre^{-1} DMDOHEMA (**11**)] in kerosene (Exxsol D80) is utilized as the extractant, has been proposed for co-extraction of actinides.[202] The first stage was co-extraction of actinides (Pu^{IV}, Np^{IV}, Np^{VI}, Am^{III}, Cm^{III}) and lanthanides. They were separated at the back-extraction stage upon application of water-soluble sulfonated bis(triazinyl)pyridine **20d** and acetohydroxamic acid.[203] The efficacy of this extractant has been proved for actinide-saturated solutions containing 0.1 to 10 g litre^{-1} plutonium. The extraction behaviour of actinides [204] and various fission products [205] has been studied; a dynamic experiment for a simulated solution containing 10 g litre^{-1} Pu^{IV} has been conducted. It is worth mentioning that the simulated solution was deprived of uranium, small amounts of which can occur in wastes. Lanthanides were represented solely by europium. A disadvantage of the tested scheme is the loss of ~30% of neptunium with the raffinate. Modification of the process flow diagram and conduction of dynamic tests on a real HLW from fast reactor spent fuel are assumed.

All the processes considered above are summarized in Table 2.

Table 2. Extraction processes for heterogenous and homogenous actinide recovery.

Concept	Process	Extractant	Back-extractant	Purpose of the process	Ref.
		Heterogenous partitioning of actinides (*reprocessing of PUREX raffinates*)			
Extraction of actinides and lanthanides from raffinates	DIAMEX	DMDBTDMA or DMDOHEMA in THP	–	Co-extraction of Am + Cm + Ln	90, 179–181
	TODGA-based	0.2 M TODGA + 0.5 M TBP in THP	–	The same	109, 182–183
	ARTIST	0.1–0.2 M TODGA + 1 M DHOA in dodecane	–	"	108, 206, 207
Separation of actinides and lanthanides	r-SANEX	$CyMe_4$-BTBP + diamide (0.25 M DMDOHEMA or 0.005 M TODGA) in octanol	–	Selective extraction of Am + Cm	185, 186
	LUCA	0.4 M $(4\text{-}ClC_6H_4)_2PS_2H$ and 0.15 M TEHP in a $PhBu^t$ and isooctane mixture	–	Selective extraction of Am	187
	i-SANEX	TODGA in kerosene + 5% octanol	0.018M **20d** + 0.35M HNO_3	Co-extraction of Am + Cm + Ln; selective back-extraction Am + Cm	188
	1-cycle-SANEX	0.015 M $CyMe_4$-BTBP + 0.005 M TODGA in a kerosene – octanol (40 : 60) mixture	–	Selective extraction of Am + Cm	189–191
	EXAM	DMDOHEMA + HDEHP in HTP (TEDGA in the aqueous phase)	HEDTA + citric acid (pH 3)	Am/Cm separation in the extraction stage; Am/Ln separation in the back-extraction stage	192
		Homogeneous partitioning of actinides (*raffinate reprocessing after uranium stripping*)			
GANEX	CEA-GANEX	DMDOHEMA + HDEHP in HTP	HEDTA + citric acid (pH 3)	Selective extraction of An; selective back-extraction of An	193, 194
	GANEX	$CyMe_4$-BTBP + TBP or DEHBA in cyclohexanone	–	Selective extraction of An	195–199
	Euro-GANEX	0.2 M TODGA + 0.5 M DMDOHEMA in kerosene Exxsol D80	**20d** + AHA + 0.5 M HNO_3	Selective back-extraction of An	202–205

Note. DHOA is dihexyl-n-octanamide, DEHBA is *N*,*N*-bis(2-ethylhexyl)-n-butanamide, AHA is acetohydroxamic acid.

Numerous processes mentioned above that utilize mixtures of malonamide or diglycolamide and nitrogen-containing extratants have been proposed for partitioning and separation of actinides and lanthanides. We believe that heterocyclic carboxylic acid amides in polar fluorinated diluents (GANEX process) are best suited for the purpose of actinide co-extraction. Among the benefits of dipicolinamides, bipyridinedicarboxamides and phenanthrolinedicarboxamides are fast equilibration, high capacity of the organic phase toward uranium, moderate or high An/Ln separation selectivity and good hydrodynamic performance. In favour of such extractant systems are feasibility of An^{III} separation from An^{IV} and An^{VI} through a change in the nitric acid concetration alone without the use of complexing agents. The optimal extractant system has not been chosen as yet and futher investigations are required; however, the prospects of the search seem rather encouraging.

The application of the proposed new extractant systems is held back by insufficient solubility of the solvates. With the aim of overcoming these limitations, a search for novel diluents is in progress. Of particular interest is the recent line of research comprising the investigation new water-soluble complexing agent.

V. Water-soluble complexing agents

Traditionally, americium and curium separation from lanthanides was accomplished by using complexing agents — polyaminoacetic acids (EDTA, DTPA, *etc.*) or similar compounds. They facilitate efficient separation of actinides and lanthanides during the back-extraction stage of the TALSPEA process, as well as in SETFICS process versions and from solutions in TODGA.[208] The search for more efficient complexing agents of this type is continued. EDTA analogues such as *N*-(2-hydroxyethyl)ethylenediaminetetraacetic (**9**) and cyclohexanediaminetetraacetic acids have been proposed. The mentioned conpounds have demonstrated high efficacy of zirconium and palladium masking during An and Ln extraction. Regarding their disadvantages, they are applicable only in dilute acid media (pH > 1.5), sparingly soluble in neutral and dilute acids and generally require a supporting salt. A recently emerging trend is to utilize complexing agents of different classes that function at nitric acid concetrations of >0.5 mol litre^{-1} and do not require supporting salts. Particularly worth mentioning are water-soluble diglycolic acid derivatives. Methyl and ethyl derivatives of diglycolamide and diglycolic acid monoamide, which have been recently proposed,[209, 210] form stable complexes with actinide and lanthanide ions in acidic media. A comparative study [124] of the influence of several complexing agents, namely DTPA, malonamide, diethyldiglycolamide and tetraethyl-3,6-dioxaoctanediamide, on the separation of americium and curium from lanthanides has been carried out. It was shown that through combination of extractants and complexing agents with different extraction capacity toward lanthanides, one can enhance the separation selectivity. Utilization of tetraethyldiglycoamide ($O[CH_2C(O)NEt_2]_2$, TEDGA) for back-extraction in the EXAM-process [192] makes possible the selective partitioning of americium. Attempts on creation of water-soluble diglycolamides,[211] which can be utilized for actinide and lanthanide separation, are being made.

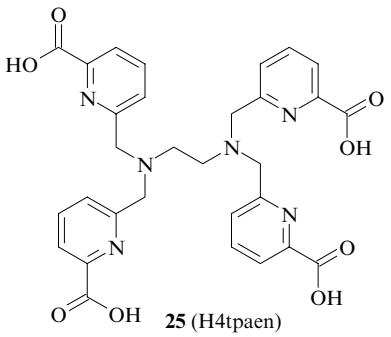
For nitrilotriacetamide (**15**) in dodecane as an extractant, it was demonstrated that the use of TEDGA as a masking agent provides efficient separation of americium from curium (with the maximum separation factor of 6.5).[127]

Various water-soluble ligands have been synthesized [212] and their impact on americium and europium distribution in a 0.2 mol litre^{-1} TODGA + 5 vol.% octanol system in a hydrogenated tetrapropylene has been investigated. For the majority of the synthesized ligands, no enhancement of americium/europium separation selectivity was observed. According to the authors, the most promising ones are 2,2′,2″-nitrilotris(*N*,*N*-dimethylacetamide) and 2,2′,2″-nitrilotris[*N*,*N*-bis(2-hydroxyethyl)acetamide], which showed the Eu/Am separation factors of 11.1 and 5, respectively. A drawback of the proposed complexing agents is that separation occurs only in the pH range of 1 – 4.

Diglycolic acid monoamides have also been used to separate plutonium(IV) and uranium(VI).[213 – 215] These ligands extract actinides(IV) with high efficiency, whereas actinides(VI) predominantly remain in the organic phase; for this reason, utilization of monoamides of diglycolic acid does not require plutonium reduction prior to back-extraction. The application of water-soluble diglycolic acid derivatives in the separation process has encouraged a thorough investigation into complex formation of these compounds in aqueous solutions.[216, 217]

Very good prospects for the separation of both An/Ln and americium/curium pairs are water-soluble complexing agents containing soft N-donor atoms. The utilization of these complexing agents enable americium back-extraction, leaving europium and other lanthanides in the organic phase. A comparison has been made of the effects of various dipicolinic acid derivatives and *N*,*N*,*N*′*N*′-tetrakis[(6-carboxypyridine-2-yl)methyl]ethylenediamine (**25**, H4tpaen,) on americium and europium distribution between the organic phase (a TODGA solution in HTP) and the aqueous phase consisting of the complexing agent in a sodium nitrate and nitric acid solution.[218] The separation factors ranged from 8 to 10 for dipicolinic acid derivatives, whereas for H4tpaen, they reached several thousand. Moreover, americium/curium separation factors of >3.5 were obtained for H4tpaen. Unfortunately, these values were achieved only in a salt solution with a sodium nitrate concetration of 1 – 3 mol litre^{-1}. One more problem is associated with low solubility of H4tpaen ($\leqslant 5$ mmol litre^{-1}).

Structure 25



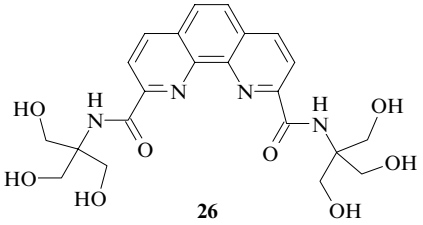
25 (H4tpaen)

High selectivity of bis(triazinyl)pyridines and bis(triazinyl)phenanthrolines toward actinides in contrast to lanthanides has aroused interest in their hydrophilic derivatives.

These complexing agents also bind to actinides more efficiently, which makes them suitable for separation in the back-extraction stage.[219] A combination of an extractant that successfully recovers lanthanides and actinides (TODGA, **12**) and a water-soluble complexant — sulfonated bis(triazinyl)pyridine **20d** — provides back-extraction of actinides, leaving lanthanides in the organic phase. The benefits of the proposed process are high separation factors and the feasibility of conducting the process in solutions with nitric acid concentrations of up to 2 mol litre^{-1}. Ligand **20d** is proposed for some versions of the SANEX process. Despite the high selectivity of the ligand, the presence of a sulfur atom in the molecule precludes considering this reagent salt-free one, as its degradation would give the poorly vitrifiable sulfate ion. Apparently, investigations should be aimed at synthesizing water-soluble BTP without sulfur atoms.

Phenanthrolinedicarboxamides efficiently recover actinides from acidic media. Hydrophilic phenanthroline derivatives have been proposed for actinide stripping from the organic phase in acidic media.[220] It was demonstrated that *N*,*N*′-bis(1,3-dihydroxy-2-hydroxymethylpropan-2-yl)-1,10-phenanthroline-2,9-dicarboxamide (**26**) is a selective complexing agent extracting americium from the TODGA–octanol (5%) in kerosene phase more efficiently than europium.

Structure 26

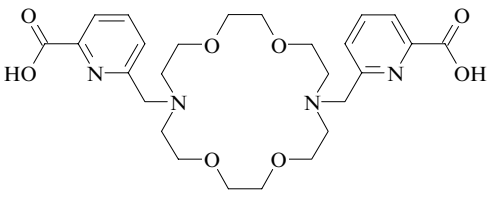


26

The distribution constants in pure 1M nitric acid and in 1 M nitric acid with addition of 0.01 mol litre^{-1} ligand **26** are >100 and 34 for europium, 23.6 and 0.82 for americium, respectively. Thus, europium/americium separarion factor of >40 is achieved. Unfortunately, under the discussed conditions, the distribution constants for light lanthanides from lanthane to neodymium are also <1, *i.e.*, the separation of americium from light lanthanides cannot be accomplished. Futhermore, the considered ligand has poor solubility in acidic media.

An interesting approach to the separation of americium and curium has been suggested.[221] A novel water-soluble ligand, *N*,*N*′-bis(6-carboxy-2-pyridylmethyl)-1,10-diaza-18-crown-6 (**27**, H2bp18c6), was used.

Structure 27



27 (H2bp18c6)

It was demonstrated that the ligand forms a more stable complex with a smaller-sized curium ion. The selectivity of americium and curium separation, defined as the ratio of stability constants of their complexes, is 4.1. It was claimed to be the highest obtained separation factor; however, a value of 6.5 had been reported previously.[124]

Studies of water-soluble complexing agents selective toward actinides have started quite recently, nonetheless, primary successes achieved give hope to finding a solution to problems of actinide and lanthanide as well as americium and curium separation. The use of complexing agents is a more attractive approach than the application of new extractants, since the chemical stability requirements are significantly lower for complexing agents: an extractant must endure hundreds of extraction cycles, while a complexant is only used once. The availability of extractants and complexing agents selective toward either actinides or lanthanides makes it possible to create extractant–complexant combinations with opposite affinity, thus enhancing the selectivity of separation.

VI. Influence of diluents

The majority of works on fractionation were conducted using hydrocarbon diluents. Since the extractants proposed for fractionation are mainly polar compounds, most of them (and this being even more pronounced for their metal complexes) have poor solubility in hydrocarbon diluents. Surpassing the solubility limit leads to precipitate (third phase) formation.

A standart method to prevent the third phase formation, as shown previously, is the addition of a modifiying agent to the diluent. Higher alcohols, TBP, carboxylic acid monoamides, *etc*. are utilized as such modifiers. The use of polar compounds, such as higher alcohols or ketones,[222] has been shown to confer high solubility of compounds like BTP and acceptable extraction performance. However, the cyclohexanone flash point (44 °C) limits its use. Hexanoic acid has been considered as an alternative.[200]

The problem can be solved by introduction of polar fluorinated diluents, commonly utilized in Russia. *m*-Nitrobenzotrifluoride originally proposed for cobald bis(dicarbollide) and carbamoylphosphine oxides contains a nitro group and is, hence, a toxic compound. Phenyltrifluoromethyl sulfone (FS-13, PTMS) [223] deprived of a nitro group is successfully used as a diluent for carbamoylphosphine oxides, pyridinedicarboxamides, BTP,[201] as well as for calixarenes [224] and malonamides.[98] In most cases, the extraction capacity and solubility of extractants in FS-13 is significantly improved, compared to hydrocarbon diluents or chloroform.

Polar fluorinated diluents, namely, fluorinated alcohol derivatives, seem exceptionally attrative.[76, 225] The strong points of such diluents are low toxicity and high chemical stability. Yet, they are surpassed by aromatic diluents in the solubility of polar extractant solvates.

Ionic liquids are a separate class of diluents. High hopes were put on these compounds in view of their low volatility and a substantial enhancement of distribution constants for several extractants in such diluents. Yet, these expectations were only partly justified.[226] Many derivatives proved to be too viscous, and in a large number of cases, back-extraction was possible only for strong complexing agents. Research on the influence of ionic liquids on extraction properties of extractants such as carbamoylphosphine oxides,[227] diglycolic acid derivatives,[228, 229] pyridinedicarboxamides [230, 231]

is in progress. The disscussion of strengths and limitations of ionic liquids, compared to traditional diluents is carried out.[118, 232] It is, however, quite evident at present that ionic liquids are still far from practical application.

VII. Conclusion

A number of works devoted to reprocessing of PUREX raffinates is rapidly growing. The interest of the scientific community in partitioning and separation of americium and curium has risen particularly sharply. This was extensively encouraged by practical importance of the task, on the one hand, and discovery of extractants selective toward actinides(III), on the other hand.

Individual extraction behaviour of neutral non-selective extractants was studied rather comprehensively. Industrial processes for partitioning of actinides and lanthanides from HLW with these extractants have been developed rather long ago. Every system, though, has its own pronounced shortcomings (low extraction capacity, possibility of third phase formation, insufficient separation of actinides from lanthanides and other); therefore, none of the extraction processes has been actually implemented on an industrial scale.

The majority of recent publications are mainly focused on modification of the existing systems, rather than the development of novel classes of extractants, which could possibly be utilized for metal partitioning, and investigation of their properties. To enhance the capacity characteristics of the ligands and to prevent the trird phase formation either novel types of diluents (polar fluorinated diluents, ionic liquids) in the presence of additives (octanol, isodecanol), or traditional aliphatic diluents (dodecane, kerosene), which increase the overall polarity of the extractant system, are proposed.

Investigations on improvement of the performance of the well-known TALSPEAK process are carried out. Various combinations of HDEHP (and its analogues) with neutral extractants have been considered. The addition of a neutral ligand provides greater capacity of the extraction mixture with regard to the stripped metals and a possibility for actinide and lanthanide separation at lower pH values.

The most efficient extractants for americium and lanthanide separation are poly-N-containing compounds [bis(triazinyl)pyridines and bis(triazinyl)bipyridines]. Various processes based on them, both for selective recovery of americium and curium (DIAMEX-SANEX) and for co-extraction of all actinides present in spent nuclear fuel (GANEX), have been developed and tested. It is worth mentioning that despite the discrepancy in approaches, the processes often employ the same ligands and selective complexing agents.

Despite the abundance of exceptionally interesting data obtained and a bulk of experiments conducted, including dynamic tests on different extractant systems, no system has been proposed that would be fully suitable for industrial application. As far as we are concerned, closest to implementation in the industry are the extractant systems based on acid diamides, diglycolamides in the first place, along with structurally similar heterocyclic acid amides.

An attractive and promising approach to HLW extractive reprocessing is the utilization of water-soluble complexing agents selective toward actinides. Combination of extractants and complexing agents with opposite affinity is one of the keys to enhance separation efficacy. This field of research is developing so rapidly that results of primary importance are expected in the nearest future.

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