NEWPART:
A EUROPEAN RESEARCH PROGRAMME
FOR MINOR ACTINIDE PARTITIONING

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Abstract
The programme NEWPART (1996-1999), was set-up in the framework of the 4PCRD European research programme “Nuclear Fission Safety” in order to develop solvent extraction partitioning processes of minor actinides, mainly americium (Am) and curium (Cm), which are contained in the high active raffinate generated during spent nuclear fuel reprocessing by the PUREX process. Owing to the difficulty of the separation problem, it was decided to design a partitioning process based on two extraction cycles: (i) the first cycle should separate the mixture of trivalent actinides (An(III)) and lanthanides (Ln(III)) fission products (FPs) from the bulk of the FPs. Malonamide extractants have been selected for this cycle, named DIAMEX process; (ii) the second cycle aims to separate selectively An(III) from Ln(III). Several extraction systems have been chosen for this goal. They include: (i) nitrogen polydendate ligands used alone or in synergistic mixtures with carboxylic acids; and (ii) sulphur bearing extractants (di-thiophosphinic acids) used alone or in synergistic combination with neutral oxygen bearing extractants. This lecture will briefly present the main achievements obtained in the framework in this research.
Introduction

In the framework of the 4PCRD “Nuclear Fission Safety” European Programme, the NEWPART research contract (1996-1999) was set-up for the definition of processes for partitioning minor actinides (MAs) contained within nuclear waste mixtures generated after reprocessing of spent nuclear fuels by the PUREX process.

The main guides for the definition of partitioning methods for MAs within NEWPART are the following: (i) the minor actinide target for partitioning are americium (Am) and curium (Cm). Neptunium is not fully considered for partitioning within NEWPART (the partitioning of this element is considered feasible by an adapted version of the PUREX process); (ii) the waste mixture to be treated is the aqueous high active raffinate (HAR) from the reprocessing of spent nuclear fuel by the PUREX process; (iii) essentially no (or only minor) modification of the composition of HAR is needed prior to implement the partitioning process. This point is a prerequisite to prevent the formation of disturbing radioactive precipitates; (iv) Am and Cm will be separated from the complex mixture of nuclear wastes (essentially the fission products, FPs) without modification of their stable oxidation state (i.e. M(III)) in aqueous nitric acid medium; (v) liquid-liquid extraction will be the preferred method of partitioning selected, owing to its potentially high efficiency for the decontamination of HAR in MAs and for the purification of the recovered MAs; and (vi) as far as possible, all the chemicals to be used, such as extractants, diluents and aqueous complexing agents, must be destructible, at the end of their uses in the process, into gases that can be released freely into the atmosphere. In this case, no secondary solid waste is expected to be generated from the partitioning operations.

The selective separation of Am and Cm from the HAR is a complex problem owing to: (i) the high concentration of nitric acid (−3 mol/L) of this effluent; and (ii) the presence of high concentrations of trivalent lanthanide FPs (molar ratio Ln/An is about 40 for the UOx1-type fuel). So, the main strategy selected in NEWPART relies in the development of a two step process: (i) the first step aims to separate the mixture of An(III)+Ln(III) from 2/3 of the FPs and from the bulk of nitric acid; and (ii) the second step is intended for the An(III)/Ln(III) group separation by selective extraction of An(III), which is the most difficult goal to achieve. To perform the first step, the DIAMEX process, based on the use of a malonamide extractant was selected, while for the second step several selective systems are under study. They include: (i) synergistic mixtures of α-substituted carboxylic acid and nitrogen polydentate ligands, like substituted oligopyridines, tri-pyridine-triazines, amino-di-pyridine-tri-azines, pyridine-bis-1,2,4-tri-azoles; (ii) pyridine-bis-1,2,4-triazines, and (iii) synergistic mixtures of substituted di-thiophosphinic acids (CYANEX 301 like) and oxygen neutral donor ligands.

The most important results obtained so far during the fundamental and process development studies will be highlighted in this lecture.

Results and discussion

DIAMEX process

Malonamide extractants, with the formula: (RR’NCO)₂ CHR”, where R, R’ are alkyl, cyclohexano or aryl groups and R’ is alkyl or oxy-alkyl groups, were selected for the design of the first An(III)+Ln(III) extraction cycle. Several types of work have been carried out: (i) synthesis of malonamide extractants, performed mainly at Reading and by small industrial companies; and (ii)
basic research involving malonamides solvent extraction mechanism, including thermodynamic and kinetic aspects, co-ordination chemistry of Am(III) and Ln(III) with malonamide ligands. This work involves, in particular, crystal structure determination and X-ray absorption spectroscopy (XAS) related to M(III) (M = An or Ln) malonamide complexes in solution, molecular modelling, DIAMEX process development, including tests of the process with synthetic spiked effluent and genuine HAR.

Fundamental studies

Extraction thermodynamics, mechanisms and kinetics

One of the major questions to be solved for the extraction of lanthanide (III) and actinide (III) from aqueous nitrate solutions by malonamide extractants concerns the knowledge of the nature of the extracted species. Is there a dual mechanism of extraction i.e. formation of solvates with formulae M(NO₃)ₓLₙ, (with M(III) = Ln(III) or An(III) and L = diamide bi-dendate extractant), for low aqueous nitric acid concentration and alkali nitrate solutions (e.g LiNO₃), and formation of ion-pairs, of formula [LH]+, [M(NO₃)ₓLₙ]⁻ for concentrated aqueous nitric acid solutions, as encountered when extracting U(VI) or actinide (IV) from nitric acid media by monoamide extractants? Several experiments, involving UV-visible and ¹³C NMR spectroscopies and solvent extraction, have been conducted to answer this question. From the data obtained so-far one can conclude that, if a dual extraction mechanism exists, the second mechanism does not seem to be an ion-pair mechanism involving a protonated diamide. So, one can conclude that the occurrence of an ion-pair mechanism is unlikely.

The M(III) extraction reaction by malonamides from aqueous nitrate solutions can thus be written as follows:

\[
M^{n+}_{aq} + 3 \text{NO}_3^-_{aq} + n \text{L}_{org} \Leftrightarrow M(\text{NO}_3)_n \text{L}_{n,org} \quad (1)
\]

n is usually 2 for most of the malonamides.

Several diamides have been compared in their ability to extract An(III) or Ln(III) from aqueous nitrate media. For a series of malonamides with different R' groups (butyl, phenyl and chlorophenyl), it was shown at Chalmers that the less basic is the malonamide the better its M(III) nitrate extracting properties. At Marcoule, new malonamides have been also studied that contain either function(s) in the central R” group. These malonamides, especially the di-methyl-di-octyl-hexylethoxy-malonamide, DMDOHEMA, exhibit better affinities for M(III) nitrates in comparison with malonamides with R” alkyl groups. DMDOHEMA has been selected to replace di-methyl-di-butyl-tetra-decylmalonamide, DMDBTDM, in a new version of the DIAMEX process (see below).

A comprehensive study of the extraction kinetics of Ln(III) and An(III) nitrates by DMDBTDM has been carried out at Marcoule (M. Dal Don Ph.D. thesis). The main conclusions of this work can be summarised as follows:

- Using a constant area stirred cell of the Lewis type, evidence of chemically limited M(III) nitrate extraction rates was obtained from the knowledge of the values of the Arrhenius activation energies, which, for all M(III) studied, were found to be close to 40 kJ/mol (while for a diffusion limited kinetic regime, this energy is generally found close to be 20 kJ/mol).
• M(III) extraction rate laws were established for Ln(III) and An(III). All of them exhibit the same form: rate : $k [M(III)] [L][NO_3^-]$. 

• Noticeable differences exist in the values of $k$ for the series of Ln(III) ions. Experimental data can be sorted out in several sections; light, medium and heavy Ln. Kinetic constant $k$ for An(III) (An= Am and Cm) was found between those of the light and middle Ln for Am, and close to that of Eu for Cm.

• Evidence was obtained for the location of the chemical limiting reaction at the interphase. This was made clear, in particular, when studying the effect of surfactants on the Nd(III) extraction kinetics; decrease of the Nd(III) extraction rate was observed with both cationic or anionic surfactants.

• Extraction kinetics of M(III) nitrates by DMDBTDMA were found much slower than extraction of U(VI) or Pu(IV) nitrates by tri-n-butylphosphate, TBP (extractant of the PUREX process). The relative slowness of the M(III) extraction rates by malonamides may have an influence on the definition of the DIAMEX process implementing conditions.

Structure determination for M(III) nitrate malonamide solvates

Numerous highly valuable structural informations have been obtained by crystal structure determination and by X-ray absorption spectroscopy.

Crystal structures related to the following complexes have been obtained at Reading: $M(NO_3)_3 L_n$ with Nd/1 DMDPHMA, Yb/1 DMDPHMA, Nd/1 DMDCHMA, Nd/2 BDMPHMA, Yb/1 BRTEMA stoichiometries (with D = di; M = methyl; Ph = phenyl; CH = cyclohexyl, E = ethyl; MA = malonamide and BR = bromo). Moreover, crystal structure of BRTEMA was also determined. Various Ln(III) co-ordination polyhedra were thus evidenced.

Experiments aiming to determine and compare M(III) ion co-ordination polyhedra in crystals and solutions have been carried out using X-ray absorption spectroscopy. Experiments were done at two synchrotron facilities, LURE (Orsay, France) and Daresbury (GB). For example, Nd(NO$_3$)$_3$ L$_{28}$ crystals or solutions in ethanol were studied for $L = tetra$-ethylmalonamide, TEMA, di-methyl-di-phenylmalonamide, DMDPhMA, di-methyl-di-butyl-ethoxyethylmalonamide, DMDBEEMA, and DMDBTDMA. For all these systems, Nd(III) co-ordination polyhedron seem to be the same with about 10 to 11 oxygen atoms at 2.55 ± 0.01 Å. It is important to note that no evidence of involvement of ether oxygen in the bonding with Nd (III) was observed for DMDBEEMA. While very interesting, these XAS data demonstrate the difficulty to precise the co-ordination modes of Ln(III) nitrate solvates with malonamides.

Molecular modelling

Molecular modelling studies have been conducted at Reading aiming:

• To compare calculated structures and X-ray determined crystal structures.

• To propose structural explanations to experimental differences observed during extraction of M(III) metallic nitrates by several malonamides.
Using Quanta/CHARM package, it was found that the lowest conformation calculated structures for DMDPhMA, DMDCDMA and BMDMDPhMA, were similar to the experimentally determined crystal structures. Differences exist between structures of DMDPhMA and BMDMDPhMA and that of DMDCDMA, which were confirmed by calculations. So, an important conclusion was drawn from that study; the differences in M(III) extraction efficiency between cyclohexano (DMDCDMA) and phenyl substituted (DMDPhMA and BMDMDPhMA) malonamides can be correlated with the difference of the preferred conformations of the malonamide extractants.

Using Gaussian 94 programme, protonation of cyclohexano (DMDCDMA) and phenyl (DMDPhMA) substituted malonamides was studied. Results are equivalent for both malonamides and show that mono-protonated malonamide contains an intramolecular hydrogen bond, while the di-protonated malonamide does not.

Quantitative Structure-Activity Relationships (QSAR) study related to the extraction of Nd(III) nitrate by a set of 17 malonamides was carried out in 1998 at Marcoule in collaboration with Reading. For each diamide in Zg-Z conformation a molecular dynamics, in vacuo, at 500 K for 200 ps has been made. Then, a conformation has been selected from the trajectory by QSAR techniques and minimised with AM1 semi-empirical method (MOPAC). The main result of this QSAR lies in the presence of an oxygen ether atom in the R’ substituent which confers to the corresponding malonamides better M(III) nitrate extracting properties.

**DIAMEX process development**

Reference DIAMEX process

The reference DIAMEX process is based on the use of DMDBT DMA in solution in TPH at a concentration equal to 0.5 mol/L.

The radiolysis and hydrolysis of DMDBT DMA were studied in parallel at the CEA/Marcoule with that of an other malonamide; the di-methyl-di-butyl-dodecylethoxymalonamide, DMDBDDEMA, which differs from the former malonamide by the presence of an ether function in 2 position within R’ group.

The main results obtained so-far can be summarised as follows:

- **Radiolysis:**
  - Degradation of malonamides is observed under radiolysis.
  - The rate of degradation is accelerated slightly by the presence of an aliphatic diluent and more importantly by that of an aqueous nitric acid solution.
  - Main radiolysis products consist mainly in amide-carboxylic acid and long chain carboxylic acids.
  - Even if degradation of the diamides occurs under a radiation field, their rates, while larger than that of the TBP, are not so important.

So, we can conclude that diamides seem to resist radiolysis sufficiently so that one can consider their use in a real process for HLLW treatment.
Hydrolysis:

- Hydrolysis of DMDBTDMA was found limited.
- Hydrolytic degradation of DMDBTDMA increases with temperature.
- Modification of the nitric acid concentration in the aqueous phase does not seem to have any influence on the DMDBTDMA degradation rate.
- The main hydrolytic products of DMDBTDMA are an amide-acid compound and a monoamide.

Next studies to be carried out in this field will concern the regeneration of the degraded solvents.

Reference DIAMEX process flowsheets have been designed for tests performed at the ITU using centrifugal contactors with real HAR. To prevent the co-extraction of Mo and Zr FPs, oxalic acid was introduced into the feed and the scrubbing solution. Several cold tests were conducted and two hot tests were performed. Most of the goals assigned to this test were reached: almost quantitative extraction of Am, and Ln; very limited extraction of most of the FPs, including Zr and Mo; and limited extraction of ruthenium. It should be noted however that some other FPs were found to be extracted. They included technetium and palladium. Solutions to prevent contamination of the purified An(III)+Ln(III) fraction will be defined in the future.

Different DIAMEX processes using DMDBTDMA or DMDOHEMA

ENEA/Polimi (Italy) developed a new version of the DIAMEX process based on the reference DMDBTDMA molecule, but for a 1 mol/L diamide solution in TPH, instead of 0.5 mol/L DMDBTDMA solution for the reference DIAMEX process. The HAR is also different; it corresponds to an UOx-2-type used nuclear fuel, whereas the fuel considered is of an UOx-1-type for the reference DIAMEX flowsheet.

The modification of the concentration of the extractant within the solvent may have at least two major advantages in:

- Minimising the occurrence of third phase problems.
- The ability to treat feeds with higher nitric acid concentrations than that of the reference DIAMEX process.

The above mentioned advantages were also observed for the flowsheet developed at CEA/Marcoule using DMDOHEMA but for a lower extractant concentration (0.65 mol/L instead of 1 mol/L for DMDBTDMA). The flowsheets designed were, like the reference DIAMEX flowsheet, based in particular on the use of oxalic acid to prevent the co-extraction of Zr and Mo fission products with the mixture An(III)+Ln(III).

ENEA/Polimi flowsheet using 1 mol/L DMDBTDMA was tested successfully in mixer-settlers in collaboration with G. Modolo and R. Odoj at Jülich on synthetic spiked solutions. DMDOHEMA flowsheet was tested at CEA/Marcoule on cold synthetic solutions. In both cases the tests were highly successful. Most of the goals were reached without noticeable problems. Computer codes of these processes were established and calculated solute concentration profiles along the cascade of extractors correspond fairly well with experimental data.
One can conclude that several possibilities exist for the selection of a DIAMEX process, either based on the reference diamide DMDBTDMA, with possible several extractant concentrations, or on DMDOHHEMA optimised malonamide. Progress should be made in the future to solve the small remaining problems that have been highlighted during the hot tests at the ITU.

**Group separation of actinides (III) from lanthanides (III)**

*Fundamental studies*

**Heterocyclic nitrogen compounds**

*Extraction thermodynamics with various molecules*

Work was done in this field at Chalmers/Göteborg, at CEA/Marcoule and FZK/Karlsruhe.

An(III)/Ln(III) selective extraction of the An(III) using mixtures of α-substituted carboxylic acids (HA) with nitrogen polydentate ligands (L) were studied. The nitrogen ligands used were from different origins:

- Prepared at Reading for most of the ligands used at Chalmers, i.e. polypyridines, amino-di-pyridyl-tri-azine (ADPTZ) derivatives.
- Prepared at Reading and obtained from French sources (PANCHIM and University laboratories) for the CEA, i.e. polypyridines, ADPTZ, pyridyl-pyrimidine, etc.
- Prepared at the laboratory for FZK work, i.e. for pyridine-bis-1,2,4-triazoles.

For HA+L mixtures, most of the experiments conducted were aiming to determine the M(III) ion extraction mechanism(s) and to expect to obtain good selectivity for the extraction of An(III) over Ln(III) for sufficiently high nitric acid aqueous feed.

The method used to determine the M(III) ion extraction mechanism(s) was generally the slope analysis method which consists in studying the effect of the variation of one chemical parameter on the distribution ratios and separation factors of the metal ions at trace levels. The determination of such extractions mechanism(s) is complicated by the following facts:

- Interaction between HA and L occurs in the organic phases.
- Protonation of L, inducing its transfer into the aqueous phase, is observed for low pH aqueous solutions.

The following preliminary conclusions can be drawn from these studies:

- Polydentate nitrogen ligands L are effective for inducing a selectivity in the separation of An(III) vs. Ln(III) when mixed in synergistic combination with a-substituted carboxylic acids.
- Substituted terpyridines are generally less effective than terpyridine itself, when one considers the DM(III).
• Substituted terpyridines are less effective than tri-tertio-butyl-pyridine-tri-azine, TtBPTZ, studied previously, in terms of DM(III), while SFAm/Eu are almost the same for both systems (≈ 10).

• Quaterpyridine are more effective than terpyridine for both DM(III) and SFAm/Eu values. This seems to be connected with the denticity of the ligand.

• ADPTZ derivatives, easy to lipophilise in comparison with TPTZ, were found to be almost as good as TPTZ derivatives. This is in particular the case for tri-methyl-hexanoyl-amino-di-pyridyl-tri-azine, BADPTZ.

• Extracted complexes are of the form MA3Ln.

• Reasonably good SFAm/Eu were obtained; 10 (terpyridines and ADPTZ), 20 (quaterpyridine), 10 to 20 (bis-1,2,4-triazole derivatives).

• None of these systems is able to perform a selective extraction of Am(III) over Eu(III) from a high nitric acid concentration aqueous solution, but BADPTZ in synergistic combination with a-cyanodecanoic acid in solution in a diluent made of TPH + a modifier was considered to be suitable for process development (see below). In this case the feed containing An(III)+Ln(III) will contain 0.2 mol/L of nitric acid, which is a reasonably high acid concentration.

Other nitrogen polydentate ligands were studied by Z. Kolarik at FZK. This is the case, in particular, for the 3-(2-pyridyl)-5-(4-ter-butyl-2-pyridyl)-1,2,4-triazole (TTP). That nitrogen polydentate ligand was found to be a cationic exchanger, which exhibits very interesting selective extraction properties for Am(III) over Eu(III). SF\textsubscript{Am/Eu} equal to 60 was observed, but unfortunately for pH = 5.7 for the feed aqueous solution. Nevertheless, this very unusual molecule seems very interesting to study.

Moreover, An(III)/Ln(III) group separation was also studied by Z. Kolarik et al. at Karlsruhe with home-made pyridine-bis-1,24-triazines derivatives (BTPs). These molecules have interesting properties. For example, they are able to extract selectively An(III) from Ln(III) with separation factor as high as SF\textsubscript{Am/Ln} = 140 and this for high aqueous nitric acid concentration. An(III) extraction proceeds through a solvation mechanism involving three molecules of BTP, as shown in the following reaction:

\[
\text{An}^{3+}_{aq} + 3 \text{NO}^{-}_{aq} + 3 \text{L}_{org} \leftrightarrow \text{AnL}_{3}(\text{NO})_{3}_{org} \quad (2)
\]

with L = BTP.

These properties of BTPs extractants correspond potentially to a breakthrough in the field of An(III)/Ln(III) group separation. Syntheses of new BTPs were carried out at CEA/Marcoule, and their M(III) extraction mechanisms were also studied. Research will be devoted in the future for the study of these very interesting extractants.

**Structural determinations and molecular modelling of the complexes**

Numerous crystal structures involving both pure new polydentate nitrogen ligands L and their solvates with Ln (III) salts have been determined at Reading.

Among them, one can cite:

• The structure of the solid TPTZ and of its Sm(III) nitrate monosolvate. For the first time, the tridentate character of the bond between the TPTZ and one Ln(III) ion was established.
• The structure of the protonated form of the 2-amino-4,6-di-(2-pyridyl)-1,3,5-tri-azine (ADPTZ).
• The structure of solvates formed between the ADPTZ and most of the Ln(III) nitrate salts. Variations of the crystal structures were observed with an increase of the atomic number of the Ln, leading to very interesting considerations about the complexation of these M(III) metal ions with these terdendate nitrogen ligands.
• The structure of ion-pairs type formed between protonated forms of the terpyridine and Ln(III) nitratocomplex anions.
• Structures of solvates formed between Ln(III) nitrates and pyridine-bis-1,2,4-tri-azoles derivatives were determined. With an increase with Ln atomic number the structural types of the crystals change. So, a systematic was carried out with respect to structures along the Ln series.

All these structures are very helpful for the design of extractant molecules.

Molecular modelling of these systems were carried out both at Reading and CEA-Marcoule. We will mention only few studies done in the field of terpyridine conformations studied \textit{in vacuo} or in a water box, alone or in the presence of protons or M(III) metal ions. The main results obtained in this field can be summarised as follows:

- The \textit{trans-trans} conformation of terpy is preferred \textit{in vacuo}.
- The presence with terpy \textit{in vacuo} of M(III) ion, induces a reorganisation of the terpy molecules which are now \textit{cis-cis}, i.e. they exhibit a potential \textit{tri}-dendate binding site.
- In a water box, terpy exhibits a \textit{cis-cis} conformation because water molecules (1 or 2) are bound to the nitrogen atoms. One can conclude that water is able to pre-organise the terpy which is a highly favourable phenomenon for subsequent ion binding.
- In a water box, M(terpy)(NO$_3$)$_3$ complexes were found to be unstable. Hydrolysis of the complexes occur leading to the complete dissociation of the M(terpy) moieties. This has been demonstrated by molecular dynamic simulations.
- On the contrary, complexes of the type M(terpy)A,$_3^\lambda$, with A = $\alpha$-bromocaprate anion, were found to be stable in a water box. This important observation is in agreement with the observed extraction efficiencies of M(III) in the corresponding experimental systems.

Sulphur bearing cation exchange extractants

Following the discovery by Zhu (Beijing, China) in 1995 of the highly efficient properties of the purified CYANEX 301, a commercial \textit{dil-thiophosphinic acid}, two partners of the NEWPART collaboration decided to work in this field. The first study was carried out at FZJ/Jülich, which involved:

- Confirmation of Zhu’s results and extension of the work in creating new CYANEX 301 like extractants with improved properties in comparison with the original molecule.
- Extension of the work towards process development, which was done in collaboration with ITU/Karlsruhe.
The second study which was carried out by CEA/ Marcoule in collaboration with PNC Japanese scientists concerns:

- The verification of the Zhu’s results.
- The determination of the mechanism for the synergistic extraction of Am (III) and Eu(III) by CYANEX 301+ TBP synergistic mixtures.

The main results obtained in this important field can be summarised as follows:

- It was confirmed at FZJ/Jülich and CEA/Marcoule, that the results obtained by Zhu are real. SF_{Am/Eu} as high as 6000 were obtained.
- The solvates formed when M(III) ions are extracted by the purified CYANEX 301 possess the following formula: M\(A_{n}H_{a}\), with M = Am(III) or Eu(III) and HA standing for the CYANEX 301 molecule. The corresponding extraction constants were determined. They are in agreement with those published by Zhu in 1996
- Extraction mechanisms of Am(III) and Eu(III) by a CYANEX 301 + TBP synergistic mixture were determined. The composition of the extracted complexes are different for Am(III) and Eu(III). Although a slight increase of the SF_{Am/Eu} is observed for low TBP/CYANEX 301 ratios, further increase of this ratio leads to an important decrease of this separation factor.
- New CYANEX 301 like extractants with electron withdrawing substituents, such as phenyl, chlorophenyl, fluoro phenyl or tolyl, exhibit, in synergistic combination with neutral organophosphorous extractant, like TBP, tri-butylphosphine oxide TBPO, tri-octylphosphine oxide TOPO, a high and selective affinity for Am(III) over Ln(III). This holds even for high aqueous nitric acid concentrations, i.e. 0.5 to 2 mol/L. These results represent an important breakthrough in the field of An(III)/Ln(III) separation. This work was done by G. Modolo and R. Odoj at Jülich.

**Process developments**

**Nitrogen polydendate extractants**

Several systems involving nitrogen polydendate extractants were considered for An(III)/Ln(III) group separation process development. The common goal of all these systems is to extract selectively the An(III) from a feed with a reasonably high concentration of nitric acid (i.e. at least higher than 0.15 mol/L), leaving the bulk of the Ln(III) in the aqueous raffinate. Up to now the most advanced system considered is based on the mixture of BADPTZ and \(\alpha\)-cyanodecanoic acid in solution in TPH in the presence of a modifier. Development work has been done to design the flowsheet which will be operated for a feed with a 0.2 mol/L nitric acid concentration, and corresponding to a An(III)+Ln(III) solution generated by the DIAMEX process. The flowsheet has been defined by P. Baron at CEA/Marcoule for runs which will be carried out in a bank of 16 miniature centrifugal-contactors installed in a hot-cell at the ITU/Karlsruhe. Hot tests are foreseen to be carried out in December 1998 or in the early beginning of 1999.

Owing to the extraordinary properties of the BTPs and of the very interesting properties of the \textit{bis}-1,2,4-triazoles derivatives synthesised by Z. Kolarik \textit{et al.} in consultation with Reading at KZK/Karlsruhe, processes for An(III)/Ln(III) group separation will be also developed by
CEA/Marcoule and ENEA/Polimi and tested in the near future. At the moment, the research concerns the scaling-up of the synthetic procedure to be able to have sufficient quantities of extractants to run the processes in centrifugal-contactor loops. Results in this field are expected in 1999.

Substituted di-thiophosphinic extractants

Experiments have been conducted at FZJ/Jülich, and also at the ITU/Karlsruhe, in order to define an An(III)/Ln(III) separation process based on the use of the outstanding properties of the di-thiophosphinic extractants.

The main results obtained so far can be summarised as follows:

- **At Jülich:**
  - The radiolytic degradation of the CYANEX 301 has been studied. It was found that the instability of the extractant was not extensive, but the radiolytic degradation products have a detrimental effect on the SF \text{An/Am}. Consequently, this point is of great importance for process design.
  - The radiolytic degradation of the substituted phenyl di-thiophosphinic acids was studied. It was found that their radiolytic instability was lower than that exhibited by the CYANEX 301 itself. These molecules can thus be considered as promising candidates for the design of an An(III)/Ln(III) separation process.
  - An(III)/Ln(III) separation test was made on synthetic spiked solution using a synergistic mixture made of bis-chlorophenyl-di-thiophosphinic acid and TOPO. The flowsheet was defined in collaboration with P. Baron from CEA/Marcoule and the test was performed using a bank of 8 stages of centrifugal contactors. Good separation performances were obtained. This represents a very encouraging result because the feed was 0.5 mol/L in nitric acid. One may observe that no such performances have been ever published to date.

- **At ITU (in collaboration with FZJ/Jülich)**
  - Tests of an An(III)/Ln(III) separation process based on the use of CYANEX 301 in synergistic combination with TBP was carried out with a genuine liquid waste. Highly successful results were obtained for purified CYANEX 301+TBP mixture; in only three stages, the effluent was decontaminated vs An(III) (Am and Cm) by a factor higher than 10 and the Am+Cm fraction was decontaminated from the Ln (III); DFAn/Ln > 400 was reached. These first results are very encouraging.

Conclusions

Considerable progress have been made in the field of minor actinide partitioning during the NEWPART research programme. Among the main achievements one can cite:

- **DIAMEX process** — Definite progresses have been made in the understanding of the basic chemistry of malonamide extractants in their ability to react with trivalent actinide and lanthanide nitrates. This was achieved with the systematic use of crystal structure determinations, X-ray absorption spectroscopy and molecular modelling. As far as the DIAMEX process development is concerned, one can mention that we extended the choice
for a good process by designing three flowsheets with the first reference malonamide extractant, DMDBTDMA, and by optimising the formula of a new malonamide, the DMDOHEMA, suitable for the design of an improved DIAMEX process flowsheet. Active tests of theses new processes are foreseen in the near future.

- An(III)/Ln(III) group separation — Here also the results obtained are quite impressive. New, very interesting nitrogen polydentate ligands were prepared and studied which exhibit far better properties than those corresponding to the previously known ligands of this type. In particular, the most important results correspond to the pyridine-bis-1,2,4-tri-azines prepared by Z. Kolarik at FZK. These molecules are able to selectively extract An(III) nitrates from Ln(III) and this for a 1 to 2 mol/L nitric acid feed. Very interesting results were also obtained in this field with bis-chlorophenyl-di-thiophosphinic acid and TOPO mixture. Good separation between An(III) and Ln(III) were obtained for a 0.5 mol/L nitric acid feed during the implementation of a counter-current test carried out with a bank of centrifugal contactors with synthetic spiked solution.

In conclusion, we can say that we are confident with the fact that the processes under study can be developed to reach the goals required for modern efficient industrial minor actinide partitioning processes.

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