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A NEW CONCEPT FOR An(III)/Ln(III) SEPARATION USING TODGA EXTRACTANT

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Abstract

One of the different options investigated by the CEA Marcoule (in the framework of the EURATOM FP7 collaborative project ACSEPT) to separate trivalent minor actinides (Am(III) to Cf(III)) directly from PUREX raffinates by solvent extraction takes advantage of both (i) the high efficiency of the TODGA diglycolamide to extract trivalent 4*f* and 5*f* elements from nitrate/nitric aqueous solutions, and (ii) the selectivity of hydrophilic polyaminocarboxylic acids that complex trivalent 5*f* elements in buffered conditions better than 4*f* elements. The extraction system was optimized (both the formulations of the organic solvent and of the aqueous scrubbing and stripping solutions) to meet the requirements of an efficient flowsheet design allowing An(III) recovery yields greater than 99.9%, with high decontamination factors *versus* Ln(III) in only one SANEX cycle.

Introduction

Recycling trivalent minor actinides by separation and transmutation is worldwide considered as one of the most promising strategies to reduce the inventory of radioactive waste, thus contributing to make nuclear energy more sustainable. Several SANEX¹ processes have been investigated at the CEA Marcoule through the past decades. Studies started with ligands containing soft donor atoms such as the tridentate nitrogen bearing TriPyridylTriazine (TPTZ) [1] and BisTriazinylPyridines (BTPs) [2], or the sulphur bearing dialkyl-dithiophosphinic acid (CYANEX 301) [3]. These second cycle systems only applied on solutions containing the trivalent minor actinides (An = Am to Cf) and the lanthanides (Ln) issued from the DIAMEX first cycle, where the An(III) and Ln(III) were selectively separated from the whole inventory of elements composing PUREX raffinates. Recently however, a binary extracting system composed of a malonamide (DMDOHEMA, *N,N'*-dimethyl-*N,N'*-dioctylhexylethoxymalonamide, used in the DIAMEX process) and a dialkylphosphoric acid (di(2-ethylhexyl)-phosphoric, HDEHP) has proved to be efficient to recover the trivalent minor actinides directly from PUREX raffinates [4]. This particular process (DIAMEX-SANEX/HDEHP) can separate the An(III) directly from PUREX raffinates in one single cycle, by (i) co-extracting the An(III) + Ln(III) fraction at high acidity ($[\text{HNO}_3] > 3\text{M}$), thanks to the malonamide DMDOHEMA as in the DIAMEX process, and (ii) selectively stripping the An(III) using an hydrophilic polyaminocarboxylate in a buffered aqueous solution (pH~3), while the Ln(III) remain extracted in the organic phase thanks to the dialkylphosphoric acid HDEHP (the malonamide being unable to extract the trivalent elements in these conditions). However, the combination of the malonamide and the dialkylphosphoric acid promotes the coextraction of some *d*-block transition metals, which must be dealt with by specific stripping steps and thus increase the volume of the process output streams.

That is why researches are currently pursued at the CEA Marcoule, within the collaborative project ACSEPT² (7th EURATOM framework program), in order to investigate new extracting agents that could present higher extracting properties than DMDOHEMA at low acidity, and could therefore replace the DMDOHEMA/HDEHP couple of extractants. Firstly developed by JAEA researchers to recover minor actinides within the ARTIST process [5], *N,N,N',N'*-tetraoctyl-diglycolamide (TODGA) extractant was recently studied during the European integrated project EUROPART³ (6th EURATOM framework program) and successfully implemented counter-currently to co-extract An(III) and Ln(III) from a genuine highly active PUREX raffinate [6]. It presents outstanding extraction properties toward trivalent actinides and lanthanides elements. The present paper describes the results of the R&D studies performed at the CEA Marcoule to optimize an extraction system based on TODGA to meet the requirements of an efficient flowsheet design allowing An(III) recovery yields from PUREX raffinates greater than 99.9%, with high decontamination factors *versus* Ln(III) in only one cycle.

Principle of the SANEX-TODGA process

The DIAMEX-SANEX/HDEHP one-cycle process, which allows the selective separation of the trivalent minor actinides (An(III) = Am(III) to Cf(III)) from PUREX raffinates, takes advantage of the combination of:

¹ SANEX: Separation of ActiNides by Extraction.

² ACSEPT: Actinide reCYcling by SEParation and Transmutation (Contract Number: FP7-CP-2007-211 267).

³ EUROPART: EUROpean research program for the PARTitioning of minor actinides from high active wastes issuing the reprocessing of spent nuclear fuels (Contract Number: FI6W-CT-2003-508 854).

1. A solvation extractant, DMDOHEMA (*N,N'*-dimethyl-*N,N'*-dioctylhexylethoxy-malonamide, the reference malonamide used in the DIAMEX process), which extracts various trivalent elements from acidic aqueous solutions (e.g., $[\text{HNO}_3] > 3\text{M}$);
2. A cation exchanger, HDEHP (di(2-ethylhexyl)-phosphoric acid, the reference dialkylphosphoric acid used in the TALSPEAK process), which extracts trivalent metallic cations at low pH by proton exchange;
3. An hydrophilic polyaminocarboxylate complexing agent, HEDTA (*N*-(2-hydroxyethyl)ethylenediamine-*N,N',N'*-triacetic acid), which can selectively strip the An(III) in buffered conditions (e.g., $\text{pH} \leq 3$, using citric acid).

As schematically described on Figure 1, the DIAMEX-SANEX/HDEHP process separates the An(III) from the Ln(III) through the following three steps (other steps, such as the stripping of *d*-block transition metals are not described hereafter):

1. Co-extraction of the An(III) and the Ln(III) by the DMDOHEMA from PUREX raffinates;
2. Selective stripping of the An(III) by HEDTA in a citric acid buffered solution, while the Ln(III) are maintained extracted in the organic phase by HDEHP;
3. Back-extraction of the Ln(III) in 1 M nitric acid.

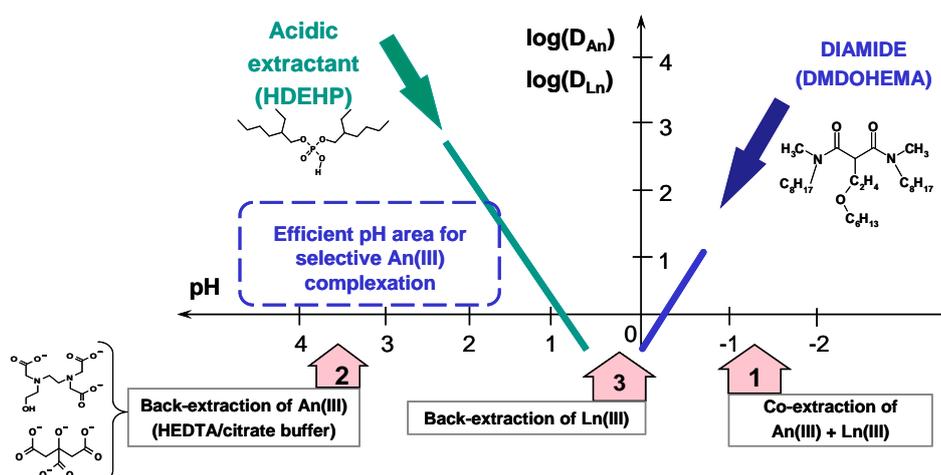


Figure 1: Principle scheme of the DIAMEX-SANEX process for An(III)/Ln(III) separation

Although the DIAMEX-SANEX/HDEHP process has proved to be efficient to separate the trivalent minor actinides from genuine PUREX raffinates [4], the combination of the malonamide and the dialkylphosphoric acid presents some drawbacks:

- There is a synergistic co-extraction of some *d*-block transition metals such as Pd(II), Fe(III), Zr(IV), and Mo(VI), which must be dealt with by specific stripping steps and thus increase the volume of the process output streams;
- The modelling of the process flowsheet is rather difficult because of the complexity of the system (two extractants presenting opposite extraction mechanisms in the organic phase, with synergism and/or antagonism depending on the acidity and metallic cation nature, and two hydrophilic molecules in the aqueous phase: a complexant and a buffer that can undergo various reactions);
- The regeneration of the spent solvent is complicated by the degradation of the two organic extractants (e.g., their respective degradation products may interact with each others).

Therefore, the teams of the CEA Marcoule have searched for an extractant that would present the advantages of both the malonamide DMDOHEMA (extraction of the trivalent elements at high acidity) and the dialkylphosphoric acid HDEHP (extraction of the trivalent elements at low acidity). *N,N,N',N'*-tetraoctyl-diglycolamide (TODGA), which was first developed by JAEA researchers to recover minor actinides within the ARTIST concept [5], presents such outstanding properties. Actually, TODGA possesses so high extraction efficiencies toward Ln(III) and An(III), as compared to DMDOHEMA, that it could replace the DMDOHEMA/HEDHP extractant couple in the DIAMEX-SANEX process, with the help of a salting-out agent used at the An(III) stripping-step to keep the Ln(III) extracted in the organic phase (the salting-out agent provides nitrates that displace the solvation extraction equilibrium of the Ln(III) at low acidity, where the An(III) are selectively stripped by the polyaminocarboxylate complexant). If DMDOHEMA was used alone the concentration of nitrate anions required to maintain the Ln(III) in the organic phase would be such that any process industrial application would become deterrent. TODGA extractant makes this application possible with relatively minor constraints. Furthermore, TODGA presents a slight selectivity toward some Ln(III), more favourable for the SANEX process application than DMDOHEMA, which extracts Am(III) better than Eu(III).

Optimization of the separation system

Solvent formulation

TODGA ligand has a rather poor loading capacity and requires the addition of a phase modifier (*e.g.* monoamide DHOA [5]) to avoid third phase formation. In the frame of the European integrated project EUROPART, studies on TODGA process development had demonstrated the possibility to recover jointly the trivalent actinides and lanthanides from a genuine PUREX raffinate. The demonstration was made by implementing at the Institute of the Transuranium Elements (ITU, Karlsruhe, Germany) a counter-current separation flowsheet designed at the CEA Marcoule, involving a solvent consisting of TODGA and TBP (to ensure sufficient solvent loading capacity especially toward the Ln(III)), dissolved in hydrogenated tetrapropene (HTP) [6].

The same kind of binary solvent was selected by the CEA researchers to optimise the formulation of the SANEX-TODGA solvent. TBP was preferred to the monoamide DHOA, as the TODGA phase modifier, because of the validation of the applicability of this binary mixture to successfully treat a genuine PUREX raffinate. Furthermore, it was observed that DHOA decreases the extraction properties of TODGA by a factor of 2. The respective concentrations of TODGA (provided by Pharmasynthèse) and TBP (provided by Sigma Aldrich) were optimized in HTP (provided by Novasep) to allow the whole inventory of An(III), Ln(III), plus Y(III) present in a UOX3 type spent nuclear fuel to be extracted (*i.e.*, the loading capacity of the SANEX-TODGA solvent should exceed 25 mM).

Aqueous solution formulations

As in the French DIAMEX process, oxalic acid and hydroxyethyl-diamine-triacetic acid (HEDTA) can be added as complexing agents in the extraction section to avoid the extraction of zirconium, iron, and palladium. Strontium extraction, which is favoured in the case of TODGA as compared to DMDOHEMA might be disabled by reducing the concentration of the scrubbing acidity.

The requirements targeted when optimizing the formulation of the aqueous solution of the An(III)/Ln(III) partitioning section, were the following:

- Distribution ratios of the Ln(III) and of Y(III) exceeding 0.5;
- Sufficiently high An(III)/Ln(III) selectivity: $SF_{Ln/An} = D_{Ln}/D_{An} > 6$;
- As low as possible sensitivity of the process performances to pH variation (due to the stripping of the nitric acid extracted with the Ln(III) and An(III) in the extraction step).

The strategy adopted has consisted in assessing the efficiency of different couples of hydrophilic An(III) complexing agents and buffers to selectively strip the An(III) from a SANEX-TODGA loaded solvent, using An(III) spiked surrogate UOX3 PUREX raffinates in test tubes. The major difficulty encountered was to minimize as much as possible the impact of the solvent acidity (nitric acid is mostly extracted by TBP) on the pH of the aqueous stripping solution and hence on the An(III)/Ln(III) separation. Various hydrophilic complexing agents have been investigated in combination with various carboxylic buffers, as shown on Figure 2. The choice ended up with diethylene-triamine-pentaacetic acid (DTPA) to complex all the An(III) potentially present in the PUREX raffinate and malonic acid to buffer the aqueous stripping solution.

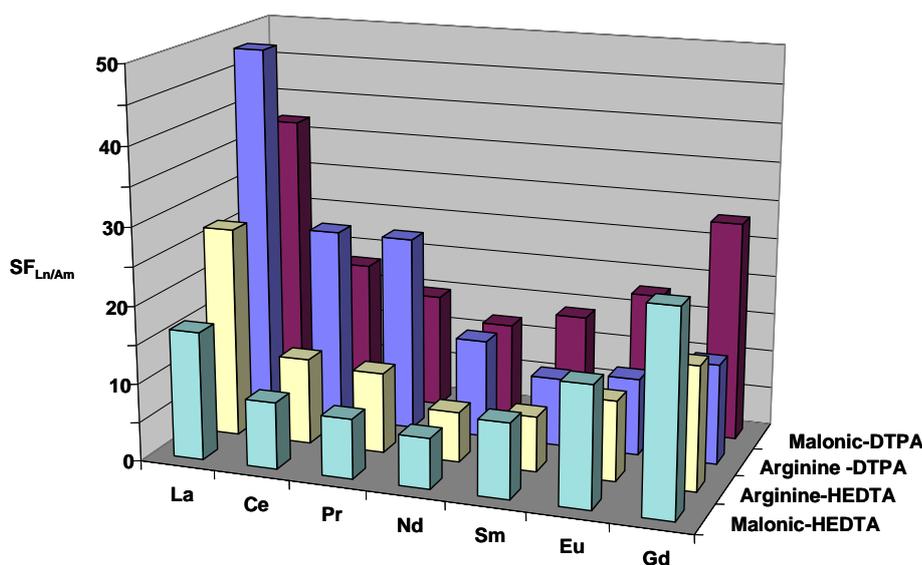


Figure 2: Optimization of the aqueous An(III) stripping solution in the SANEX-TODGA process for An(III)/Ln(III) separation

Since the extraction performances appeared to be very sensitive towards pH variations, it was decided to process the flowsheet at a rather low pH to reduce the amount of nitrate anions required to maintain the Ln(III) in the organic solvent while the An(III) are selectively stripped by DTPA. As a matter of fact, the higher the pH is in the aqueous phase the stronger is the complexation of the trivalent metallic cations with DTPA and hence the worse is the extraction efficiency of Ln(III) by TODGA, thus requiring more nitrate anions to compensate. Ln(III) distribution ratios vary with different powers of $[HNO_3]$ ranging from 1 to 4 as shown on Figure 3. Therefore, the pH value of the buffered An(III) stripping solution and the concentration of nitrate anions were optimized to allow

both good An(III)/Ln(III) selectivities and comfortable margins for process operation in case some nitric acid was carried over the extraction/scrubbing section into the An(III)/Ln(III) partitioning section by TBP. In the process, the nitrate anions are introduced either through the addition of sodium nitrate or hydroxylamine nitrate.

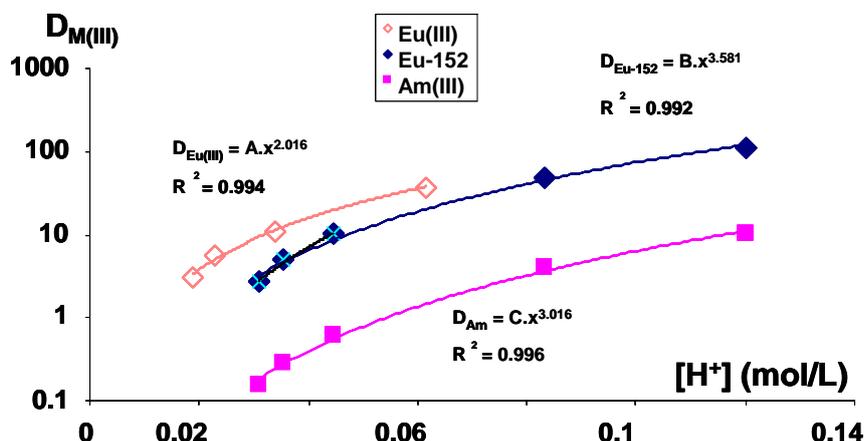


Figure 3: Variation of the distribution ratio of Eu(III) with regard the acidity of the buffered An(III) stripping solution (malonic acid + DTPA) in the SANEX-TODGA process

Conclusion

CEA researchers have imagined a one-cycle An(III)/Ln(III) separation process based on the TODGA/TBP solvent, since it provides sufficiently high extraction efficiency toward trivalent *4f* and *5f* elements as compared to DMDOHEMA to allow the selective stripping of the An(III) by a hydrophilic polyaminocarboxylic complexing agent (DTPA) in a buffered solution (malonic acid), while the Ln(III) remain extracted in the solvent thanks to the salting-out effect of nitrate ions.

Based on the promising results obtained in test tube experiments carried out on An(III) spiked surrogate UOX3 PUREX raffinates a SANEX-TODGA process flowsheet will be elaborated and proposed for further validations through counter-current cold and hot tests.

Acknowledgments

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