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Results of recent counter-current tests on An(III)/Ln(III) separation using TODGA extractant

Xavier Hérès, Christian Sorel, Manuel Miguirditchian, Béatrice Camès, Clément Hill, Isabelle Bisel, Denis Espinoux, Catherine Eysseric, Pascal Baron, Brigitte Lorrain
CEA/DEN/MAR/DRCP, Marcoule, BP17171, 30207 Bagnols/Cèze, France
Tel: 33.4.66.79.16.10, Fax: 33.4.66.79.65.67, Email: clement.hill@cea.fr

Abstract – One of the different options investigated at the CEA Marcoule to separate trivalent minor actinides (An(III) = Am(III) to Cf(III)) directly from PUREX raffinates by solvent extraction takes advantage of both the high efficiency of the diglycolamide, *N,N,N',N'*-tetraoctyl-diglycolamide (TODGA), to extract trivalent 4f and 5f elements from nitrate containing aqueous solutions, and the selectivity of hydrophilic polyaminocarboxylic acids, which better complex trivalent 5f elements than 4f elements in buffered conditions, and hence allow the former elements (An(III)) to be selectively stripped, whereas the latter elements (Ln(III)) remain in the solvent and are further back-extracted in diluted nitric acid. The major difficulty of this separation process is to tune the pH in a very narrow range of operating conditions, at the An(III) selective stripping step, because of the high sensitivity of the performances of the flowsheet. The extraction system was optimized to meet the requirements of an efficient process flowsheet allowing recovery yields greater than 99.9% to be obtained for the An(III), with high decontamination factors vs Ln(III), in only one cycle after the PUREX process implementation. A cold test was successfully carried out in small scale mixer-settlers in the Marcel testing loop, using a surrogate feed composed of major fission products. A medium activity test was further implemented in similar laboratory contactors, in the glove boxes of the ATALANTE facility, on a surrogate feed spiked with Am-241, Cm-244, and Eu-152. This paper describes the results of these two counter-current tests.

I. 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 SANEX^b processes have been investigated at the CEA Marcoule during the past two decades. Studies started with ligands containing soft donor atoms, such as the tridentate nitrogen bearing TriPyridylTriazine (TPTZ) and BisTriazinylPyridines (BTPs)¹, or the sulfur bearing dialkyl-dithiophosphinic acid (CYANEX 301)². These systems could only be implemented as second cycles, after the DIAMEX process that co-extracts trivalent 4f and 5f elements (respectively Ln(III) and An(III)). More recently, a binary extracting system composed of a malonamide (*N,N'*-dimethyl-*N,N'*-dioctyl-hexylethoxy-malonamide, DMDOHEMA, used in the DIAMEX process) and a dialkylphosphoric

acid (di(ethyl-2-hexyl)-phosphoric acid, HDEHP, used in the TALSPEAK process) has proved to be efficient to selectively recover trivalent minor actinides from genuine PUREX raffinates in only one cycle³⁻⁵. Nevertheless, new extracting agents are still under investigation at the CEA Marcoule to develop simpler An(III) partitioning processes. This is the case of *N,N,N',N'*-tetraoctyl-diglycolamide (TODGA), an extractant which was first developed by JAEA researchers to recover minor actinides within the ARTIST concept.

TODGA ligand presents a very high extraction affinity toward trivalent actinides. However, its rather poor loading capacity requires the addition of a phase modifier (e.g., monoamide, DHOA⁶, or TBP⁷). For example, studies carried out at FZ Jülich and the ITU (Karlsruhe) during the EUROPART collaborative project (led by the CEA Marcoule from 2003 to 2007 within the 6th EURATOM Framework Program) to develop a viable TODGA process have validated the possibility to recover jointly Ln(III) and An(III) from a genuine PUREX raffinate, using a solvent consisting of TODGA and TBP dissolved in hydrogenated

^b SANEX : Separation of ActiNides by EXtraction

tetrapropene (HTP). More than 99.9% of americium and curium, along with the lanthanides and yttrium, could be separated from the genuine feed⁷. As in the French DIAMEX process, oxalic acid and N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) were added as masking agents, both in the extraction and in the fission products scrubbing sections, to avoid zirconium, iron, and palladium extractions. Strontium extraction (much higher for TODGA than for DMDOHEMA, the malonamide used in the DIAMEX process) was disabled by adding a second scrubbing section at low acidity.

II. PRINCIPLE OF SANEX-TODGA PROCESS

CEA researchers have imagined a one-cycle An(III)/Ln(III) separation process based on the same TODGA/TBP solvent as used at the ITU, in view of the fact that it provides such a high extraction affinity toward trivalent 4f and 5f elements as compared to DMDOHEMA, that the selective stripping of the An(III) appears feasible by a hydrophilic polyaminocarboxylate complexing agent (e.g., DTPA as in the reverse-TALSPEAK process) in a buffered solution, while the Ln(III) remain complexed by TODGA in the organic solvent thanks to a salting-out agent (e.g., nitrates). The 4-step SANEX-TODGA process was elaborated, as described on Fig.1. It consists in, first, co-extracting the 4f and 5f elements from a PUREX raffinate (3M<acidity<4M) by a mixture of TODGA and TBP dissolved in HTP, then, stripping the trivalent minor actinides selectively thanks to a complexing polyaminocarboxylic acid in a buffered aqueous solution, while the trivalent lanthanides and yttrium remain in the solvent thanks to the salting-out nitrate anions, (III) and finally, stripping Ln(III) and Y(III) in an acidic solution of low ionic strength, before recycling the spent solvent after appropriate clean-up treatment.

III. OPTIMIZATION OF THE SEPARATION SYSTEM

III.A. Solvent formulation

In order to allow the whole inventory of An(III), Ln(III), and Y(III) to be fully extracted from PUREX raffinates^c, the loading capacity of the SANEX-TODGA solvent should exceed 25 mM. This is achieved by adding TBP to TODGA in HTP, since almost 80 mM of Ln(III) and Y(III) can be extracted from UOX3 PUREX raffinate surrogate solutions. This organic phase formulation allows possible saturation of the solvent by the lanthanides during the process without any risk of third phase formation.

^c Raffinates issued from the treatment of UOX3 spent nuclear fuels by the PUREX process.

III.B. Aqueous solution formulation

The requirements to be fulfilled when optimizing the formulation of the aqueous solution used for the An(III)/Ln(III) partitioning step, are the following:

- Distribution ratios of the Ln(III) and of Y(III) exceeding 0.5;
- Sufficiently high An(III)/Ln(III) selectivities: $SF_{Ln/An} = D_{Ln}/D_{An} > 6$;
- As low as possible sensitivity of the process performances to pH variations (the nitric acid co-extracted with the Ln(III) and An(III) at the extraction step can be stripped at the An(III)/Ln(III) partitioning step and hence modify the pH of the aqueous stripping solution).

The strategy adopted 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 in test tubes, using surrogate solutions of UOX3 PUREX raffinates, spiked with An(III).

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 yields. Various hydrophilic complexing agents have been investigated in combination with various carboxylic buffers. The choice ended up with diethylene-triamine-pentaacetic acid (DTPA) and malonic acid, the concentrations of which have been optimized respectively to complex all the An(III) potentially present in the PUREX raffinate and to buffer the aqueous stripping solution. Since the extraction performances appeared to be very sensitive toward pH variations, it was decided to process the flowsheet at a rather low pH to reduce the amount of nitrate anions (introduced either through the addition of sodium nitrate or hydroxylamine nitrate in the stripping solution) 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 in the aqueous phase, the stronger the complexation of the trivalent metallic cations with DTPA, and hence, the worse the extraction of Ln(III) by TODGA, thus requesting more nitrate anions to compensate for DTPA complexation.

IV. COUNTER-CURRENT TESTS

Based on the thermodynamic constants reported in the literature for the complex formation of trivalent 4f and 5f elements with DTPA and assuming the stoichiometry of potentially extractable acidic complexes of nitric, oxalic, and malonic acids with TODGA and TBP, a process flowsheet was calculated with the PAREX simulation code (Fig. 1) in order to reach more than 99.9% An(III) recovery, with less than 5%_{mass} Ln(III). The whole process

flowsheet (except solvent treatment step) was implemented on a cold surrogate feed, but only a part of the whole process flowsheet was implemented on a surrogate feed spiked with Am-241 and Cm-244.

IV.A. Cold test

The objectives of the cold counter-current test performed in the MARCEL testing-loop (Fig. 2) of the CEA Marcoule were:

- to assess the hydrodynamic behavior of the SANEX-TODGA separation system (all steps of Fig. 1, except that of spent solvent treatment) in the same laboratory-scale mixer-settlers as the ones that should be implemented in the shielded cells of the ATALANTE facility for the hot test on a genuine PUREX raffinate;
- to determine the decontamination factors of the fission products;
- to (in)validate the model and code calculations.

The cold surrogate feed contained all the fission products potentially present in a genuine PUREX raffinate (Table I).

The counter-current test ran for 30 hours without any hydrodynamic problem. The pH value in the stripping section remained fairly stable all along the test and the separation performances were satisfactory:

- Less than 1%_{mass} of the initial quantity of elements present in the feed (including Fe, Sr, Y, Mo, Zr, Pd and the Ln) followed the expected An product (absent in this cold test).
- Ln elements, supposed to mimic An elements, were effectively extracted from the feed; their final concentrations in the raffinate and the spent solvent were lower than the detection limit (0.5 mg/L).
- Around 2.5% of Pd and more than 99% of Y followed the Ln production flux.

Comparisons of experimental and calculated concentration profiles of nitric acid, in the extraction and scrubbing sections, and of europium, in the whole flowsheet, are shown on Fig. 3.

IV.B. Spiked test

The objectives of the counter-current test performed in the glove boxes of the ATALANTE facility on a surrogate feed spiked with Eu-152, Am-241, and Cm-244 were:

- to assess the An(III)/Ln(III) separation efficiency on a reduced number of stages in the An(III) stripping section (see Fig. 4);
- to determine the influence of pH variation on the process performances;
- to (in)validate the model and code calculations.

Prior to the counter-current test, the organic solvent was loaded with nominal amounts of Ln(III) using a surrogate feed, the composition of which is displayed in Table II. The loaded solvent was then spiked with Eu-152, Am-241, and Cm-244 for gamma/alpha analyses.

In-line UV-Visible spectrophotometric measurements allowed Am(III) and Nd(III) concentrations to be followed during the transient and steady state periods. Three tests were performed by varying the pH in the An-stripping section. The flowsheet sensitivity towards pH could thus be evaluated and the comparisons between the experimental and the calculated concentration profiles were satisfying for americium and europium, respectively in the An(III)-stripping and in the Ln(III)-stripping banks, as shown on Fig. 5.

V. CONCLUSIONS

Good results were obtained during the counter-current inactive and spiked tests performed in mixer-settler banks at the CEA Marcoule to validate the An(III)/Ln(III) separation in one cycle after the PUREX process, using a TODGA/TBP solvent. A hot test is planned in the hot cells of the ATALANTE facility in 2009 in order to confirm the process performances on a genuine PUREX raffinate. The reference flowsheet with the nominal number of An-stripping / Ln-stripping stages should achieve recovery yields of An(III) larger than 99.9% with high decontamination factors towards lanthanides(III).

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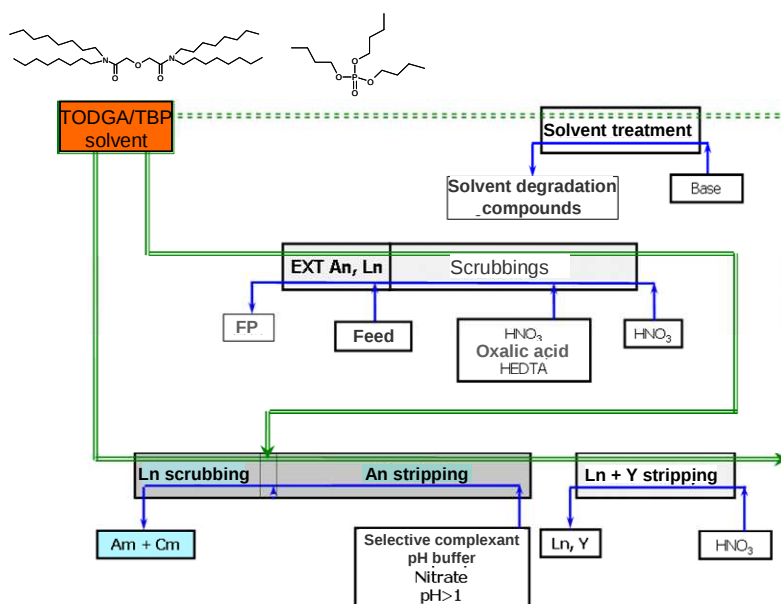


Fig. 1. Principle scheme of the SANEX-TODGA process for An(III)/Ln(III) separation.

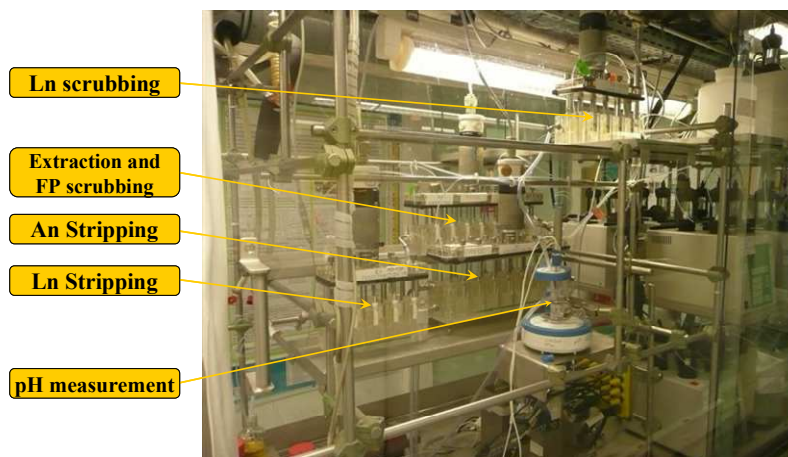


Fig. 2. MARCEL testing-loop used for the cold SANEX-TODGA test.

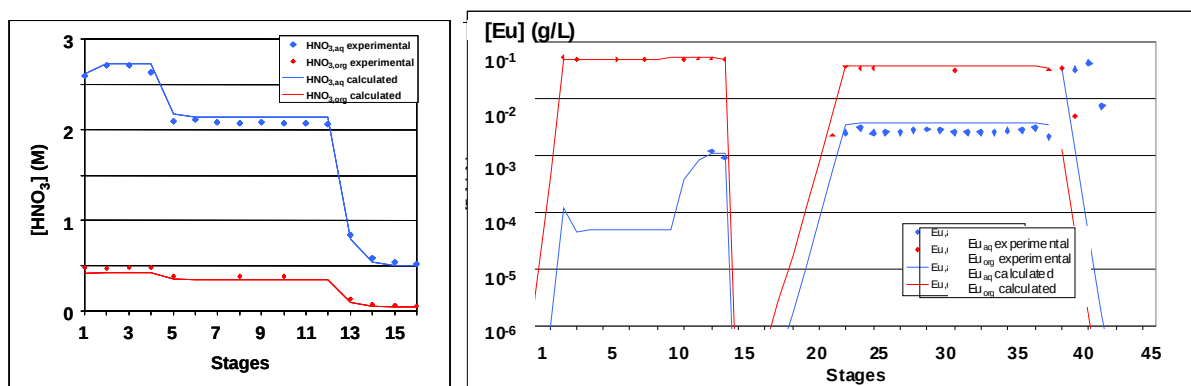


Fig. 3. Comparisons of experimental and calculated concentration profiles of nitric acid in the extraction and fission product scrubbing sections and of europium in the whole flowsheet.

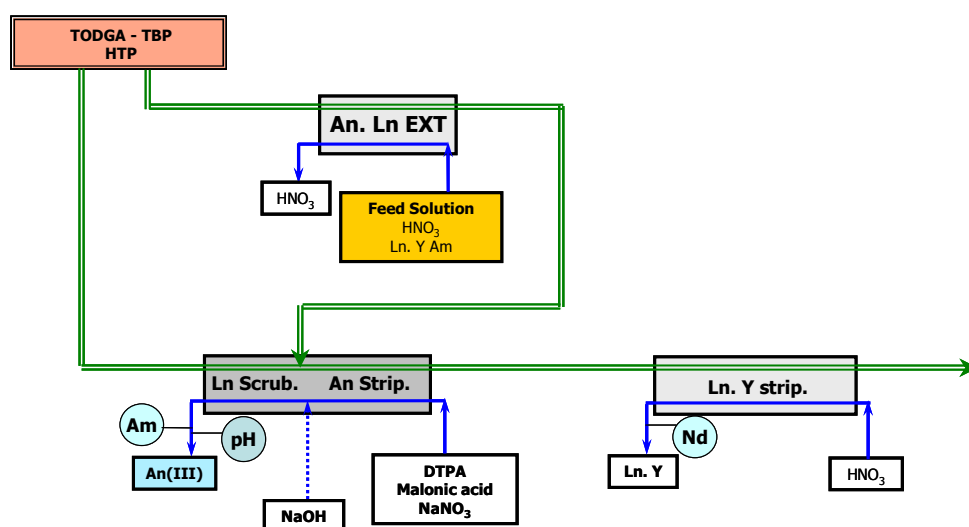


Fig. 4. Partial SANEX-TODGA flowsheet implemented to validate the An(III)/Ln(III) separation step in spiked counter-current test (ATALANTE).

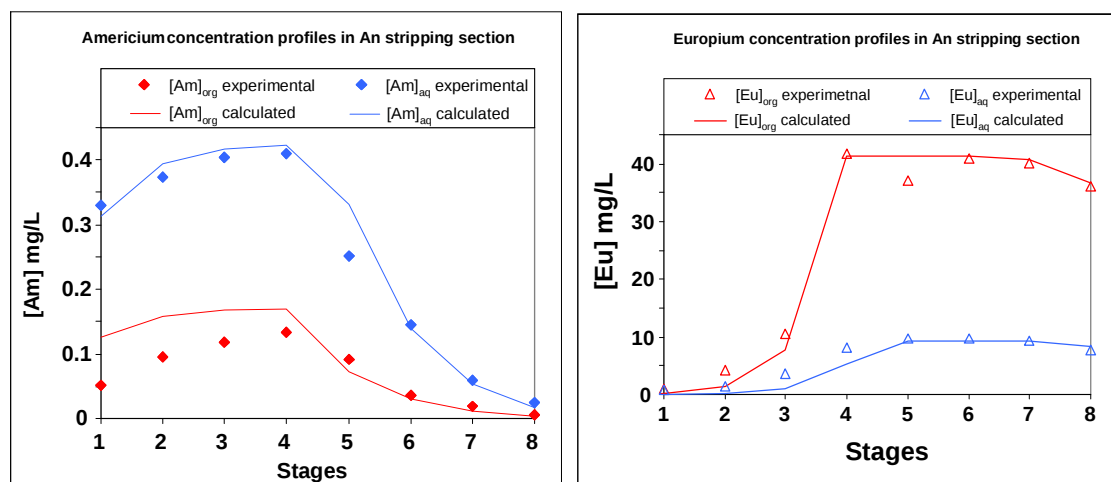


Fig. 5: Comparisons of experimental and calculated concentration profiles for americium and europium in the An(III)-stripping and in the Ln(III)-stripping banks.

TABLE I

Composition of the surrogate feed used in the SANEX-TODGA cold test

Element	Fe	Sr	Y	Mo	Zr	Pd	La	Ce	Pr	Nd	Sm	Eu	Gd
[mg/L]	92	257	145	1141	886	529	406	780	401	1311	287	50	48

TABLE II

Composition of the surrogate feed used in the SANEX-TODGA spiked test

Element	Y	La	Ce	Pr	Nd	Sm	Eu	Gd
[mg/L]	130	410	805	320	1250	260	51	52