

INACTIVE DIAMEX TEST WITH THE OPTIMIZED EXTRACTION AGENT DMDOHEMA

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Abstract

In the frame of the development of the DIAMEX process, first studies including counter-current hot tests were performed, with the DiMethyl-DiButylTetraDecylMAlonamide as reference extractant. In parallel, the diamide formula has been optimised so that a new extractant was proposed: the DiMethylDiOctylHexylEthoxyMAlonamide. This new reference extractant was used in two inactive flowsheets. The performances obtained were satisfying and confirmed the choice of DMDOHEMA as the new reference extractant for the DIAMEX process

Introduction

As part of the SPIN program, the CEA has undertaken the development of the DIAMEX process, which uses diamide extractants to separate minor actinides from fission products in High Level Liquid Waste. DIAMEX is the first step of the strategy adopted and leads to the coextraction of actinides(III) and lanthanides(III). Actinide/lanthanide separation will be achieved by another specific process.

Preliminary counter-current hot tests had confirmed the feasibility of the concept with the DMDBDTMA (DiMethyl-DiButyl-TetraDecyl-MalonAmide) [1].

Then, two routes have been studied to prevent from zirconium and molybdenum extraction ; two inactive flowsheets were performed with DMDBDTMA as extractant and finally oxalic scrubbing was preferred [2].

In parallel, studies have then been undertaken to optimise the diamide formula, so that performances would be improved. Distribution coefficients of actinides and lanthanides(III) have been enhanced, third phase boundary occurs at higher acidities and metal concentrations and degradation products are shorter and then easier to manage. Two inactive tests using mixer-settlers were carried out in order to qualify the DIAMEX reference flow-sheet with the new proposed DiMethyl-DiOctyl-HexaEthoxy-MalonAmide molecule (DMDOHEMA).

The objectives of the first test were to check :

- The quantitative extraction of lanthanides (simulating actinides).
- The high values of the decontamination factors towards Zr and Mo.
- The high value of the decontamination factor towards Fe.

The objective of the second test was to study the behaviour of Ruthenium.

Flow-sheet elaboration

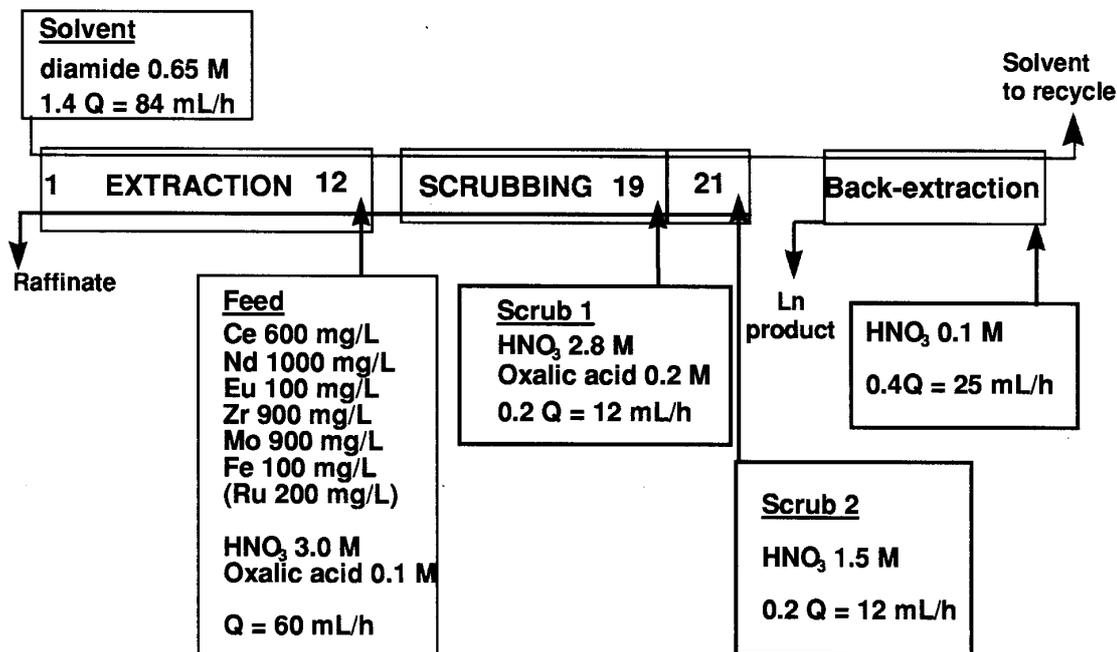
The “reference flow-sheet” was adapted to the new organic solvent, thanks to the PAREX code. The possible improvements of the “reference” flow-sheet using the DMDBDTMA were related to the better affinity of DMDOHEMA towards An(III) and Ln(III) :

- Decrease of nitric acidity in extraction and scrubbing sections (3 mol/L instead of 3.5 mol/L), to prevent from iron extraction.
- Decrease of the organic/aqueous flowrate ratio, so that solvent consumption was reduced.

In addition, concerning the stripping section, aqueous flowrate has been optimised (reduced), so that “An, Ln product” is recovered more concentrated.

The flow-sheet tested is presented in figure 1.

Figure 1 New DIAMEX flow-sheet designed for the inactive runs with DMDOHEMA



Experimental

The runs were conducted in mixer-settlers, composed of 21 stages for the “extraction-scrubbing” section and 8 stages for the back-extraction.

Hydraulic behaviour of the solvent in the mixer-settlers was satisfying for both runs.

Though, a black precipitate (probably RuO₂) occurred at the feed introduction stage, during the second run with Ruthenium. Nevertheless, this precipitate did not perturb the hydraulic behaviour of the mixer-settlers batteries.

Results of the cold runs

Both flowsheets which were similar, except the presence of ruthenium in the second one, achieved good and similar performances :

- Lanthanides extraction :
More than 98.5 % of Eu and more than 99.8 % of Nd and Ce were extracted.
- Disturbing fission products removal :
More than 99.7% of Zr and Mo were eliminated.
More than 98.1 % of Fe was eliminated.
Ru was eliminated at 79 %.
- Lanthanides pollution :
Less than 0.05 % of Zr.
0.11 % of Mo.
0.45 % of Fe.
3.4% of Ru.

Besides, experimentally measured metal ion concentration profiles were in good agreement with the calculated ones, except for iron and ruthenium, as it can be seen on figures 2 to 7 :

Figure 2 **Comparison between the Experimental and Calculated Nitric acid Profiles in the Extraction-Scrubbing Section (Test 2)**

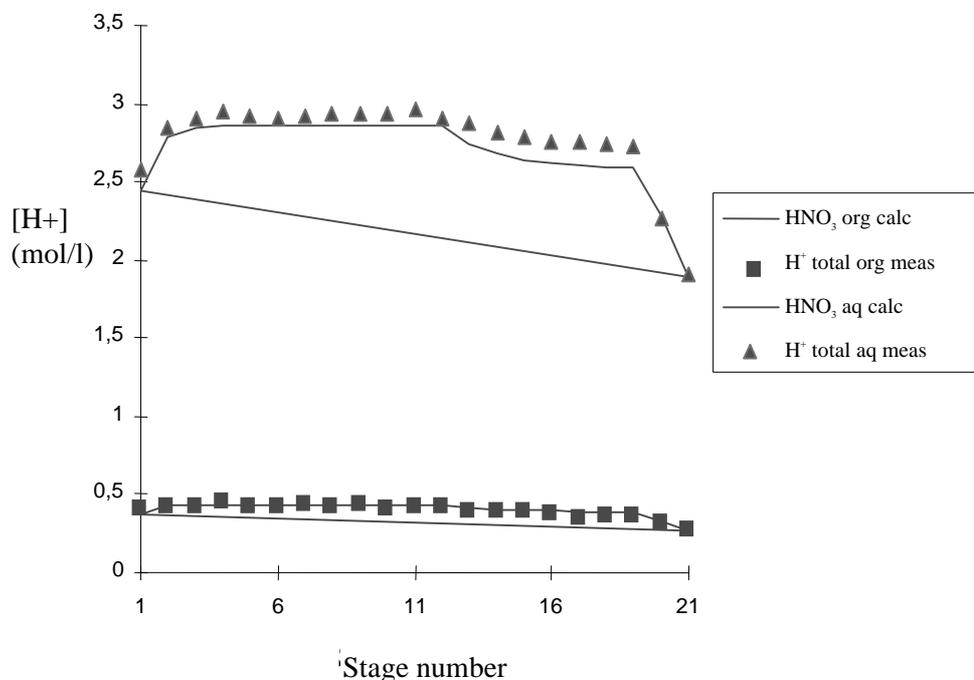


Figure 3 **Comparison between the Experimental and Calculated Neodymium Profiles in the Extraction-Scrubbing Section (Test 2)**

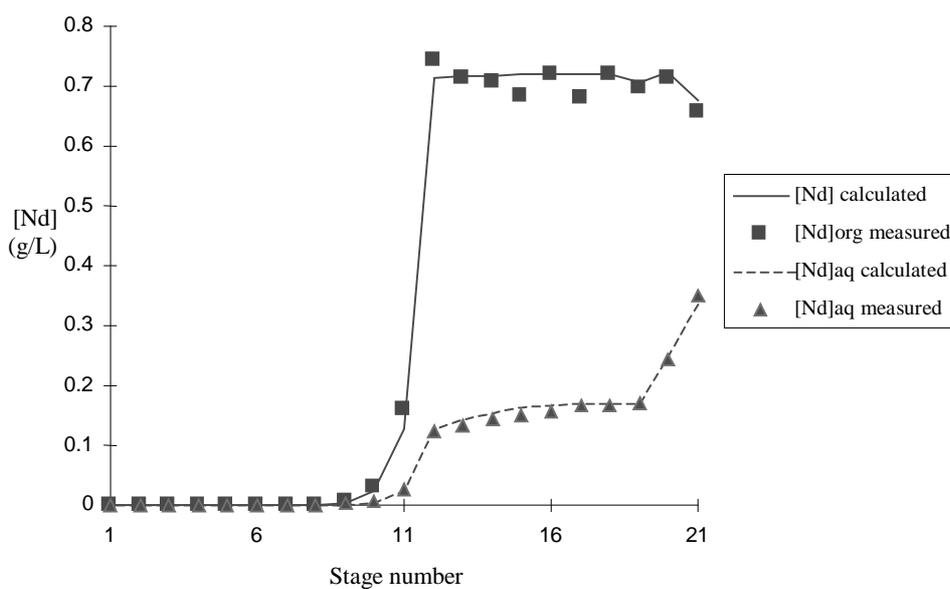


Figure 4 Comparison between the Experimental and Calculated Zirconium Profiles in the Extraction-Scrubbing Section (Test 2)

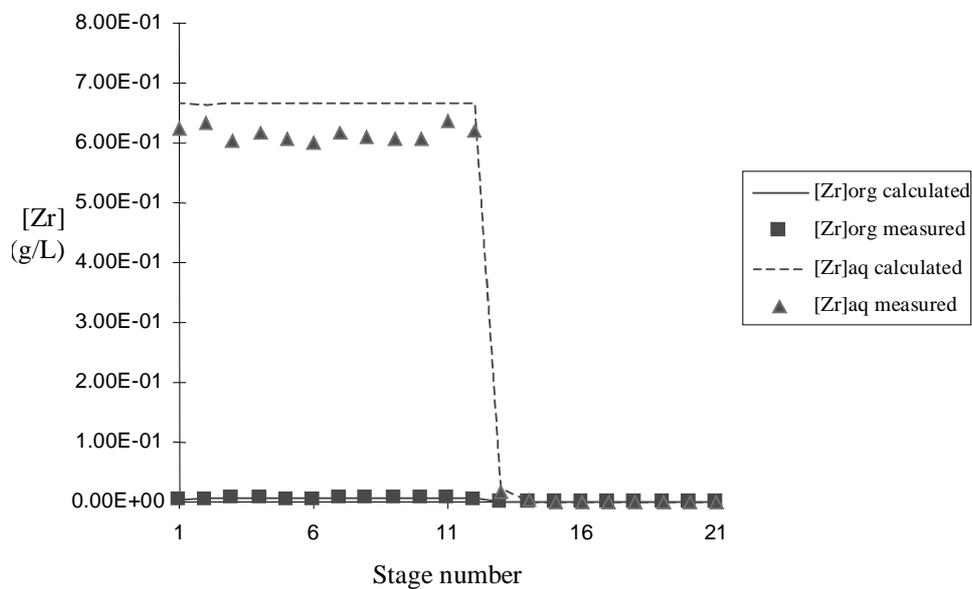


Figure 5 Comparison between the Experimental and Calculated Molybdenum Profiles in the Extraction-Scrubbing Section (Test 2)

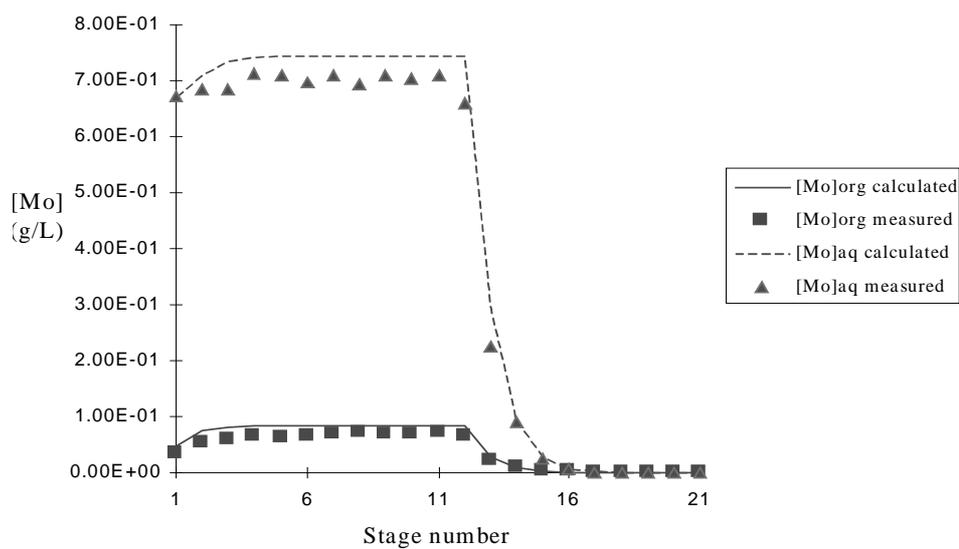


Figure 6 Comparison between the Experimental and Calculated Iron Profiles in the Extraction-Scrubbing Section (Test 2)

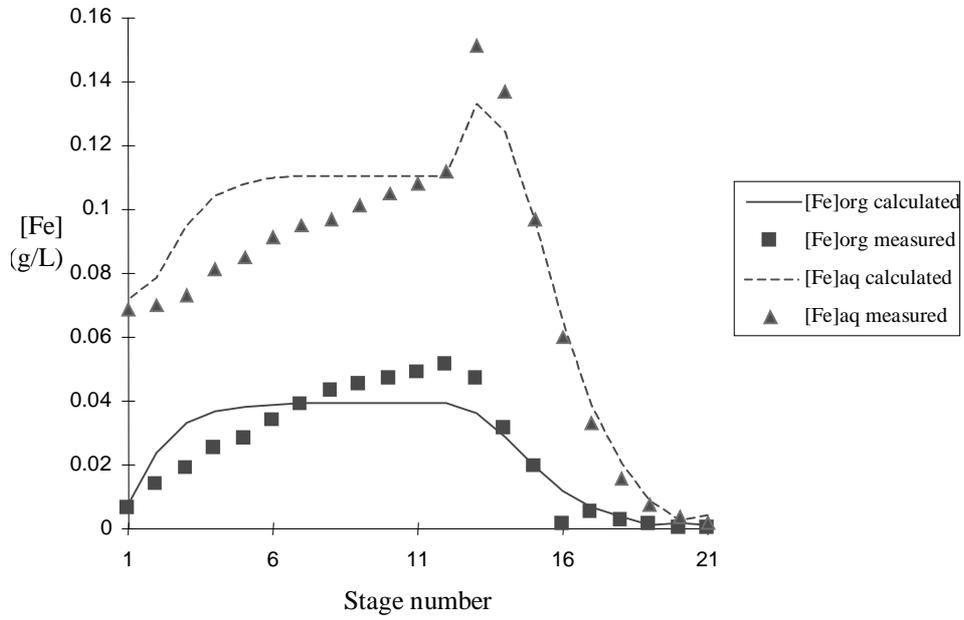
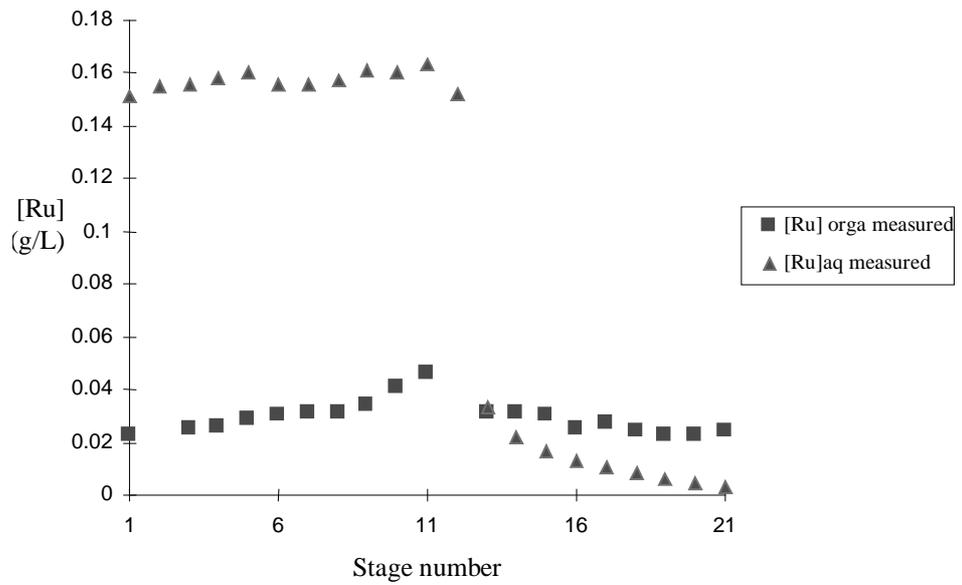


Figure 7 Experimental Ruthenium Profiles in the Extraction-Scrubbing Section (Test 2)



Conclusion

The inactive runs enabled us to confirm the choice of DMDOHEMA as a new extracting agent for the DIAMEX process, because :

- The hydrolytic behaviour was correct,
- The performances regarding lanthanides extraction were excellent and as good as those obtained with DMDBTDMA.
- The elimination of Zirconium was quantitative as with DMDBTDMA.
- The elimination of both Molybdenum and Iron was improved :
 - 99.7 % for Molybdenum (to be compared to 95 % for DMDBTDMA)
 - 98.1 % for Iron (to be compared to 27 % for DMDBTDMA)
- The efficiency to remove ruthenium was encouraging ; it is better than in the case of the run performed in the CYRANO hot cell (50 % of Ru only were eliminated in the CYRANO run, whereas 79 % of Ru were eliminated in these runs).

Nevertheless, these runs have also shown that the chemistry of Iron, and most of all that of Ruthenium, still had to be investigated and our knowledge deepened, because a good simulation of their chemical behaviour was not yet obtained for synthetic solutions.

Acknowledgements

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