



## DIAMEX SOLVENT REGENERATION STUDIES

C. NICOL, B. CAMES, L. MARGOT, L. RAMAIN  
Commissariat à l'Energie Atomique  
DCC/DRRV/SEMP/LNE

BP 171, 30207 BAGNOLS sur CEZE Cédex (France)

Tél. : 33 4 66 79 65 24 FAX : 33 4 66 79 16 49 E-mail : christine.nicol@cea.fr

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### ABSTRACT

The CEA has undertaken the development of the DIAMEX process as the first step in the strategy aiming at recovering minor actinides which could then be transmuted or separately conditioned (1, 2).

The scientific feasibility of this process was demonstrated during counter current hot tests operated in 1993 (3). Then experimental works were conducted, on one hand to optimise the extractant formula, on the other hand to improve the flowsheet. Reference extractant and flowsheet were then chosen, respectively in 1995 and 1996 (4, 5).

The next step, still in progress, is the demonstration of the DIAMEX technical feasibility (in 2002) ; this means that the flowsheet should include solvent regeneration treatments. In this aim, degradation studies were performed to quantify main degradation products, and identify those which could be disturbing in the process.

This paper deals with experimental studies performed with intend to propose a regeneration treatment, included in the flowsheet, so that the solvent could be recycled. It comprises :

- Quantification of the main degradation products issued from radiolysis or hydrolysis, which are methyl octyl amine (MOA) and carboxylic acids,
- Effects of these products on extracting and hydrodynamics performances of the process,
- Study of methods able to remove mainly disturbing degradation products. Acidic scrubbing, which are performed in the scrubbing and stripping sections of the DIAMEX process, should allow the quantitative removal of methyl octyl amine. Then basic scrubbing, which were more especially studied, should eliminate at least 80% of carboxylic acids, and part of the cations remaining in the solvent.

### INTRODUCTION

As part of the SPIN program, the CEA has undertaken the development of the DIAMEX process, which is the first step in the reference strategy aiming to separate minor actinides from fission products in high liquid wastes. It consists in coextracting actinides(III) and lanthanides(III) by the use of a diamide extractant.

Preliminary counter current hot test, conducted at laboratory scale in the CYRANO hot cell in 1993, has demonstrated the feasibility of the concept (3) : quantitative extraction and stripping of actinides(III) (>99%). Then the formula of the extractant was optimised to improve solvent affinity for actinides(III) and solubility of metallic extracted complexes in the diluent (hydrogenated tetrapropylene). A reference extractant was then chosen : the dimethyl dioctyl hexylethoxy malonamide, symbolised by DMDOHEMA (4). Oxalic scrubbing were developed to improve the flowsheet ; they lead to inhibit some fission products extraction such as Zr, Mo and Fe (5).

The last main aspect lacking for the technical feasibility demonstration was then the solvent clean up. Batch studies were started in this field in late 1998. The objective is to define a treatment able to restore the solvent properties.

To highlight the work performed, three majors aspects are presented here :

- Characterisation of the radiolysed or hydrolysed solvent by quantification of the main degradation products and effect on its properties
- Various scrubbing studies to remove main disturbing products
- Effect of the most efficient scrubbing on cations remaining in the solvent (after stripping).

### CHARACTERISATION OF RADIOLYSED OR HYDROLYSED SOLVENT

Degradation products issued from radiolysis and/or hydrolysis were identified using gas chromatography (GC) coupled to Fourier Transform InfraRed Spectroscopy (FTIR) or Mass Spectrometry (MS) (6). Main solutes were quantified using potentiometric titrations and gas chromatography (with flame ionisation detector) (Fig. 1). These are :

- Carboxylic acids,
- Light amides,
- Methyl octyl amine,
- N-methyl N-octyl hexyl oxybutanamide,
- 2-(methyl(octyl)carbamoyl) 4-hexyl oxy butanoic acid, which is a bifunctional compound subsequently symbolised as acidic amide or AA,
- secondary diamides (loss of methyl or octyl chain on the nitrogen of one amide function).

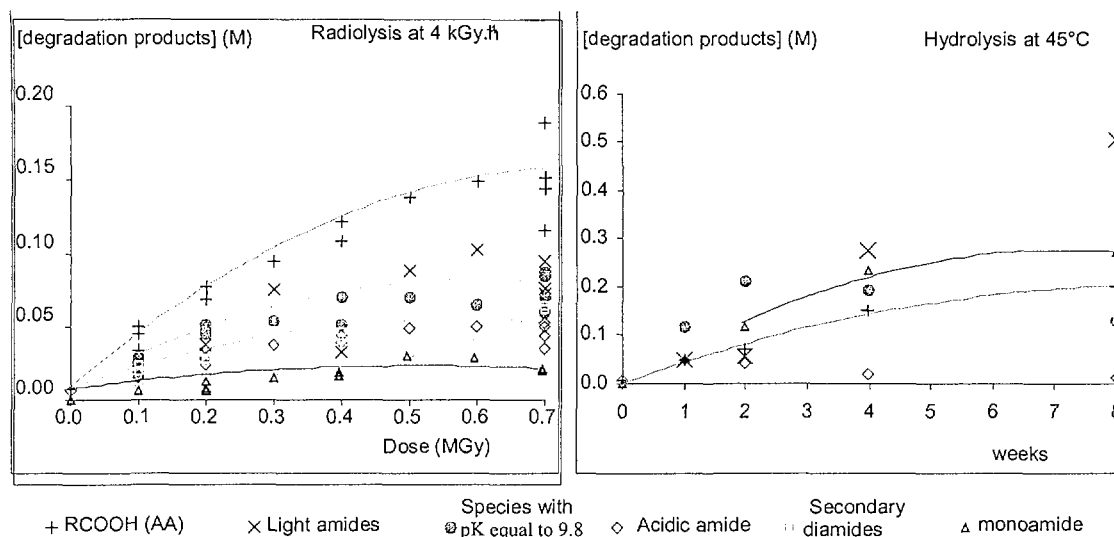


Figure 1 : Concentrations of main degradation products in the organic phases in function of absorbed dose or hydrolysis time.

RCOOH (AA) : includes acidic amide

Degradation conditions : [DMDOHEMA] 0.65 mol/L in HTP, [HNO<sub>3</sub>] 3 mol/L,  $V_{org}=V_{aq}$

A simplified degradation scheme for diamide radiolysis and hydrolysis was proposed (6). The first rupture is the breaking of one amide function which leads to :

- Methyl octyl amine, which has a basic character ( $pK \sim 9.8$ ) and is symbolised by MOA
- 2-(methyl(octyl)carbamoyl) 4-hexyl oxy butanoic acid, which has an acidic character and is symbolised by AA.

Hydrolysis or radiolysed solutions show a decrease of actinides(III) and lanthanides(III) distribution ratios. This decrease in solvent extraction properties can be explained by the decrease of the diamide concentration and by the presence of the main degradation products. So various scrubbing, respectively acidic and basic have been studied to remove respectively MOA (basic species) and AA (acidic species).

### ACIDIC SCRUBBING EFFICIENCY

Species removed by acidic scrubbing (nitric acid 0.1 mol/L), which simulates stripping step in DIAMEX flowsheet, were analysed.

In the case of hydrolysed solvent, basic species - which  $pK$  is close to 9.8 in the titration media (water/ethanol 50/50) is quantitatively eliminated (Fig. 2).

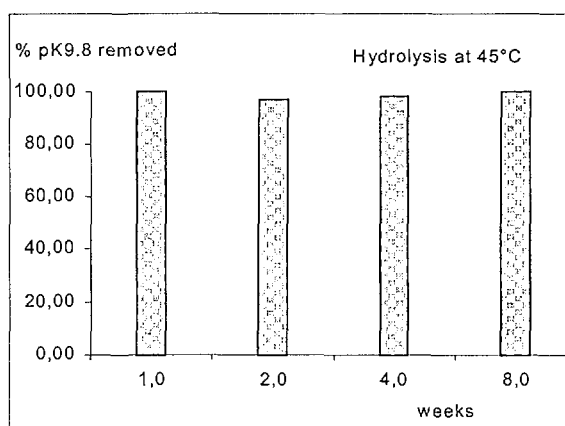


Figure 2 : Percentage of species with  $pK$  about 9.8 (mainly methyloctylamine) removed by scrubbing with nitric acid 0.1 mol/L, in function of hydrolysis time at 45°C (other conditions : see Fig. 1)

In the case of radiolysed solvent, large fraction of basic species is removed (from 60% to 100%, depending on samples). This dispersion could be due to :

- Concentration next to detection limit, for low irradiated samples,

- Samples from various sources,
- Presence of other species with pK close to 9.8 which are not distinguishable by potentiometry.

It has been checked on synthetic organic solutions, doped with MOA, that this species is totally removed by 0.1 mol/L nitric acid scrubbing.

### BASIC SCRUBBINGS IMPLEMENTATION

Various basic scrubblings (with sodium hydroxyde or carbonate, ammonium carbonate and tetramethylammonium hydroxyde) with concentration between 0.1 mol/L to 1 mol/L were studied in function of irradiation dose or hydrolysis time to remove carboxylic acids, including acidic amide (AA).

Experimental conditions are mentioned in figure 3. It must be noticed that basic scrubbing settling is difficult ; it is necessary to centrifuge the phases after mixing to get good separation. Settling seems more favourable when organic/aqueous volume ratio > 1.

### BASIC SCRUBBINGS EFFICIENCY VERSUS ORGANIC SPECIES

#### INFLUENCE ON CARBOXYLIC ACIDS

Neither the nature of the base nor its concentration seem to influence the basic scrubbing efficiency which varies from 70% (for radiolysis) to 90% (for hydrolysis) as it can be seen figure 3. Concerning the acidic amide, efficiency is most often about 80%. It can be specified that only the first basicity is efficient (in the case of carbonates).

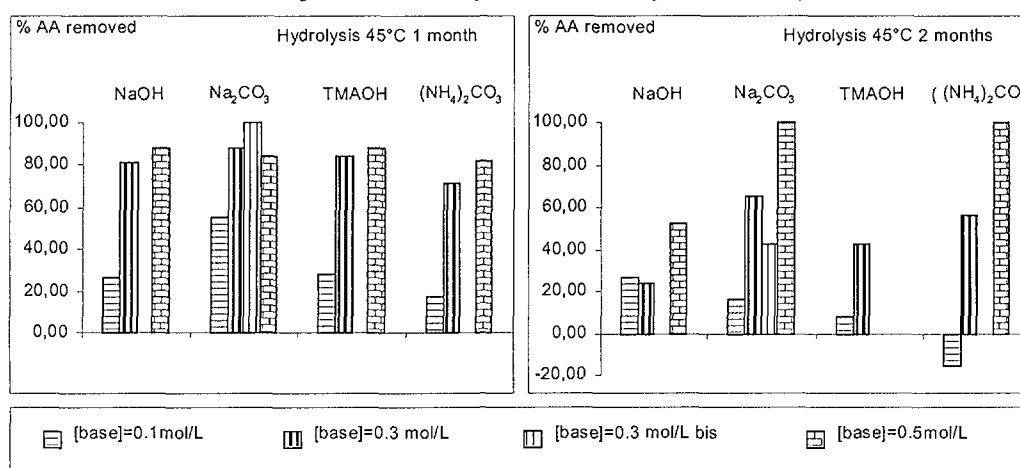


Figure 3 : Percentage of acidic amide removed in function of the base and its concentration for diamide hydrolysed solutions (other conditions see fig.1).

[AA]<sub>ini</sub> = 0.025 mol/L (after 1 month) ; 0.01 mol/L (after 2 months)

The efficiency of a second basic scrubbing was tested : it seems much less efficient (about 20%). An hypothesis to explain this phenomena is that a little part of carboxylic acids is very difficult to strip with such basic scrubbing, so that a small fraction of acids remains in the solvent.

#### INFLUENCE ON SOLVENT PROPERTIES

Basic scrubbing effects on solvent properties were observed in terms of hydrodynamics and extracting properties. For example, after two successive scrubblings with sodium carbonate 0.3 mol/L :

- Hydrodynamics properties are partially restored : settling time is shorter, but is not as fast as with no degraded solvent.
- Extracting properties are slightly improved in the case of radiolysed samples, so that the fall in the distribution ratios can be explained by the diamide concentration decrease. But in the case of hydrolysed samples, the drop in the distribution ratios cannot be completely explained by diamide concentration lowering. An hypothesis is that in those samples, rather high monoamide concentration (removed neither by acidic nor by basic scrubblings) inhibits partially cations extraction. Anyway, if monoamide is issued from acidic amide, we can expect its formation will be very limited if acidic amide is quickly enough removed.

### BASIC SCRUBBINGS EFFICIENCY VERSUS CATIONS

Hot test performed in TUI (Trans Uranium Institute), in 1998, in the frame of an European contract, showed that ruthenium and palladium were partially remaining in the solvent, even after stripping. To prevent from solvent saturation during successive recycling, it is necessary to remove these cations. It is the reason why basic scrubblings efficiency versus these cations was determined.

The best reagent for palladium is ammonium carbonate, which allows to removed about 70% of Pd, while about 20% of Pd removed is got with other bases.

For ruthenium, the efficiency of the various bases is similar, except with ammonium carbonate in the case of degraded samples. In comparison, 20 to 30% of Ru is removed instead of 70% with the other reagents (Fig. 4).

A second scrubbing is little efficient. This phenomena could be imputed to no strippable palladium and ruthenium species.

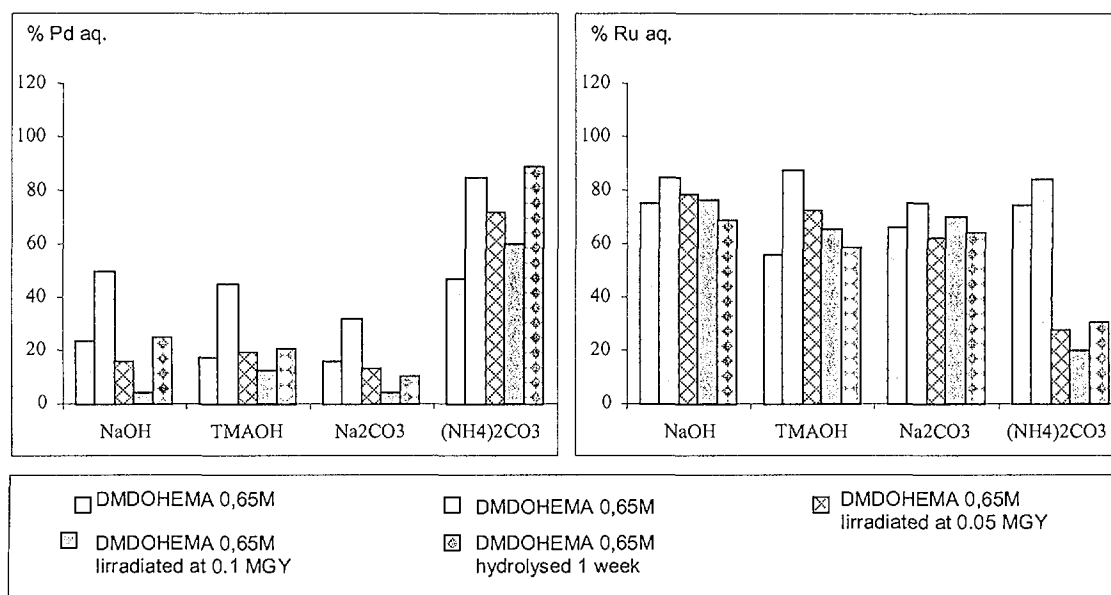


Figure 4 : Proportion of Pd and Ru in aqueous basic phases after each scrubbing by the 4 bases (other conditions : see figure 1)

## CONCLUSION

Among main degradation products of DIAMEX reference solvent (dimethyl dioctyl hexylethoxy malonamide 0.65 mol/L in hydrogenated tetrapropylene), batch experiments incline to think that methyl octyl amine will be quantitatively removed in the stripping section of the flowsheet (by nitric acid scrubbing), while carboxylic acids (especially acidic amide) will be eliminated by basic scrubbing. It can be expected that if clean up is continuously performed, neutral degradation products, such as monoamide, will not be formed and accumulate.

Some disturbing fission products (Pd and Ru) which are partially remaining in the solvent after stripping, are not totally removed by basic scrubbing. It will be useful to test complexing reagents, such as citric acid, to remove quantitatively these two cations.

Then a complete flowsheet, including solvent clean up will be elaborated and tested.

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