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RESEARCH FOR ACTINIDES EXTRACTANTS FROM VARIOUS WASTES

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# RESEARCH FOR ACTINIDES EXTRACTANTS FROM VARIOUS WASTES

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## Summary

This paper is an overview of the actinides solvent extraction research undertaken in Fontenay-aux-Roses. Two kinds of extractants are investigated ; those usable for the improvement of the nowadays nuclear fuels reprocessing and those necessary for advanced fuels cycles which include the minor actinides (Np, Am) recovery for a further elimination through nuclear reactions. In the first class the mono and diamides, alternative to the organophosphorus extractants, TBP and polyfunctional phosphonates, showed promising properties. The main results are discussed. For the future efficient extractants for trivalent actinides-lanthanides group separations are suitable. The point about the actinides (III) - lanthanides (III) group separation chemistry and the development of some of these extractants are given.

## 1. INTRODUCTION

Improvement of the back-end of the nuclear fuels cycle can be achieved by using new actinides extractants. Wastes amounts limitation as well as process simplification are suitable. In this paper we classified the extractants according to the goals for which they could be used. The N,N-dialkylamides are an alternative to TBP and could be employed in the existing plants ; in order to limit the amounts of the wastes generated by the solvent.

The N,N'-tetraalkyle 2-alkyle 1,3-diamide propane, could be used to remove the actinides contained in various wastes and this help to limit the quantities of the deep underground storable wastes. The chemistry leading to the choice of the extractants efficient for the trivalent actinides-lanthanides group separations is presented. This group separation is necessary in view of the minor actinides (Am, Cm) recycling for their elimination by nuclear reactions (complete reprocessing). Emphasis is put on the extraction chemistry which leads to the extractants choice. The number of investigations and the level of development of those different reagents are quite different going from several bench-scale separations to just laboratory tests. The results of practical continuous separations will be given in order to illustrate this last point.

## 2. EXTRACTION OF THE ACTINIDES IONS BY N,N-DIALKYLAMIDES

### 2.1. Choice of the extractant as a function of $UO_2(NO_3)_2$ -amide solvate solubility into alkanes

N,N-dialkylamides ( $RCONR'_2$ ) have been proposed as alternative to TBP for a PUREX type process (1,2). Long time the interest of N,N-dialkylamide has been hindered by the necessity to use aromatic diluents for U(VI) large loading capacity of the organic phase. We demonstrated (3) that the proper choice of the R' radical permits to extract  $120 \text{ g.l}^{-1}$  of U(VI) into 1M N,N-dialkylamide diluted into TPH (tetrapropylène hydrogéné, a commercial branched dodecane). Some of the results dealing with the third phase formation are given into Table 1.

Amide	Organic solubility (U g.l <sup>-1</sup> )	Aqueous acidity $C_{HNO_3}^{aq}$
$(C_4H_9)_2NCOC_{11}H_{23}$	80 71	0 4
$(C_2H_5CH(CH_3))_2NCOC_{11}H_{23}$	64 36	0 4
$\begin{array}{c} C_2H_5 \\   \\ (C_4H_9CH-C^H_2)_2NCOC_5H_{11} \end{array}$	> 120	0 and 4
$\begin{array}{c} C_2H_5 \\   \\ (C_4H_9CH-CH_2)NCOCH_3C(CH_3)_3 \end{array}$	> 120	0 and 4

Table 1 - Solubility of  $UO_2(NO_3)_2$  in various N,N-dialkylamides solutions into TPH

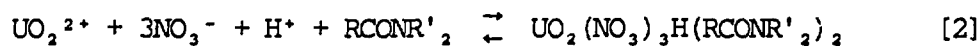
It can be seen that the best results are obtained for  $R' = -CH_2-\overset{C_2H_5}{\underset{|}{CH}}-C_4H_9$

## 2.2. Extraction chemistry of U(VI) and Pu(IV)

The following extraction equilibria were found for U(VI) and Pu(IV), (4,5).

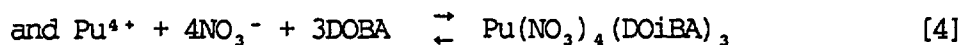
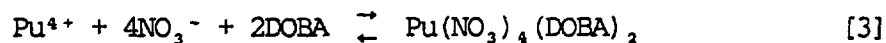


(Extraction from low acidic solutions  $0 < C_{HNO_3}^{aq} < 1N$ )



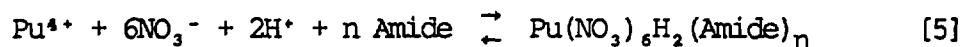
(Extraction from high acidic solutions  $C_{HNO_3}^{aq} > 8N$ )

The substituents R and R' have no qualitative effect upon the extraction equilibria of U(VI), but they influence the Pu(IV) organic species. One found from low acidic solutions



DOBA and DOIBA are the acronym of :  $C_3H_7CO N(CH_2CH(C_2H_5)C_4H_9)_2$  and  $(CH_3)_2CHCO N(CH_2CH(C_2H_5)C_4H_9)_2$  two N,N-dialkylamides differing only by the nature of R which is a propyl or isopropyl substituent.

The extraction of Pu(IV) from acidic medium leads to the same organic complex for the two amides, according to :



## 2.3. First cycle PUREX bench scale separations in mixer-settlers

Separations mimicking a first cycle of the PUREX process have been carried out with three batteries of mixer-settler according to the flow sheet shown figure 1.

The solvent was a mixture of 0.5M DOBA and 1M DOiBA into TPH and the goal was to achieve the U-Pu partition without Pu(IV) reduction. The results are contained Table 2.

Flux	U % of feed	Pu	Zr	Ru	Np
Extraction (Solvent)	> 99.99	99.999	0.01	0.05	95
Extraction (Aqueous)	< 0.0005	0.0008	99.99	99.95	5
Partition (Solvent)	99.89	0.006			not detected
Partition (Aqueous)	0.11	99.994			95
U desextraction (Solvent)	not detected	not detected			not detected
U desextraction (Aqueous)	99.89	0.006			not detected

Table 2 - Results of the first cycle PUREX process using N,N-dialkylamides

It can be seen that the Ru and Zr decontamination are quite satisfactory. The U(VI)-Pu(IV) partition was good but less efficient than expected by the calculations.

Some technical trouble (wrong flow rate at the beginning of the experience) may be at the origin of this discrepancy. However this experiment was quite encouraging and no draw-back of the amide was observed.

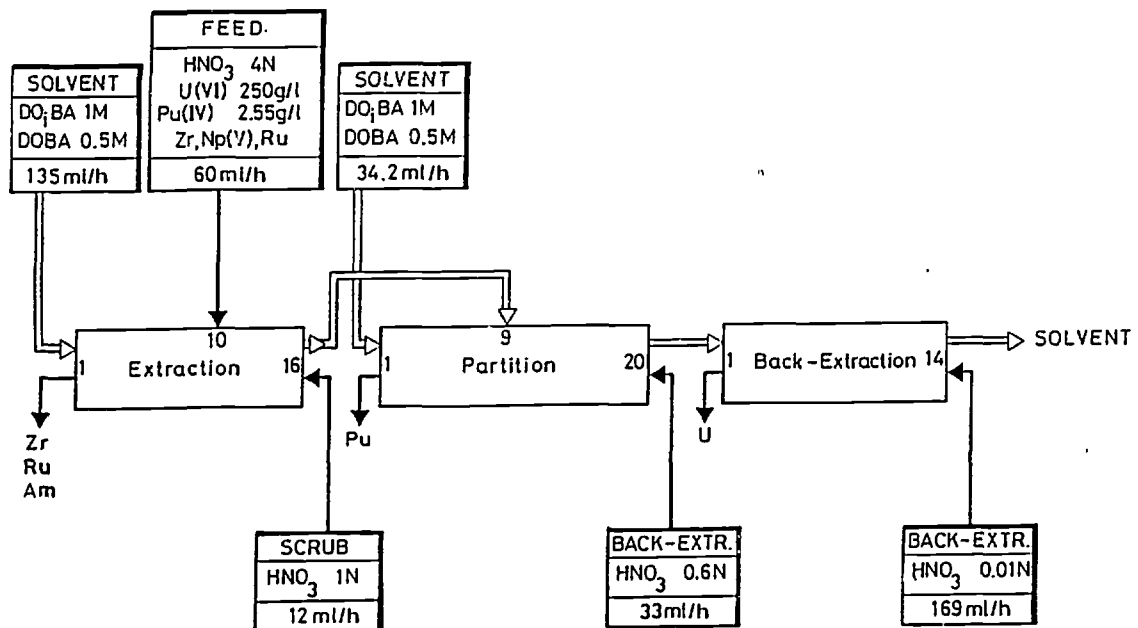


Figure 1 - Flow sheet for a PUREX process first cycle using a N,N-dialkylamide as a solvent

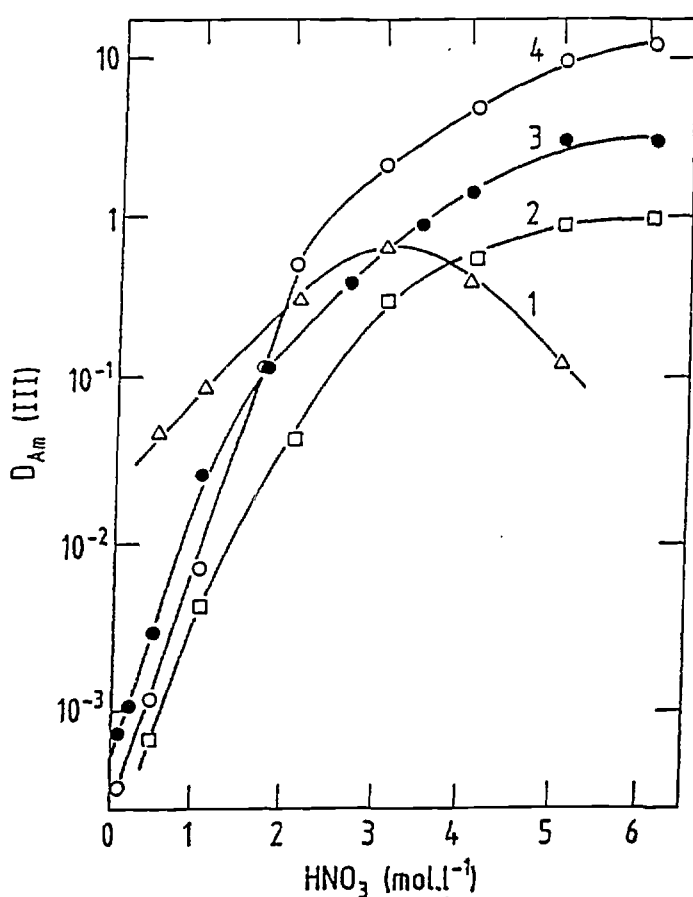
### 3. N,N'-TETRAALKYLE ALKYLE PROPANE DIAMIDES

It has been claimed than N,N'-tetrabutylmalonamide ( $C_4H_9$ )<sub>2</sub>NCOCH<sub>2</sub>CO N(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub> does not extract Ce(III) from HNO<sub>3</sub> solutions (6). However we found out (7) that the nature of the N substituent was important for the Am(III) extraction (Table 3). A short substituent is necessary to observe good Am(III) extraction.

Malonamide acronyme	R	R'	D <sub>Am(III)</sub> *
DCHDEMA	C <sub>6</sub> H <sub>11</sub>	C <sub>2</sub> H <sub>5</sub>	0.11
TEMA	C <sub>4</sub> H <sub>9</sub>	C <sub>4</sub> H <sub>9</sub>	0.18
DPDOMA	C <sub>3</sub> H <sub>7</sub>	C <sub>8</sub> H <sub>17</sub>	0.45
DMDEMA	CH <sub>3</sub>	C <sub>4</sub> H <sub>9</sub>	0.55
DMDOMA	CH <sub>3</sub>	C <sub>8</sub> H <sub>17</sub>	1.18

\* Distribution ratios at the maximum of the curve D<sub>Am(III)</sub> as a function of aqueous HNO<sub>3</sub>.

Table 4 - Influence of the substituents R,R' upon Am(III) distribution ratios between HNO<sub>3</sub> solutions and 0.5M malonamide into benzene



Furthermore the effect of various substituent bear by the central methylene groupe upon the distribution ratios of Am(III) as a function of  $\frac{D_{Am(III)}^{ac}}{HNO_3}$  is important (8) (figure 2). A maximum in the distribution ratios value is observed only in the case of no substituent. This effect has been correlated to the competition of Am(III) with HNO<sub>3</sub> for the coordination site of the diamide. If it is so we have to measure a higher basicity for the diamide with no substituent. A scale of basicity of different amides in acetic anhydride has been established (Table 4).

It can be seen that the most basic diamide has no methylene substituent. The presence of an oxygen into the R'' substituent depress further the basicity.

Figure 2 - Distribution ratios of Am(III) between various 0.5M diamide solutions into t-butylbenzene and aqueous nitric acid solutions

1.  $(CH_3C_8H_{17}NCO)_2CH_2$
2.  $(CH_3C_4H_9NCO)_2CH C_6H_{13}$
3.  $(CH_3C_4H_9NCO)_2CHC_2H_4OC_2H_5$
4.  $(CH_3C_4H_9NCO)_2CHC_2H_4OC_2H_4OC_6H_{13}$

Malonamide acronyme	Formula	pH <sub>1/2</sub>
DEDMMA	(C <sub>4</sub> H <sub>9</sub> CH <sub>3</sub> NCO) <sub>2</sub> CH <sub>2</sub>	3.43
DEDMEMA	(C <sub>4</sub> H <sub>9</sub> CH <sub>3</sub> NCO) <sub>2</sub> CHC <sub>4</sub> H <sub>9</sub>	3.1
DEDM3ONMA	(C <sub>4</sub> H <sub>9</sub> CH <sub>3</sub> NCO) <sub>2</sub> CHC <sub>2</sub> H <sub>4</sub> OC <sub>6</sub> H <sub>13</sub>	2.72

Table 4 - pH at half neutralization by HCCl<sub>4</sub> into acetic anhydride for various malonamides (pH<sub>1/2</sub> for isobutyramide was taken as the origin of the scale).

One mixer-settler bench scale experimental separation of the actinides contained in a real waste is presented in this meeting (9). Improvements suitable for industrial applications are better Am(III)-Fe(III) separations and higher solubility of the [HNO<sub>3</sub>. Diamide] solvates into aliphatic hydrocarbons.

#### 4. TRIVALENT ACTINIDES-LANTHANIDES GROUP SEPARATIONS

Neutrophage trivalent lanthanides must be separated from the actinides in view of the recycling of these latest in "nuclear actinide burner reactors". This separation could be achieved either at the first cycle of the PUREX process by using an extractant selective of the (VI), (IV) and (III) actinide or after the classical PUREX process by treating the first cycle extraction effluent in two steps : first extraction of the actinides (VI), (IV), (III) plus lanthanide (III) and then separation of the trivalent actinides from trivalent lanthanides. With the present knowledge of actinides extractants there is no possibilities of doing the first kind of treatment which is the more interesting because of one single step involving high level of β, α radioactivity. The second kind of process has been proposed (10,11) but its complexity is unsuitable for real applications. The amounts of wastes generated by these processes are so high that the interest of the separation is questionable. So progress must be done in trivalent actinides-lanthanides group separations. In order to do so we investigated the difference in stability for different kind of complexes of the 5f and 4f trivalent ions. A simple way to compare different ligands is to measure the quantity S, defined for a trivalent actinide-lanthanide pair (12).

$$S = 2 (\Delta G_{\text{Actinide}} - \Delta G_{\text{Lanthanide}} / (\Delta G_{\text{Actinide}} + \Delta G_{\text{Lanthanide}}).$$

The highest value of S corresponds to the best difference in complex stability. Such values of S are given in Table ±. It can be seen that the presence in the ligands of donor atoms with low electronegativity is in favor of actinides (III) selective complexation. One application of this observation is shown by figure 3 distribution ratios of Am(III), Ce(III) and Eu(III) between a 0.125N nitric acid solution and organic solution of CCl<sub>4</sub> containing HDNNS ((C<sub>9</sub>H<sub>19</sub>)<sub>2</sub>C<sub>10</sub>H<sub>5</sub>SO<sub>3</sub>H) plus (tris-2,4,6(2-pyridyl)1,3,5-triazine), the last reagent being the active ligands for group separation. A mixer-settler separation of Am(III) from Eu(III) plus Ce(III) has been tested with this system (13). The flow sheet and the results are given into figure 4.

The results were encouraging however it must be stressed out that extractants efficient in actinides (III) selective extraction at the industrial scale are not yet available and this subject might be an interesting challenge for the actinide chemists.

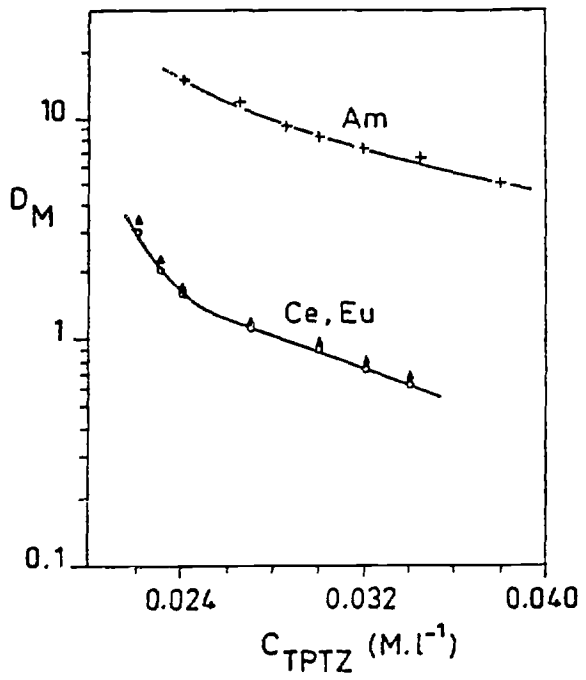


Figure 3 - Distribution ratios of Am(III)<sup>+</sup>, Ce(III)<sup>Δ</sup>, Eu(III)<sup>◦</sup>, between HDNNS 0.05M, TPTZ into CCl<sub>4</sub> and 0.125N aqueous HNO<sub>3</sub> as a function of the initial TPTZ concentration into the organic phase.

Ligand	Complexes	S <sub>Am-Nd</sub>	S <sub>Am-Eu</sub>	Donor Electronegativity
F <sup>-</sup>	MF <sup>2+</sup>	- 0.05	- 0.084	4
CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	MCH <sub>3</sub> COO <sup>2+</sup>	0.074	0.03	3.5
N <sub>3</sub> <sup>-</sup>	MN <sub>3</sub> <sup>2+</sup>	0.95	0.93	3.0
Phen	MPhen <sup>3+</sup>	0.84	0.69	3.0
DEHDTP*	M(DEHDTP) <sub>3</sub> .TBP		4.6	2.5 (6) 3.5 (1)

\* DEHDTP = (C<sub>4</sub>H<sub>9</sub>CH(C<sub>2</sub>H<sub>5</sub>)CH<sub>2</sub>O)<sub>2</sub>PSS<sup>-</sup>

Table 6 - S values for selected donors for the Am-Nd and Am-Eu couple. (Ionic radius : Am<sup>3+</sup> 0.99 Å, Nd<sup>3+</sup> 0.99 Å, Eu<sup>3+</sup> 0.99 Å)

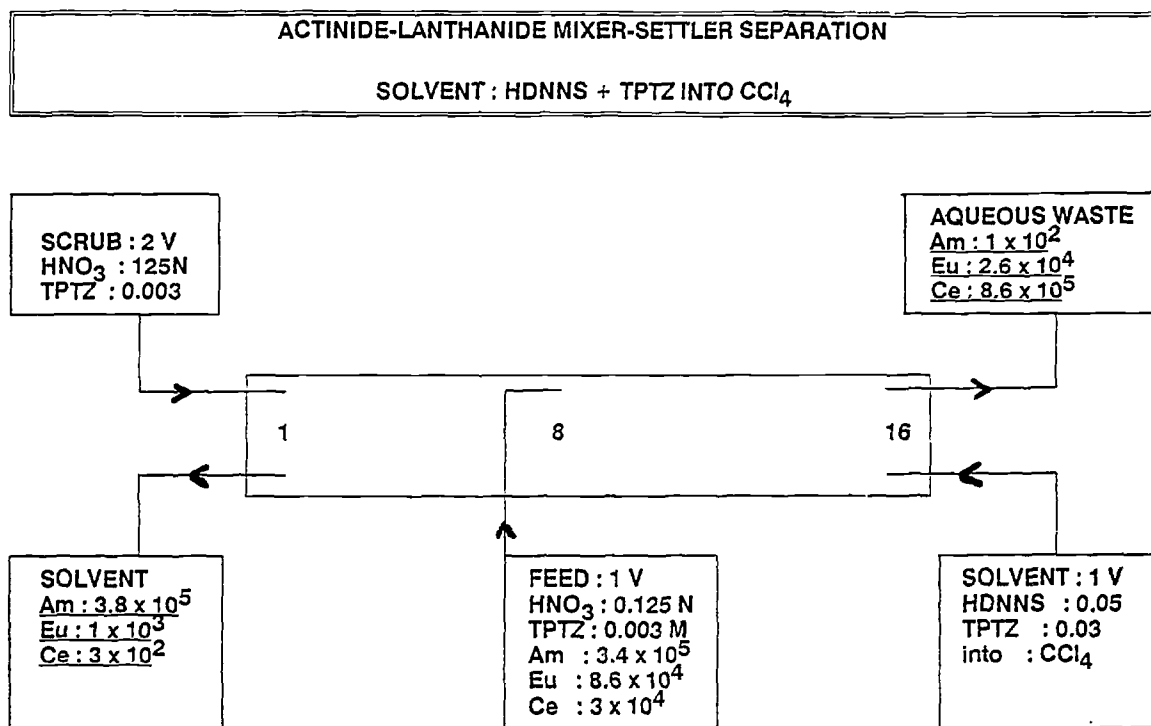


Figure 4 - Flow sheet and results fo mixer-settler actinide(III) - lanthanide (III) group separation using a solvent TPTZ + HDNNS into CCl<sub>4</sub>

6. CONCLUSIONS

The nuclear cycle has been one of the first industrial applications of solvent extraction. Today new concepts of the back-end nuclear fuels cycle may need another efforts in basic solvent extraction research to find new extractants which match the requirements of environmentalists.

The amides seem one good alternative to waste generating organophosphorus extractants. For the future, complete reprocessing has been proposed in several instances. Solvent extraction is potentially interesting to achieved such chemical separations but the problem of the waste must be taken into account when one designs the process and selects the extractants.

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