THE FRENCH SITUATION
ON LONG LIVED RADIOISOTOPE SEPARATION STUDIES
(Puretex and Actinex program-s)

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ABSTRACT

Even if the optimal choice of a disposal site and its installation may, by themselves, guarantee the reliability of long-term waste management, any reduction of long-lived elements could only improve the protection of man and the environment and consequently contribute to the enhancement of nuclear as far as the public is concerned.

The first step before transmutation includes chemical separation. In France separation studies make up a part of the SPIN program (Separation - Transmutation) and especially of the ACTINEX program.

Examining the noxiousness of wastes leads to favoring the separation of actinides if only the potential noxiousness of wastes is considered, i.e. that which considers radionuclides as being immediately ingestible, without taking either the quality packaging or the retention at the disposal site into account.

On the other hand, if the activity at the outlet is considered, the effect of solubilities and the rock/radionuclides interaction will limit the weight of these actinides, giving increased importance to the fission products such as iodine 129, technetium 99, selenium 79, cesium 135, etc.

The ACTINEX program involves the separation of both actinides and fission products. However, owing to the French experience in nuclear fuel reprocessing and the knowledge acquired because of the need to separate certain actinides for the fabrication of sources (smoke detectors, californium reactor startup sources), the actinide separation program is the most advanced technique today.

1- SEPARATION OF ACTINIDES

Current reprocessing plants use liquid-liquid separation processes to recover plutonium and uranium. These techniques will be preferred in the separation processes since they can be more easily integrated into today's technologies. Moreover, the considerable knowledge on the behavior of radioelements in an aqueous medium potentially offers greater short-term possibilities.

This does not mean that dry processes are not to be investigated.

Three methods are currently under consideration:

■ Modify the valence state of the elements considered to make them simultaneously extractable with the uranium and plutonium in the PUREX process, slightly modified. At present, only the separation of neptunium maybe considered (see below).

■ Completely replace the current solvent by a solvent that will pick up the long-lived elements, in other words to replace **the** PUREX process by another process having the same reliability. This is a difficult objective.

■ Work only on the fission products solution coming from the first stage of the PUREX process, i.e. add a new stage to the current process.

2- MODIFY THE PUREX PROCESS: SEPARATION of the NEPTUNIUM

In the PUREX process the solvent selectively extracts, from the fuel dissolution solutions, both the uranium at valence (VI) and the plutonium at valence (IV), whereas practically all the fission products and minor actinides (Am and Cm) and part of the neptunium remain in the original solution. In a second step, plutonium is separated from uranium by reducing it from the extractable valence (IV) to the non-extractable valence (III).

The neptunium exists under two valencies in the dissolution solutions:

. about 40°/0 at valence (V), non-extractable, remain in the solution of fission products to be vitrified,

. about 60°/0 at valence (VI) is coextracted with Pu and U. First it follows the uranium and then goes into the raffinate of the 2nd uranium cycle (2CU) which is currently joined with the fission products solution.

It is clear that if this raffinate is no longer sent to vitrification, 60% of the NP is immediately recovered. It is, however, possible to go beyond this by making extractible the **40%** of the neptunium which is not, i.e. by oxidizing it at the state of Np (VI).

The whole problem lies in the selection of an oxidant that should oxidize Np (V) and Np (VI) without making Pu(IV) go to Pu (VI) which **is** hardly extractable.

At the present time, vanadium salts seem to offer a possibility based on different oxidation kinetics between Np and Pu. This possibility is tricky but it would barely modify the present facility. Apparently the Soviets recover α part of Np this way. Japanese are currently investigating a photochemical oxidation.

New Extractants:

TBP is an extractant that has proven its reliability for several decades in the PUREX process. Its only drawback lies in the generation of secondary waste owing to the presence of phosphate ions.

The research earned out at CEA shows that monoamides constitute a class of molecules capable of replacing TBP. They are compatible with the aliphatic diluents and present strong affinity for uranyl nitrate and Pu (IV) and low affinity for the metallic ions of the fission products. This affinity maybe greatly modulated according to the groups linked to the carbonyl function. Thus, the DEHMBA with formula $(CH_3)_3$ CCH_2CO N $(CH_2$ CH C_4H9 $C2H_5)_2$ enables an excellent extraction of U and Pu in a concentrated nitric medium and allows a U/Pu separation at low nitric acidity without changing the oxidation states.

If future studies were to confirm the feasibility of such a method at the industrial level, a major simplification would be obtained for the re-extraction of Pu which, in today's PUREX process implies a reduction to valence (III) 'which is hard to master.

At present, the accumulated knowledge on these monoamides is still insufficient to propose a replacement for TBP but does provide interesting prospects.

3- SEPARATION USING SOLUTIONS of FISSION PRODUCTS : DIAMEX Process

The difficulty in recovering actinides from fission product solutions lies in the similarity in the properties of actinides and lanthanides. Therefore, most processes begin with a simultaneous separation stage for actinides and lanthanides, stable at valence (III), followed by a separation of the two groups.

The American TRUEX process using CMPO (Carbonyl Methylene Phosphine Oxide) or the processes with HDEHP (di 2 ethylhexylphosphoric acid) separate An (III) and Ln (III).

These processes present several drawbacks. Consequently, a new process with the following objectives has been looked into at CEA:

. good separation factor in a highly acidic medium,
. easy re-extraction,
. soluble in alkanes, particularly the TPH used in La Hague

. easy synthesis to obtain inexpensive product,
. total incineration to limit secondary wastes, therefore containing only the elements : C, H, O, N.
. resistant to irradiation with formation of harmless radiolytic compounds.

This leads to choosing diarnides and especially malonamides.

3.1. DIAMEX Process

A good balance has been found with Dimethyl Dibutyl Tetradecyl methyl amide.
The methyl and butyl radical, on account of their restricted steric hindrance, promote americium extraction.

The tetradecyl radical gives:

. a very low solubility in nitric acid medium ($< 1.7 \times 10^{-4}$ M)
. a good extraction of the metal and the nitric acid before the formation of a third phase in the aliphatic diluent.
. the ability of a kinetic partition (americium/iron) avoids the use of oxalic acid. Separation is possible using this acid in the TRUEX process as well as with diamides.
. good radiolytic and hydrolytic stability.

If the DMDBTDMA amide is currently the one chosen in furthering applied studies of the DIAMEX process, we nevertheless continue our search for molecules of diamides with still higher performances.

The theoretical studies by NMR have shown that in a neutral or very low acid medium the species extracted were dimers (diamide) or oligomers. On the other hand, in an acidic medium, only the monomers were present.

The extraction mechanisms follow the general equation below:

$$q(\text{diamide}) + m \, Am^{3+} + TH^{+} + (3m+T)(NO_3) = (\text{diamide})q(Am)m(NO_3)3(H_T)3m+T$$
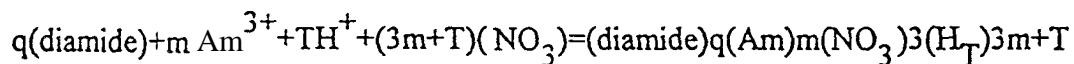
which shows that the extracted species depend upon the acid and the concentration in nitric acid, with protons included in the complexes.

Curve 1 shows the variations of the partitioning of americium versus groups linked and the reason for choosing malonamides.

Curve 2 shows the variation of the extraction coefficients for americium, uranium, plutonium and iron. At high acidity, a K_d of around 10 is excellent and will allow, in a process, a good decontamination to be achieved.

Conversely, a K_d of 10-4 at low acidity will result in a very good re-extraction.

The DIAMEX process has been tested with success on low and medium activity waste. It is currently being tested using mixer-settlers on "synthetic wastes" (non radioactive fission products with actinides at nominal value). At the end of 1993, it will be tested on actual fission product solutions.

TRUEX - DIAMEX Comparison :

Here, some troublesome aspects of the TRUEX process are considered and the available performances of diamide solvents are compareed.

Nitric acid and americium extraction
Curves 3 and 4 compare HNO_3 and Am(III) extraction for TRUEX solvents and diamides.

Note that nitric acid is less extracted and also that Am is more easily stripped at intermediate acidity ($\leq 1M$) with diamides than with CMPO/TBP.

This is really **in favor of diamides because it could prevent the trivalent actinides and rare-earth accumulation observed with Truex solvent in mixer-settler experiments.**

Of course the fact that Am extraction at high acidity must be enhanced by improving the diamide formula is kept in mind but, contrary to CMPO, the degradation products due to hydrolysis and radiolysis do not cause actinide retention or the formation of precipitates.

Ruthenium and technetium nuclides
Provided aqueous nitric acid does not exceed 4 M, ruthenium is clearly less extracted by diamides than by different Truex solvents for which even oxalic acid cannot prevent the extraction. Curve 5.

The case of technetium is more troublesome for the two solvents. Distribution coefficients are equal to or greater than one and CMPO, like diamides, exhibit a coextraction (Tc/actinide) and (Tc/lanthanide) Curve 6.

Oxalic acid
Oxalic acid may be used with diamides and CMPO to obtain an Am/Fe partition or to maintain the Zr (IV) ions in aqueous solutions. Extracted by **Truex** solvent to a certain extent during Am extraction, it may induce rare earth precipitation at the very low acid. level used for Am stripping. The problem is less acute with diamides due to the lower $D(H_2C_2O_4)$.

Actinide/Lanthanide Separation
The second phase consists in separating lanthanides and actinides. The Tall Speak process has been proposed in the USA and the DIDBA by JAERI. A system based on diamides with a diamides trilaurylamine thyocyanate synergy is currently under study.

Specific extraction:
The simultaneous separation An (111 / Ln (111) presents the great disadvantage of extracting a majority of lanthanides compared to actinides (about **10 to 1),** and therefore to handle high activities and large volumes even in the second phase.

A selective extraction is considered in two different ways:

. find a specific extractant, which implies electron donor atoms that are "softer" than oxygen. Interesting results have been obtained with picolinamides that selectively complex *the* actinides in aqueous phase.

. separate oxidized actinide forms. The general principle of the process consists in oxidizing actinides to differentiate them from the group of lanthanides, essentially trivalent. However, this process has two drawbacks :

the difficulty in oxidizing curium which will not be extracted. This is minor for the reprocessing of PWR fuels where its concentration is low.

. the separation of oxidized ruthenium before the actinides.

Electrovolatilization has been tested with success on a raffinate solution. It remains to be demonstrated on a concentrated HA solution.

For oxidation, 2 possibilities are offered:

. valence (VI), hard to keep stable in a nitric medium, hence the necessity of working at low acidity, unless a polyanionic complexant is found,

. valence (IV) that could be complexed by the phosphotungstic complexant.

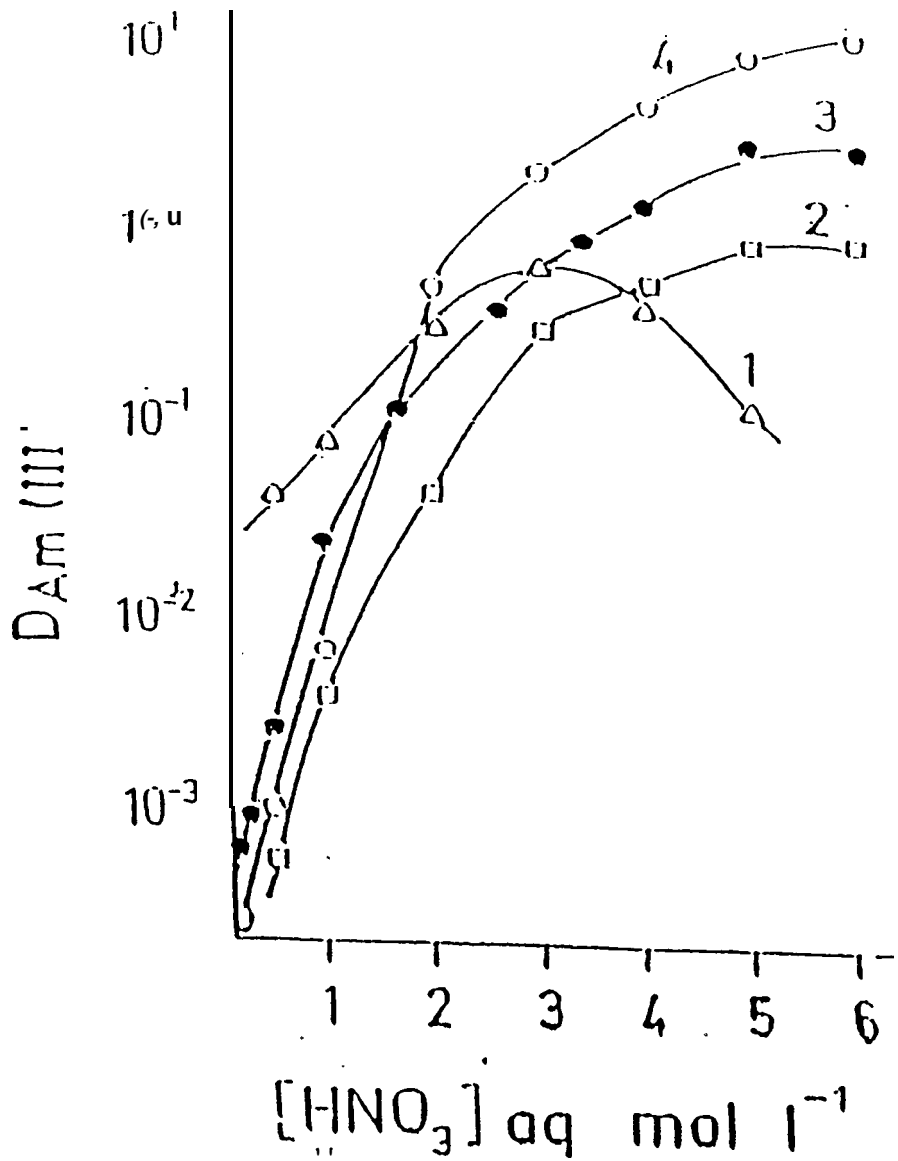The complex Am (IV) $(PN)_2$ is extractable by amines.

Other extractants:
The possibilities of macrocycles to extract long-lived elements and possibly actinides are being investigated.
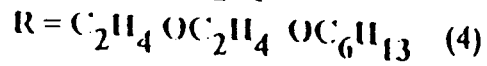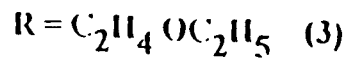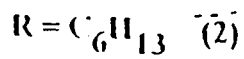

4- CONCLUSION
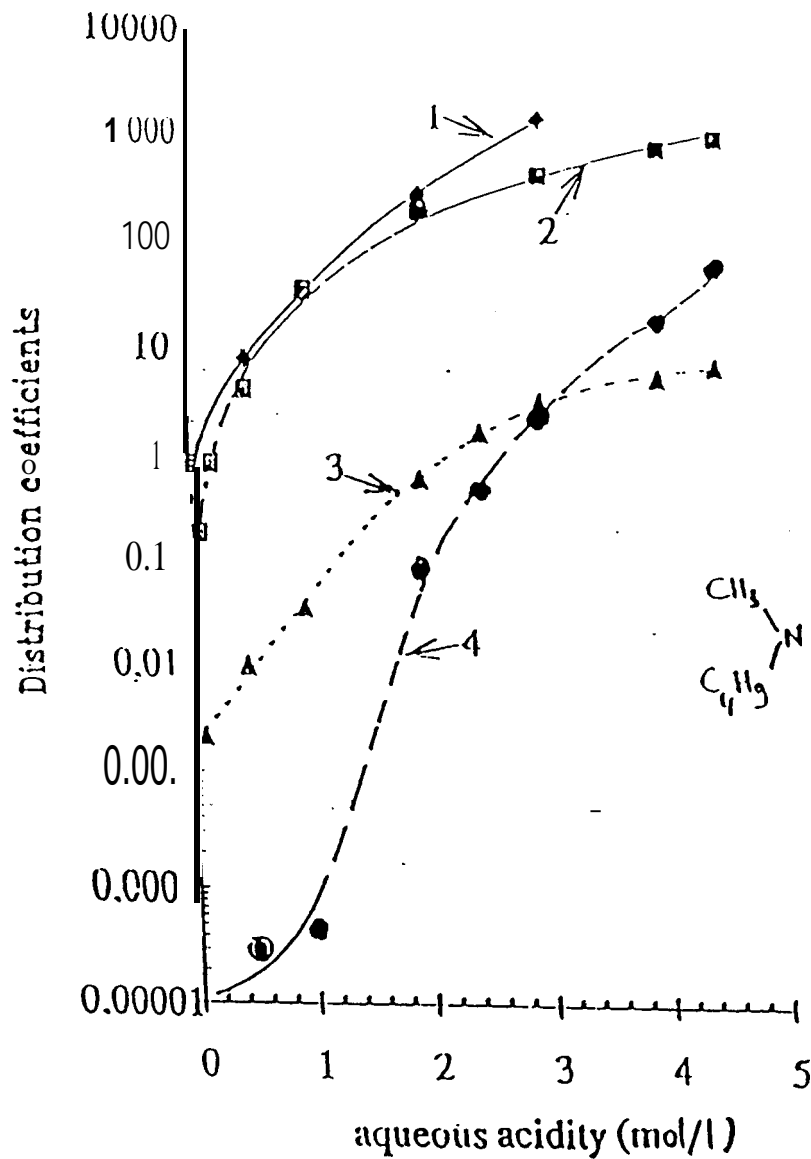
The basic research and the first tests show that the DIAMEX process *offers* interesting possibilities for extraction in an acidic medium, at least equal to those of the TRUEX process, and at lower costs.

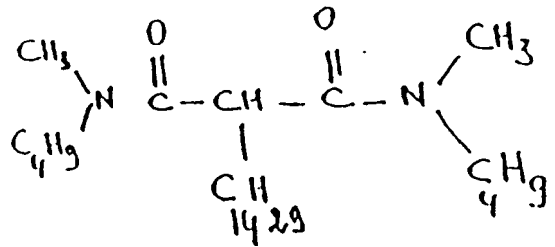Selective extraction still requires numerous studies, but interesting prospects are starting to be outlined.

Curve 1

D1 S["I([BUTION CO EFFICIENTS WITH DIFFERENT
LINKING GROUPS

1 - $C_8 H_{17} CH_3 NCOCH_2 CONCH_3 C_8 H_{17}$

2 à 4 - $(C_4 H_9 CH_3 NCO)2 CHR$

$R = C_6 H_{13}$ (2)

$R = C_2 H_4 OC_2 H_5$ (3)

$R = C_2 H_4 OC_2 H_4 OC_6 H_{13}$ (4)

Extraction of metallic cations
by DMDBTDMA 0.5 M in TPH

$n = 1$

1- uranium   2- plutonium
3- americium   4- iron

a

americium distribution coefficient

10

1

0.1

0.01

0.001

" — "

0   1   2   3   4   5

●queous nitric acidity (mol/l)

b

10^{3}

10^{2}

10^{1}

10^{0}

D_{Am}

^{241}Am

10^{-2} 10^{-1} 10^{0} 10^{1}

H N O$_3$ [mol/l]
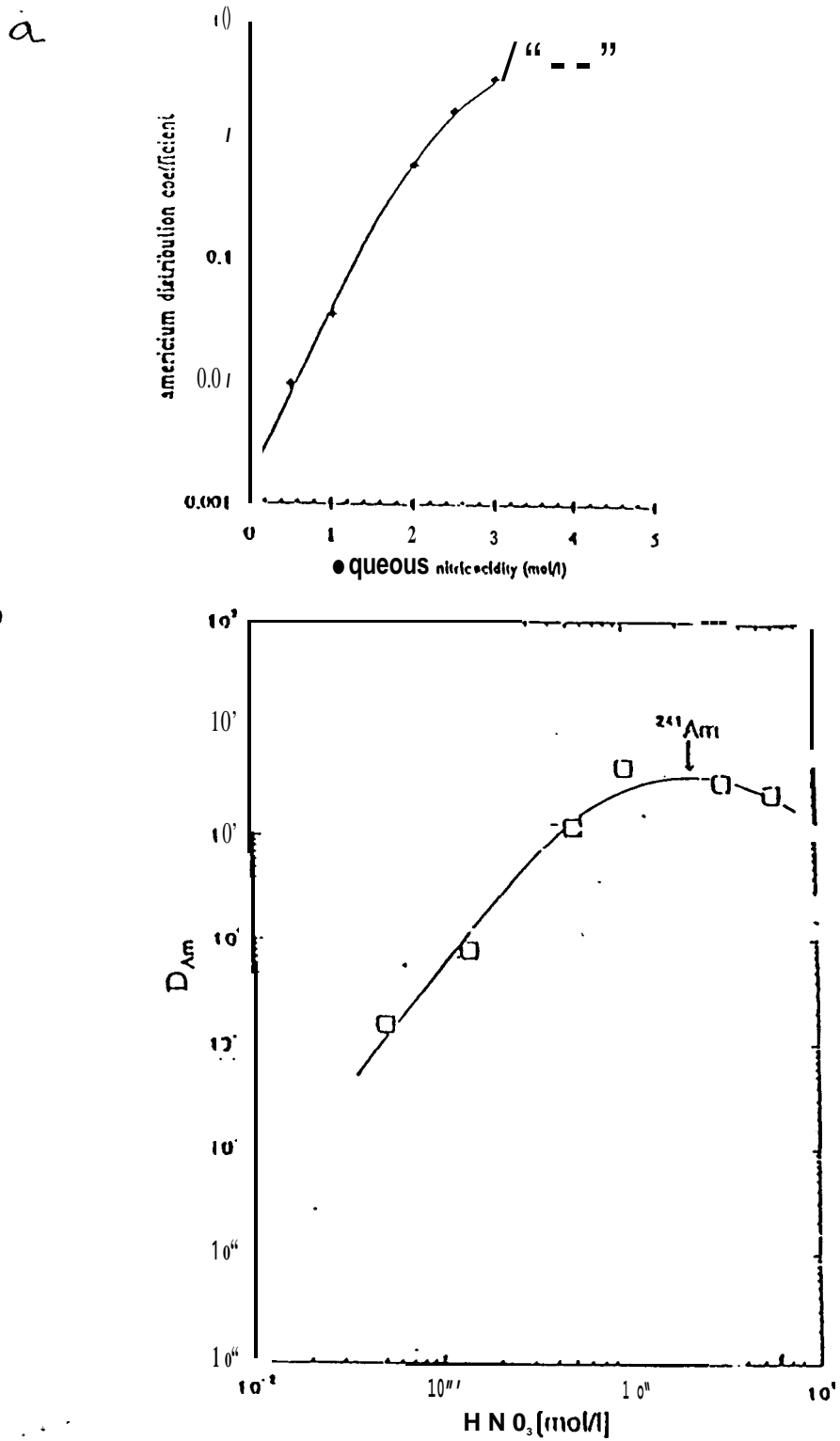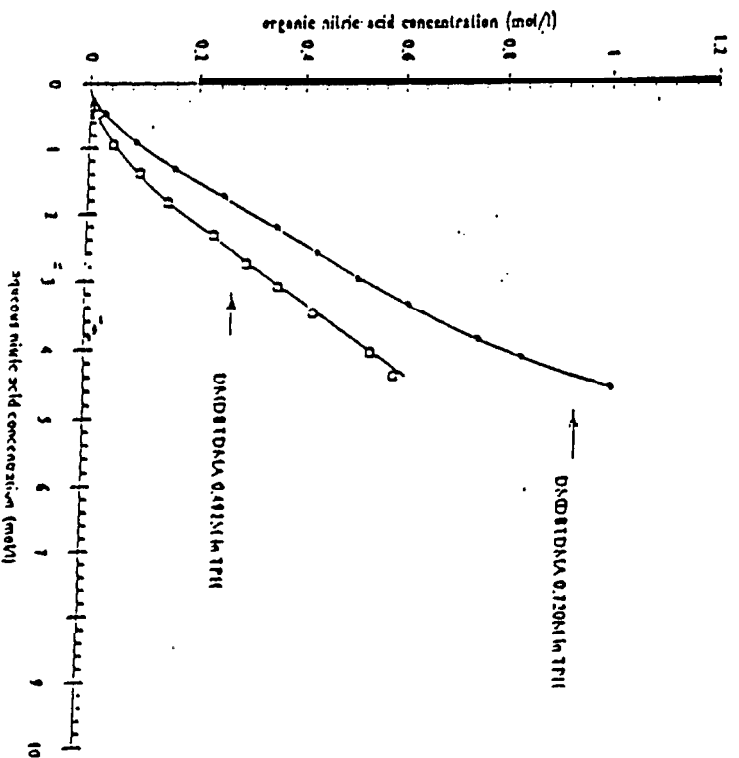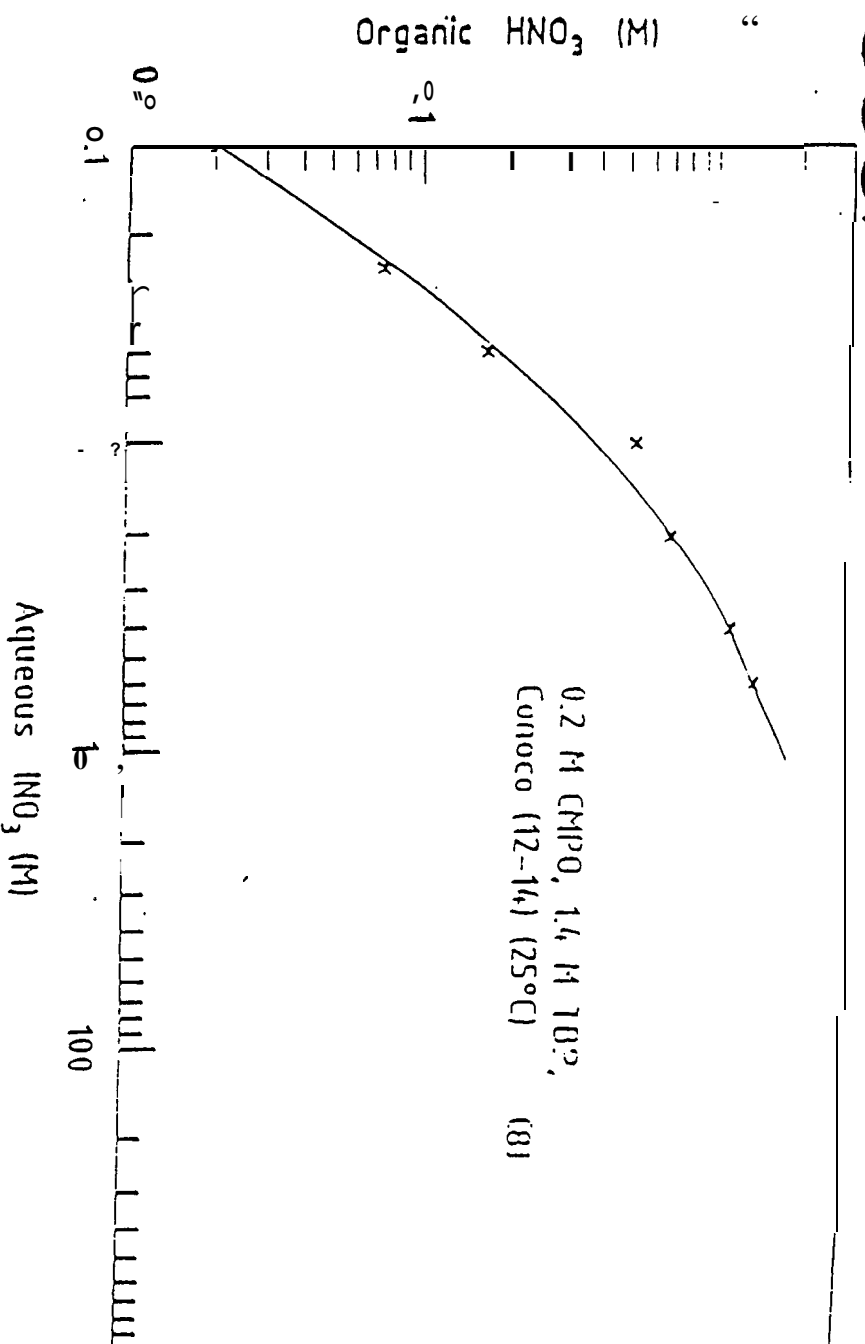
FIGURE 11 b : Am(III) extraction by :   CURVE 3

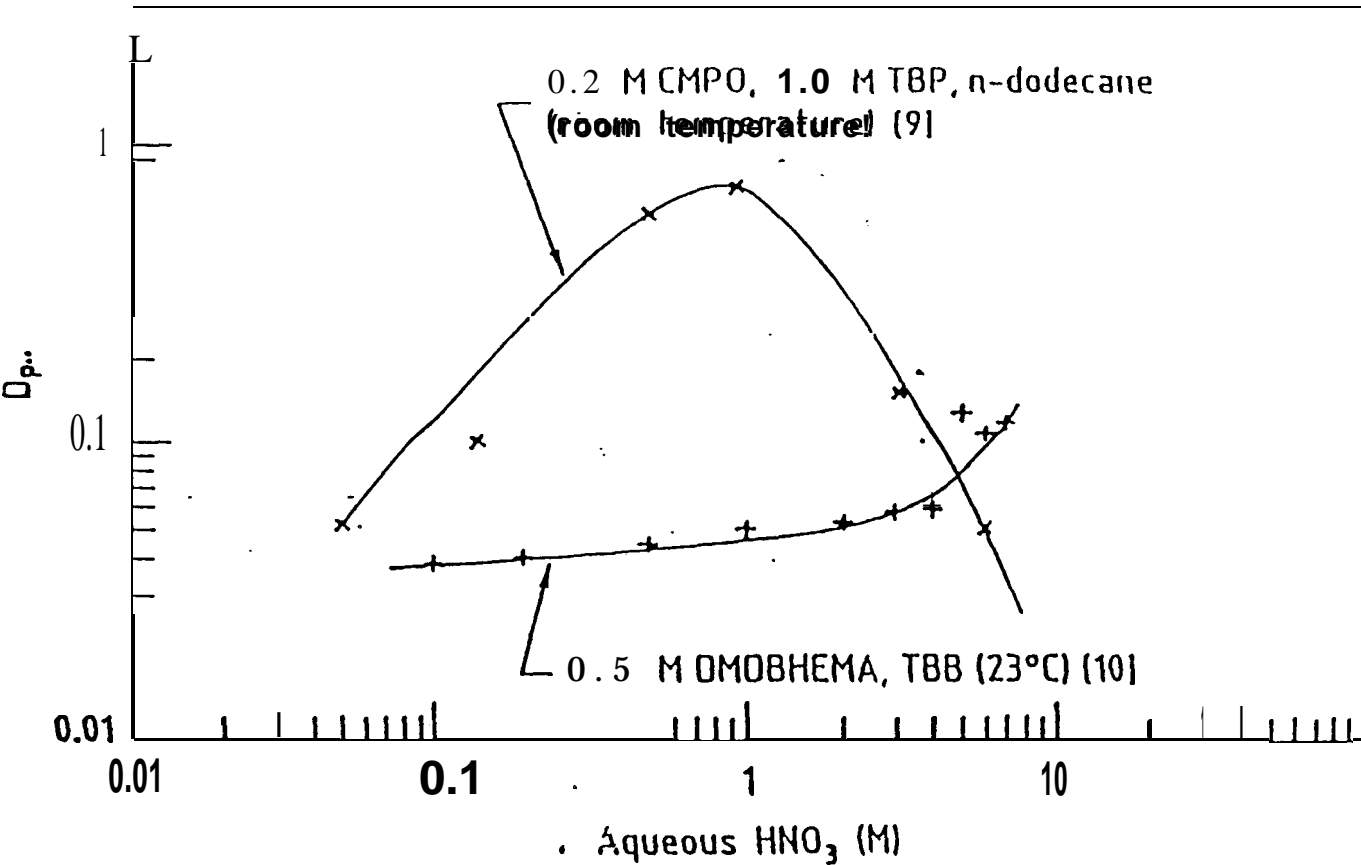a- 0.5M DMDBTDMA in TPH [1]

b- 0.2M CMPO, 1M TBP in dodecane (room temperature) [9]

Organic HNO$_3$ (M)

0.1 0^0 0^{-1}

Aqueous HNO$_3$ (M)

1b 100

0.2 M CMPO, 14 M TBP,
Conoco (12-14) (25°C) (8)

organic nitric acid concentration (mol/l)

0 0.2 0.4 0.6 0.8 1 1.2

aqueous nitric acid concentration (mol/l)

DMDBTDMA 0.493M in TPH

DMDBTDMA 0.730M in TPH

FIGURE 11 a : HNO$_3$ extraction by Truex solvent and dianide
DMDBTDMA

CURVE 4

FUEL CYCLE DIRECTION —————— WE WORK FOR THE FUTURE

L

D_{Ru}

0.2 M CMPO, **1.0** M TBP, n-dodecane
(room temperature) [9]

0.5 M DMDBHEMA, TBB (23°C) [10]

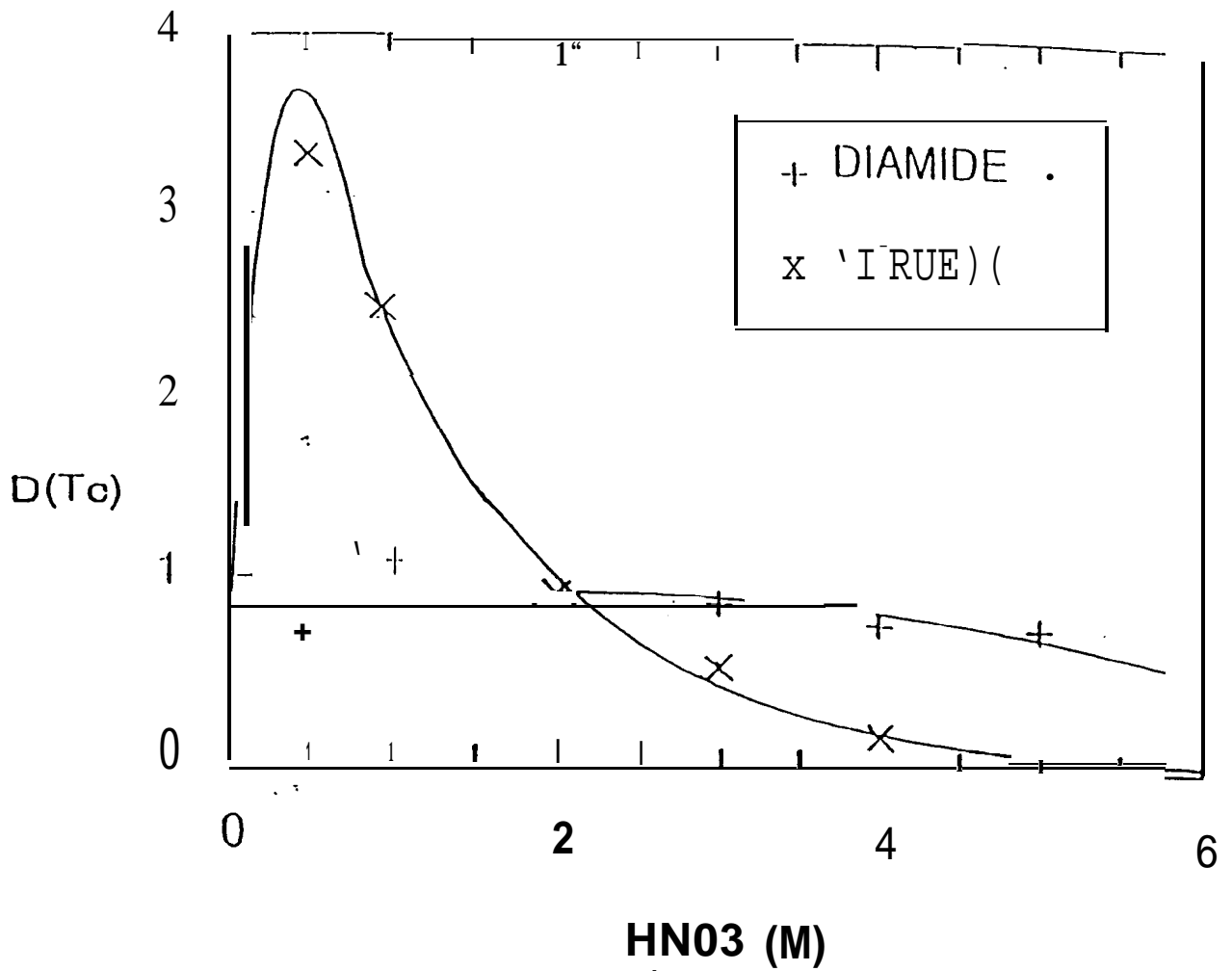. Aqueous HNO_3 (M)

$[H_2C_2O_4]$ (M)	0.05	0.1	0.2
'Ru	0.39	0.38	0.30

Extraction of Ru from a dissolved sludge waste(DSW) by 0.2 M CMPO, 1.4 M TBP, Conoco 12-14 diluent, (40°C,O/A = 0.5) as a function of oxalic acid in the feed (from [7]).

FIGURE 12: Extraction of Ru by diamides and Truex solvents.

CURVE 5

Tc(VII) extraction by diamides and Truex solvent

CURVE 6

- + 0. 5M DMDBHEMA, TBB (25°C, O/A=1) [2] .

× 0.2M CMPO, 1.4M T B P , Conoco C_{12} - C_{14} (40°C) [8]