MML i+e

Annexe III de la circulaire DPR 005

94100 15 96

MML 60 MN. FR9601279

C.E.A.

DEMANDE D'AUTORISATION
EN VUE D'UNE PUBLICATION OU D'UNE COMMUNICATION
à faire parvenir, par la voie hiérarchique pour accord

Direction : DCC
Centre : Marcoule
Réf. : . 12297

Titre du document[1] **:** Actinide Partitioning from high level liquid waste using the DIAMEX process -

AUTEURS	AFFILIATION[2]	DEPT./SERV./SECT. (ex. ../../...)	VISA (d'un des auteurs)	DATE
C. MADIC et al.	CEA	DRDD/SEMP		6/12/93

Nature[3]**:** 94 00 976

RAPPORT	THESE	REVUE	CONF/CONGRES	MEMOIRE DE STAGE	LIVRE	POLYCOPIE DE COURS	AUTRE
☐	☐	☐	☒	☐	☐	☐	☐

4. Int. Conf on Nuclear Fuel Reprocessing and Waste Management

TITRE (Revue, Congrès) : RECOD'94

ORGANISME OU ORGANISATEUR :

PAYS : UK **VILLE :** LONDON **Date :** 24-28 Avril 1994.

EDITEUR : –

COLLECTION : -

N° Vol :
Date Parution :

LANGUE : Anglais

Elément Programme

Les visas portés ci-dessous attestent que la qualité scientifique et technique de la publication proposée a été vérifiée et que la présente publication ne divulgue pas d'information brevetable, commercialement utilisable ou classée.

	SIGLE	NOM	DATE	VISA	OBS.
CHEF DE SERVICE	SEMP	B. BCULLIS	9/12/93		Régularisation (+)
CHEF DE DEPARTEMENT	DRDD	Po CAUCHETIER	16/12/93		

Un exemplaire du résumé est à joindre à chaque destinataire : D.O,INSTN/MIST/CIRST, Doc-Unité.

---

1 Titre en français suivi du titre en langue étrangère
2 Entité d'appartenance de l'auteur : Ex. CEA, CNRS, ISERM...
3 Cocher la case correspondante

VOL 27 № 14

(+) envoi / directement aux organisateurs

94001596
CEA-CONF-12297
FR9601279

RECOD '94 24-28 April 1994
London, UK

ACTINIDE PARTITIONING FROM HIGH LEVEL LIQUID WASTE USING THE DIAMEX PROCESS

C. MADIC[a], P. BLANC[a], N. CONDAMINES[a], P. BARON[a], L. BERTHON[a]
C. NICOL[a], C. POZO[a]
M. LECOMTE[b], M. PHILIPPE[b], M. MASSON[b], C. HEQUET[b]

and M.J. HUDSON[c]

CEA, DCC/DRDD
[a]SEMP, Section des Etudes de Chimie
[b]SPHA, Section des Procédés de Retraitement et d'Assainissement
CEN-FAR, B.P. n° 6, 92265 Fontenay-aux-Roses (FRANCE)
[c] Department of Chemistry - University of Reading
Whiteknights, PO.Box 224, Reading RG6 2AD (U.K.)

Abstract

The removal of long-lived radionuclides, which belong to the so-called minor actinides elements, neptunium, americium and curium, from the high level nuclear wastes separated during the reprocessing of the irradiated nuclear fuels in order to transmute them into short-lived nuclides, can substantially decrease the potential hazards associated with the management of these nuclear wastes.

In order to separate minor actinides from high-level liquid wastes (HLLW), a liquid-liquid extraction process was considered, based on the use of diamide molecules, which display the property of being totally incinerable, thus they do not generate secondary solid wastes. The main extracting properties of dimethyldibutyltetradecylmalonamide (DMDBTDMA), the diamide selected for the development of the DIAMEX process, are briefly described in this paper.

Hot tests of the DIAMEX process (using DMDBTDMA) related to the treatment of an MOX type HLLW, were successfully performed. ~~using the CYRANO hot cell in June 1993;~~ The minor actinide decontamination factors of the HLLW obtained were encouraging. The main results of these tests are presented and discussed in this paper.

86

mixed oxide fuels

authors. 9 figs. [illegible] pp, 4 tables.

94001596
CEA-CONF-12297
FR9601279

RECOD '94 **24-28 April 1994**
London, UK

ACTINIDE PARTITIONING FROM HIGH LEVEL LIQUID WASTE USING THE DIAMEX PROCESS

C. MADIC[a], P. BLANC[a], N. CONDAMINES[a], P. BARON[a], L. BERTHON[a]
C. NICOL[a], C. POZO[a]
M. LECOMTE[b], M. PHILIPPE[b], M. MASSON[b], C. HEQUET[b]

and M.J. HUDSON[c]

CEA, DCC/DRDD
[a]SEMP, Section des Etudes de Chimie
[b]SPHA, Section des Procédés de Retraitement et d'Assainissement
CEN-FAR, B.P. n° 6, 92265 Fontenay-aux-Roses (FRANCE)
[c] Department of Chemistry - University of Reading
Whiteknights, PO.Box 224, Reading RG6 2AD (U.K.)

Abstract

The removal of long-lived radionuclides, which belong to the so-called minor actinides elements, neptunium, americium and curium, from the high level nuclear wastes separated during the reprocessing of the irradiated nuclear fuels in order to transmute them into short-lived nuclides, can substantially decrease the potential hazards associated with the management of these nuclear wastes.

In order to separate minor actinides from high-level liquid wastes (HLLW), a liquid-liquid extraction process was considered, based on the use of diamide molecules, which display the property of being totally incinerable, thus they do not generate secondary solid wastes. The main extracting properties of dimethyldibutyltetradecylmalonamide (DMDBTDMA), the diamide selected for the development of the DIAMEX process, are briefly described in this paper.

Hot tests of the DIAMEX process (using DMDBTDMA) related to the treatment of an MOX type HLLW, were successfully performed using the CYRANO hot cell in June 1993. The minor actinide decontamination factors of the HLLW obtained were encouraging. The main results of these tests are presented and discussed in this paper.

I. Introduction

The reprocessing of irradiated nuclear fuels, in order to recover the fissile materials, uranium and plutonium, which are valuable for power generation, allows the separation of the nuclear wastes composed of fission and activation products, and of the minor actinides neptunium, americium and curium. After separation, these wastes are conditioned in the form of glass blocks intended for future disposal in an underground repository. Considering the potential hazards associated with the storage of these vitrified nuclear wastes in the repository, it can be calculated that, for a period exceeding three centuries (time required for the decay of the major fission products ^{137}Cs and ^{90}Sr) the main potential hazards lie in the presence, in these blocks, of the alpha-emitting minor actinide nuclides : ^{237}Np, $^{241,243}Am$ and ^{244}Cm. Thus, an improvement can be expected in the management of these wastes by removing the minor actinides followed by their transmutation into short-lived nuclides. In France, under the law passed by parliament on 30 December 1991, the CEA launched a major research programme in this field, called the SPIN (SéParation-INcinération) programme.

In connection with the SPIN programme, two cases can be considered for the minor actinide separation processes (1).

Firstly, the removal of neptunium is the simplest problem to be solved. In COGEMA's UP3 reprocessing plant at La Hague, for example, most of the neptunium initially present in the irradiated fuel is co-extracted with uranium and plutonium in the first extraction cycle, and is then separated from the uranium in the second uranium separation cycle. After separation, the neptunium-bearing aqueous solution is mixed with the HLLW raffinate. Thus, with minor changes in the PUREX process flow-sheet and to the plant design, not described in the present paper, a quasi-quantitative separation of neptunium from HLLW can be achieved.

Secondly, for the removal and separation of the americium and curium, which is a far more difficult problem, a two-step strategy was considered, both steps based on the use of extracting agents composed only of C, H, O and N atoms, thus minimizing the amount of secondary solid waste generated, owing to the total incinerability of these extractants. The first step of this strategy, the so-called DIAMEX process (DIAMide EXtraction), is based on the use of diamide extractants, belonging to the malonamide sub-group, which, owing to their bidendate character, display the ability to extract trivalent actinide nitrates from nitric acidic effluents (HLLW). Since trivalent lanthanide nitrates, which account for about a third of the total fission products, are also co-extracted by the diamide, a second separation step is necessary, for which alkylated derivatives of tripyridyltriazine (RTPTZ) can be employed.

This paper focuses on the DIAMEX process and provides :

- a summary of the main extracting properties of the diamide molecule selected for the development of the process,
- the results of the first hot tests of the DIAMEX process, conducted in June 1993, related to the treatment of a MOX-type HLLW.

II. Results and discussion

II.1. Summary of the extracting properties of dimethyldibutyltetradecylmalonamide

In designing solvent extraction processes for nuclear fuel reprocessing or liquid waste treatment, it has long been recognised that neutral extractants, which enable the easy reversible extraction and stripping of the metallic salts of interest from aqueous solutions with high and low nitric acidities respectively, are the preferred molecules. A problem encountered in the extraction of trivalent americium and curium nitrates present in HLLW generated by nuclear fuel reprocessing by the PUREX process, using neutral extractants, is the competitive extraction of nitric acid. Neutral bidentate extractants can be used to circumvent this problem, .

Years ago, C. Musikas. (2-5) proposed the use of diamide extractants, and among them those belonging to the malonamide sub-group, with the general formula $(RR'NC(O))_2CHR''$, where R, R' and R" are hydrogen or hydrocarbon substituents. The bidentate character of malonamides arises from the ability of the two oxygen atoms of the amide functions to be bonded to metallic ions. The other criteria considered for selecting the best malonamide were :

- the solubility of the extractant in the industrial diluent TPH (hydrogenated tetrapropene) used in COGEMA's reprocessing plants. TPH is a complex mixture of branched hydrocarbons with an average of 12 carbon atoms in the skeleton of the molecule,
- the low ability shown by solvents consisting of malonamides dissolved in TPH to form third phases during the extraction of various solutes, such as nitric acid and metallic nitrates.

So far, dimethyldibutyltetradecylmalonamide (DMDBTDMA) of formula $(CH_3C_4H_9NC(O))_2CHC_{14}H_{29}$ is considered to be one of the best malonamides (6-7). It was selected for the development of the DIAMEX process.

Solubility in TPH

DMDBTDMA is a yellow liquid at room temperature and is highly soluble in TPH. Its solubility at 22°C, is higher than 1.5 mol/L, suggesting high potential extracting capacities for the solvent.

Extraction of metallic nitrates at low concentration.

Actinides

Figure 1 shows the distribution coefficients (D_{Mn+}) of various metallic nitrates of interest vs aqueous nitric acidity at equilibrium during extraction by a solution of DMDBTDMA 0.5 mol/L in TPH, at room temperature. For all the metallic nitrates investigated, an increase in the aqueous nitric acid concentration causes an increase in the distribution coefficients. Thus, for example, for Am(III) nitrate, the solvent demonstrates a high affinity at high aqueous nitric acidities, whereas low distribution coefficients are obtained at low nitric aqueous acidities. These properties are ideal for the effective extraction and stripping of this salt. Figure 1 also shows that U(VI) and Pu(IV) nitrates are extracted better than Am(III) nitrate. The affinity sequence is : U(VI) > Pu(IV) > Am(III).

In conducting hot tests of the DIAMEX process (see below), it was found that the affinity of DMDBTDMA for Cm(III) nitrate is similar to that exhibited for Am(III) nitrate. Nervertheless, for 4 mol/L nitric aqueous solution, the separation factor $D_{Am(III)}/D_{Cm(III)}$ was found to be close to 1.6, perhaps allowing their separation in a multi-stage process.

Fission products

Among fission products, special attention was paid to lanthanides, zirconium and molybdenum, the nitrate salts of which exhibit high affinities for DMDBTDMA.

Extraction of lanthanide (III) nitrates is similar to that of An(III) nitrates : high and low affinities are observed for high and low aqueous nitric acid concentrations respectively. Thus it appears quite impossible to separate An(III) from Ln(III) using the DIAMEX process. Among the lanthanide series, the affinity of DMDBTDMA decreases with increasing atomic number of the element. For example, a $D_{Nd(III)}/D_{Er(III)}$ separation factor close to 5 was observed. A comprehensive study in this field is now underway, and will be published later.

The extraction of Zr(IV) nitrate by DMDBTDMA is also a function of the aqueous nitric acid concentration. The affinity of the extractant for Zr(IV) nitrate is higher than for An(III) (or Ln(III)) nitrate(s). To prevent the extraction of this abundant fission product, it is possible to use oxalic or ketomalonic acid as specific Zr(IV) "salt-free" complexing agents.

The affinity of DMDBTDMA for molybdenum (VI) nitrate is also high for concentrated aqueous nitric acid solutions. Nevertheless, the extraction of Mo(VI) can be prevented by the presence, in the aqueous solutions, of hydrogen peroxide ("salt-free" reagent), which is able to complex Mo(VI) selectively.

Further details on the extraction of other fission product nitrates, especially of the ruthenium, are provided in section II.2. of this paper (see below).

Iron (III)

Special attention must be paid to the extraction of Fe(III) nitrate by DMDBTDMA. In effect, this salt is always present in the effluent owing to corrosion of the process equipment, exhibits a high affinity for DMDBTDMA, as shown in Figure 1. Contrary to the extraction and stripping of the nitrates of most of the salts that display a strong affinity for DMDBTDMA, the rates of the kinetics of Fe(III) nitrate transfer between the organic and aqueous phases are very low. If this property can be considered advantageous for the separation of Fe(III) due to the slow extraction rate, it is also a disadvantage, in view of the possible accumulation of Fe(III) nitrate in the solvent. Specific solutions must therefore be devised to deal with this problem.

Third phase formation

In designing liquid-liquid extraction processes one of the major points to be studied is third phase formation, i.e. the splitting of the organic phase into two layers, when extracting solutes in macro amounts. This phenomenon is often particularly acute when aliphatic hydrocarbon diluents are used. Third phase formation also occurs with diamide extractants. As DMDBTDMA is the present result of the optimization of the diamide formula, especially in connection with third phase formation, its properties in this area can be considered to be satisfactory. Data on third phase boundaries for the extraction of various solutes, such as nitric acid and Nd(III), U(VI) and Fe(III) nitrates by DMDBTDMA solutions in TPH at room temperature, are given in Table 1. Third phase formation was also noted, qualitatively, in the extraction of Zr(IV) nitrate.

Extraction mechanisms

Nitric acid

The extraction of nitric acid by DMDBTDMA solutions in TPH is rather complex. If the mechanism can be represented by the following simple equation :

$$\overline{xL} + yH^+ + yNO_3^- \Leftrightarrow \overline{L_x(HNO_3)_y}$$

where L represents DMDBTDMA, the complexity is evident when considering the number of solvates formed. They possess the stoichiometries (x/y) 2/1, 1/1, 1/2 and 1/3. None of these species are hydrated, but the formation of each can induce the solubilization of some water in the organic phase.

Metallic nitrates

The extraction mechanisms of various metallic nitrates, U(VI), Pu(IV), Am(III), Ln(III), etc., were determined using several methods, including: U.V.-visible and FTIR spectroscopies, slope analysis, and organic phase saturation studies. The results obtained can be summarized as follows :

- the bidendate character of DMDBTDMA is established : the two amidic oxygen atoms are always bonded to the metal ion in the neutral solvates formed (9),

- the principal extraction mechanism corresponds to the formation of neutral solvates, with the following stoichiometries (metal nitrate/ligand) : U(VI) (1/1) ; Pu(IV) (1/1 and 1/2) ; Am(III) and Nd(III) (1/1 and 1/2),

- a comparison of the results obtained by slope analysis and organic metal ion saturation methods shows that for neutral solvates, diamide molecules are present in a second coordination sphere of the metal, certainly bonded to the diamide molecules present in the metal ion inner-sphere of coordination,

- an ion pair extraction mechanism is also observed in the extraction of Am(III) and Nd(III) for high nitric acid concentrations, with the formation of the acidic species with the general formula $H_yM(NO_3)_{3+y}L_x$.
- the extraction of Fe(III), and certainly that of Zr(IV), proceeds via the formation of ion pair(s).

The co-existence of two mechanisms for the extraction of metallic nitrate complexes is one of the salient features among the properties of diamide extractants.

II.2. First tests of the DIAMEX process : treatment of an MOX type HLLW.

General considerations

Since DMDBTDMA displays reasonable extracting properties, probably matching those required for the design of the first step of a minor actinide partitioning process, it was the diamide selected for the development of the DIAMEX process.

In order to identify the main problems to be solved in process development, it was considered important to first conduct counter-current integrated tests in mixer-settlers using real HLLW, instead of studying synthetic solutions spiked with radionuclides, which is more conventional. These tests had limited objectives :

- demonstration of the quantitative removal of alpha emitters (americium and curium radionuclides) from the HLLW,
- proof of the feasibility of the non-extraction of Zr(IV) and Mo(VI) species when adding specific "salt-free" complexing agents to the aqueous solutions : ketomalonic acid for Zr(IV), and hydrogen peroxide for Mo(VI),
- study of the behaviour of the main metallic species in the different steps of the tests : extraction, scrubbing and stripping,
- demonstration of the quantitative stripping of extracted actinide (III) nitrates from the loaded solvents, by contact with dilute nitric acid solutions,
- study of the hydraulic behaviour of the solvent in the different steps of the hot tests.

For this study, an MOX type HLLW, available in the CYRANO hot-cell, was used for the three hot tests.

HLLW composition

The HLLW used was generated by the PUREX process in the treatment of a sample of MOX fuel, irradiated to a burn-up of 34 GWd/t of initial (U+Pu), and cooled for five years. PUREX treatment of the fuel was performed in February 1993, and the HLLW amounted to 5.2 m^3/t of initial (U+Pu).

This effluent was analyzed by acid-base titration, nuclear (alpha and gamma counts and spectrometry) and Induced Coupled-Plasma-Atomic Emission Spectrometry (ICP-AES) measurements. The main results obtained are given in Table 2.

Preliminary studies

Hydraulic behaviour of the solvent

Some years ago, a 5 kg batch of DMDBTDMA was prepared by IRCHA (Vert-le-petit, 91, France). 1.7 kg of this batch was made available for hot tests of the DIAMEX process.

To define the experimental conditions to be used in the countercurrent mixer-settler tests, hydraulic experiments were performed using test-tubes or a mixer-settler battery identical to the one to be used in the CYRANO hot-cell (8 stages, each stage having a total volume of 25 mL and a mixer volume of 5.6 mL)

It was first found that the DMDBTDMA had to be purified, because of the poor settling behaviour of the emulsions formed with organic solutions of DMDBTDMA in TPH and aqueous solutions, especially those made with pure water or soda solutions. This was thought to be due to the presence of a minute quantity of surfactant in the batch of DMDBTDMA. While no direct evidence of such an impurity was obtained, the diagnosis was certainly correct. The settling time of emulsions prepared in standardized conditions, was substantially reduced after purification of the DMDBTDMA solutions in TPH. Several purification methods were examined :

- chromatography on columns containing the following solid phases : alumina A, alumina B, charcoal, Actisil ^{R}, silica and zirconia,

- washing with acidic and basic aqueous solutions.

The most effective method, chromatography with alumina B, was accordingly used to treat the entire batch of DMDBTDMA solution.

Test-tube settling experiments, using 0.5 mol/L DMDBTDMA purified solution in TPH, were performed for emulsions formed with various aqueous solutions. The corresponding results are given in Table 3. For aqueous nitric acid solutions with concentrations > 0.5 mol/L, the settling times can be considered to be satisfactory. On the contrary, the settling times for 0.1 mol/L nitric acid solution or water are too long for practical purposes. Thus, reasonable settling times can be predicted for emulsions formed in the extraction (nitric acidity close to 4 mol/L, see Table 2) and actinide stripping steps, during hot countercurrent tests. In the later case, the stripping aqueous solution is 0.5 mol/L nitric acid.

Cold mixer-settler experiments were performed to determine the flowrates of the feed (4 mol/L nitric acid solution was used to simulate the HLLW) and stripping solution (0.5 mol/L HNO_3), to be used in the hot tests. Residence times 2 and 4 min respectively for the feed in the extraction section, and for the stripping solution in the stripping section, were found to be satisfactory : the aqueous phase entrainment rates into the settled organic phases were only 0.3 % (in volume) and 0.7 %, respectively. These residence times correspond to the following flowrates : * 84 mL/h for the feed and * 42 mL/h for the stripping aqueous solution.

Qualitative experiments were performed to estimate the effect of possible solvent degradation owing to hydrolysis and radiolysis on its hydraulic behaviour. The time scale considered corresponded to the total residence time in the mixer-settlers. No change was observed in the hydraulic properties of the solvent during these tests.

Distribution coefficients of the main metallic species and third phase formation.

The distribution coefficients of the main metallic species contained in the MOX type HLLW were determined for extraction from the HLLW (4 mol/L nitric acidity) and for back-extraction from the loaded organic phase into a 0.5 mol/L nitric aqueous solution. The results are given in Table 4.

As expected from the results of tracer scale experiments, high distribution coefficients were obtained for extraction from HLLW, for An(III), Ln(III), Zr(IV), Fe(III) and Mo(VI) species, but no extraction was observed for Sb and Cs(I) species. Ruthenium is an intermediate case : the distribution coefficient of the Ru species (D_{Ru} = 0.5) is sufficiently high to create a separation problem from the mixture An+Ln. No problems in back-extraction of the extracted species from the loaded organic phase were encountered, except for Fe(III) and, more importantly, for Ru species.

In order to prevent the coextraction of Zr(IV) and Mo(VI) species with the An(III)+Ln(III) mixture, these metallic ions can be converted into aqueous soluble complexes with the following "salt-free" ligands : ketomalonic acid for Zr(IV), and hydrogen peroxide for Mo(VI).

These data suggested good general extraction-stripping behaviour of the main species of interest, except for the inactive Fe(III) species, present in the HLLW in low concentration, and for Ru species (containing the radionuclide ^{106}Ru), for which specific solutions would be required to solve the problems.

The effect of the Vo/Va ratio (with Vo and Va the volume of the organic and aqueous phases, respectively), of organic 0.5 mol/L DMDBTDMA (TPH) phase to HLLW, on third phase formation was studied. For Vo/Va > 0.9, no third phase occurs, but for Vo/Va = 0.83 , 0.66 and 0.5, third phase formation was observed, with a larger volume of heavy phase at lower Vo/Va. For Vo/Va = 1, a third phase also occurs if the organic phase is contacted twice with HLLW. Consequently, to prevent the occurrence of third phase formation during the hot counter-current tests in mixers-settlers, sufficiently high Vo/Va ratios are necessary for the extraction section of the battery.

Flowsheets tested and main results

The flow conditions of the three hot tests performed are listed in Table 5.

Since the fluids moved with difficulty in the CYRANO type mixers-settler battery with the solvent DMDBTDMA, a limited number of stages was selected : 6, 2 and 8 for the extraction, scrubbing and stripping sections, respectively. This accordingly limited the expected separation performance. In tests 2 and 3, the feed was adjusted prior to its introduction into the mixer-settler battery. This was designed to prevent any destruction of ketomalonic acid (Zr(IV) complexant) owing to radiolysis. In test 2, an attempt was made to strip the extracted metallic species "on line" with the extraction and scrubbing steps, thus cutting by half the residence time of the solutions in the mixers of the stripping section stages recommended from the results of the cold hydraulic tests.

The behaviour of alpha-emitters in the three tests is indicated in Table 6, while Figure 2 presents an example of the alpha activity profiles in the extraction and scrubbing sections of the mixer-settler battery, in the second test. For the three tests, the alpha-emitter decontamination factors are excellent (Table 6). If necessary, these figures can be improved because, as shown in Figure 2, the alpha activity profiles (in semi-log plots) are quasi-linear in the extraction section, this is due in particular to the small variations in nitric acid concentration along the stages, so that the same behaviour can be expected with extra stages. From Figure 2, it was also observed that very little accumulation of metallic species occurs during the test. Stripping of the actinides from the loaded solvent, by contact with 0.5 mol/L nitric acid solution, performed "on-line" in test 2, was excellent (Table 6). For test 1, the actinides were stripped batch-wise with the loaded solvent aged for 24 hours. While a settling problem of the emulsion formed was evident, no retention of actinide alpha emitters in the stripped solvent was observed.

The behaviour of the main fission products and of Fe(III) is shown in Table 7. As expected, in the absence of complexant, Ln(III), Zr(IV)and Mo(VI) are coextracted with the actinides. The Ru and Fe(III) species are also partially co-extracted. The presence of ketomalonic acid in the feed and in the aqueous scrubbing solution helps to prevent the extraction of Zr(IV) species (test 2). The small decrease in the alpha decontamination factor (comparison with test 1) of the effluent (see Table 6) is not related to the presence of ketomalonic acid in the scrubbing solution, but to the modifications of the flowrates. As shown in Table 7, the expected non-extraction of Zr(IV) and Mo(VI) species owing to the presence in the scrubbing solution of ketomalonic acid and hydrogen peroxide, was not confirmed : about half of these species were extracted. This extraction is certainly due to the mutual destruction of these two reagents (redox reaction). The stripping of fission products from the loaded solvent was excellent, except for the Ru species : 11% of the total Ru inventory remained in the solvent.

The hydraulic behaviour of the solvent in the 8 stage CYRANO type mixer-settler battery was satisfactory for tests 1 to 3. Nevertheless, progress in this area is required, for the use of more stages to improve performance. It was also found that the stripping operation could not be run with aged loaded solvent (test 1) owing to the formation of a stable emulsion.

III. Conclusions

The first hot tests of the DIAMEX process conducted during the treatment of an HLLW can be considered to have been successful. The main goals of these tests were attained : °good alpha decontamination factor of the effluent, ° good stripping of the actinide alpha emitters from the loaded solvent, even if the solvent was aged after loading, ° prevention of the extraction of Zr(IV) species by the addition of ketomalonic acid, ° reasonable hydraulic behaviour of the solvent. However, a number of problems were identified, including : ° separation of ruthenium, and especially its stripping from the solvent, ° separation of molybdenum, feasible by using two separate scrubbing sections with complexing agents (ketomalonic acid and hydrogen peroxide), ° improvement of the hydraulic behaviour of the solvent in the battery. Obviously, the procedure for regenerating of degraded solvent needs to be defined to design an entire process flow-sheet.

For the development of the DIAMEX process, it is considered that the use of the diamide DMDBTDMA is a satisfactory strategy. Nevertheless, studies of other diamides are underway (8). In comparison with DMDBTDMA, some of the new diamides investigated display improved extracting properties, especially for their loading capacities without third phase formation.

Acknowledgement

Part of this study was carried out with CEC financial support under the Fourth Research and Development Programme on the Management and Disposal of Radioactive Waste, Contract F.012W-CT91-0112 performed jointly by the CEA (France) and the University of Reading (U.K.)

References

1. J.M. ADNET, L. NIGOND, N. CONDAMINES, J. BOURGES and C. MADIC
   Proceedings of SAFEWASTE 93 International Conference 13-16 June 1993
   Avignon (France), vol.2 323 SFEN Ed.
2. C. MUSIKAS
   "Actinide-lanthanide separations", G.R. CHOPPIN, J.D. NAVRATIL, W.W. SCHULZ Eds. Word Scientific (1984)
3. C. MUSIKAS
   Proceedings of "ISEC 90" Kyoto (1990).
4. C. CUILLERDIER, C. MUSIKAS, P. HOEL, L. NIGOND and X. VITART
   Separation Science and Technology. 26.(9) 1229-1244 (1992)
5. C. CUILLERDIER, C. MUSIKAS and L. NIGOND
   Separation Science and Technology. 28,(1-3) 155-175 (1993)
6. L. NIGOND
   Thèse de Doctorat de l'Université Blaise Pascal (1992).
   Published as CEA-R-5610
7. L. NIGOND, C. MUSIKAS and C. CUILLERDIER
   To be published in Solvent Extraction and Ion Exchange 12 (2) (1994)
8. L. NIGOND, N. CONDAMINES, P-Y. CORDIER, J. LIVET, C. MADIC, C. CUILLERDIER, C. MUSIKAS, and M.J. HUDSON
   "Recent advances in nuclear wastes treatment via the use of diamide and picolinamides extractants", Eighth Symp. on Separation Science and Technology for Energy Application, Gatlinburg (October 1993)
9. P. BYERS, M.G.B. DREW, M.J. HUDSON, N.S. ISAACS and C. MADIC
   Will be published in Polyhedron (1994).

$[DMDBTDMA]^b$	Third phase boundaries							
	HNO_3		Nd(III)		U(VI)		Fe(III)	
	$[HNO_3]$	$[HNO_3]^b$	$[HNO_3]$	$[Nd]^b$	$[HNO_3]$	$[U]^b$	$[HNO_3]$	$[Fe]^b$
0.5	4.7	N.D.[a]	/	/	3	0.02	/	/
0.65	5.7	1.2	4.0	0.041	/	/	/	/
0.67	/	/	/	/	/	/	3.5	0.026

[a] : N.D. = Not Determined

[b] : species present in the organic phases are overlined.

Table 1 . Third phase boundaries for the extraction of various solutes by DMDBTDMA in solution in TPH at room temperature.
(the figures in the table represent the concentrations of the various species in aqueous or organic solutions expressed in mol/L)

Alpha counting and spectrometry		**Gamma counting and spectrometry**		**ICP-AES**	
Species	**Activity[a] (concentration[b])**	**Species**	**Activity[a]**	**Species**	**Concentration[b]**
^{244}Cm	5.97 (73)	^{137}Cs	19.1	Nd	633
^{241}Am	1.23 (367)	^{134}Cs	6.5	Zr	456
^{242}Cm	0.05	^{106}Ru	4.2	Ce	394
^{243}Am	0.03 (150)	^{144}Ce	3.9	Mo	387
		^{154}Eu	1.4	Fe	23
		^{125}Sb	0.47	U	<10
				Pu	< 0.5
				Np	<10
Total	7.28		35.6		1900

[a] : activities of alpha and beta, gamma radionuclides are expressed in Ci/L,

[b] : concentrations of metallic species are expressed in mg/L.

Table 2 . Composition of MOX type HLLW used for hot tests of the DIAMEX process.
(the nitric acid concentration of the effluent was 4 mol/L)

Aqueous phase composition[a]	**Settling time of aqueous phase (s)**	**Settling time of organic phase (s)**
HNO_3		
4	64	35
1	68	48
0.5	130	120
0.1	no settling	no settling
H_2O	210	250
NaOH		
1	220	120

[a] : figures in the table correspond to the nitric acid or caustic soda concentrations expressed in mol/L

Table 3 . Settling time of various emulsions made by 0.5 mol/L DMDBTDMA solution in TPH mixed with various aqueous solutions.
(room temperature, mechanical mixing with a propeller, rotation 4000 rpm)

Species	$D_{M^{n+}}$	
	HNO_3 4 mol/L	HNO_3 0.5 mol/L
^{241}Am(III)	4.3	$< 10^{-3}$
^{244}Cm(III)	2.8	$< 10^{-3}$
Zr(IV)	35 (0.9[a])	< 0.05
Fe(III)	26	0.55
Mo(VI)	4.5 (0.3[b])	< 0.05
^{144}Ce(III)	3.3	$< 10^{-2}$
Nd(III)	3.2	< 0.05
^{154}Eu(III)	1.7	$< 10^{-2}$
^{106}Ru	0.5	2.5
^{125}Sb	$< 10^{-3}$	N.D.[c]
$^{137-134}$Cs(I)	$< 10^{-3}$	N.D.[c]

[a] : presence of 0.05 mol/L of ketomalonic acid in the HLLW
[b] : presence of 0.1 mol/L of hydrogen peroxide in the HLLW
[c] : Not Determined

Table 4 . Distribution coefficients of the main metallic species contained in the MOX type HLLW.

(experimental conditions : DMDBTDMA 0.5 mol/L in TPH, Vo/Va = 1, temperature : 30 °C, emulsion time = 25 mn. For 4 mol/L nitric acid, the distribution coefficients correspond to extraction from HLLW, whereas for 0.5 mol/L nitric acid, the distribution coefficients correspond to back-extraction from the previously loaded organic phases)

Test N°	Feed	Feed adjustment	Solvent	Scrub
1	MOX type 34 GWd/t 5 years cooling 5.2 m^3/t HNO_3 = 4 mol/L		DMDBTDMA 0.5 mol/L TPH	HNO_3 2 mol/L
	56 mL/h		84 mL/h	11.2 mL/h
2	MOX type 34 GWd/t 5 years cooling 5.2 m^3/t HNO_3 = 4.8 mol/L	HNO_3 5 mol/L KMA[a] 1 mol/L	DMDBTDMA 0.5 mol/L TPH	HNO_3 2 mol/L KMA[a] 0.1mol/L
	56 mL/h	5.6 mL/h	84 mL/h	33.6 mL/h
3	MOX type 34 GWd/t 5 years cooling 5.2 m^3/t HNO_3 = 4.8 mol/L	HNO_3 5 mol/L KMA[a] 1 mol/L	DMDBTDMA 0.5 mol/L TPH	HNO_3 2 mol/L KMA[a] 0.1 mol/L H_2O_2 0.1 mol/L
	56 mL/h	5.6 mL/h	84 mL/h	33.6 mL/h

[a] : KMA = ketomalonic acid

Table 5. **Flow conditions for the hot countercurrent tests of the DIAMEX process**
Temperature : test 1 : 35.5 °C ; test N°2 : 37 °C for the extraction-scrubbing sections and 36 °C for the stripping section ; test N°3 : 38 °C.
Total run time (number of test): 15.6 h (1) ; 11.5 h (2) ; 7.5 h (3).
Time required for steady state conditions : 6H

Test N°	D.F (alpha) [a]		
	Total	Am	Cm
1	900	1100	800
2	290	2000	250
3	180	210	180

[a] : DF (alpha) = ratio of initial alpha activity of effluent to final alpha activity

N.B : stripping of alpha emitters from the loaded solvent is excellent : the remaining solvent alpha activity represents only 0.003 % of the total. (test 2).

Table 6 : DIAMEX. : General behaviour actinide alpha emitters Am and Cm.

Test N°	Extracted species (% of feed content)								
	Ce	Nd	Eu	Zr	Mo	Ru[a]	Fe	Sb	Cs
1	100	99.9	100	99.8	99.6	54	86.4	< 0.2	< 0.02
2	99.5	99.4	100	0	73.4	50	66.2	< 0.2	< 0.02
3	99.4	99.2	100	47.2	57.4	44	59.8	< 0.2	< 0.02

[a]: stripping is excellent for all extracted species except Ru : 11% of total Ru remains in the solvent.

Table 7. DIAMEX. Behaviour of main fission products and of Fe (III)

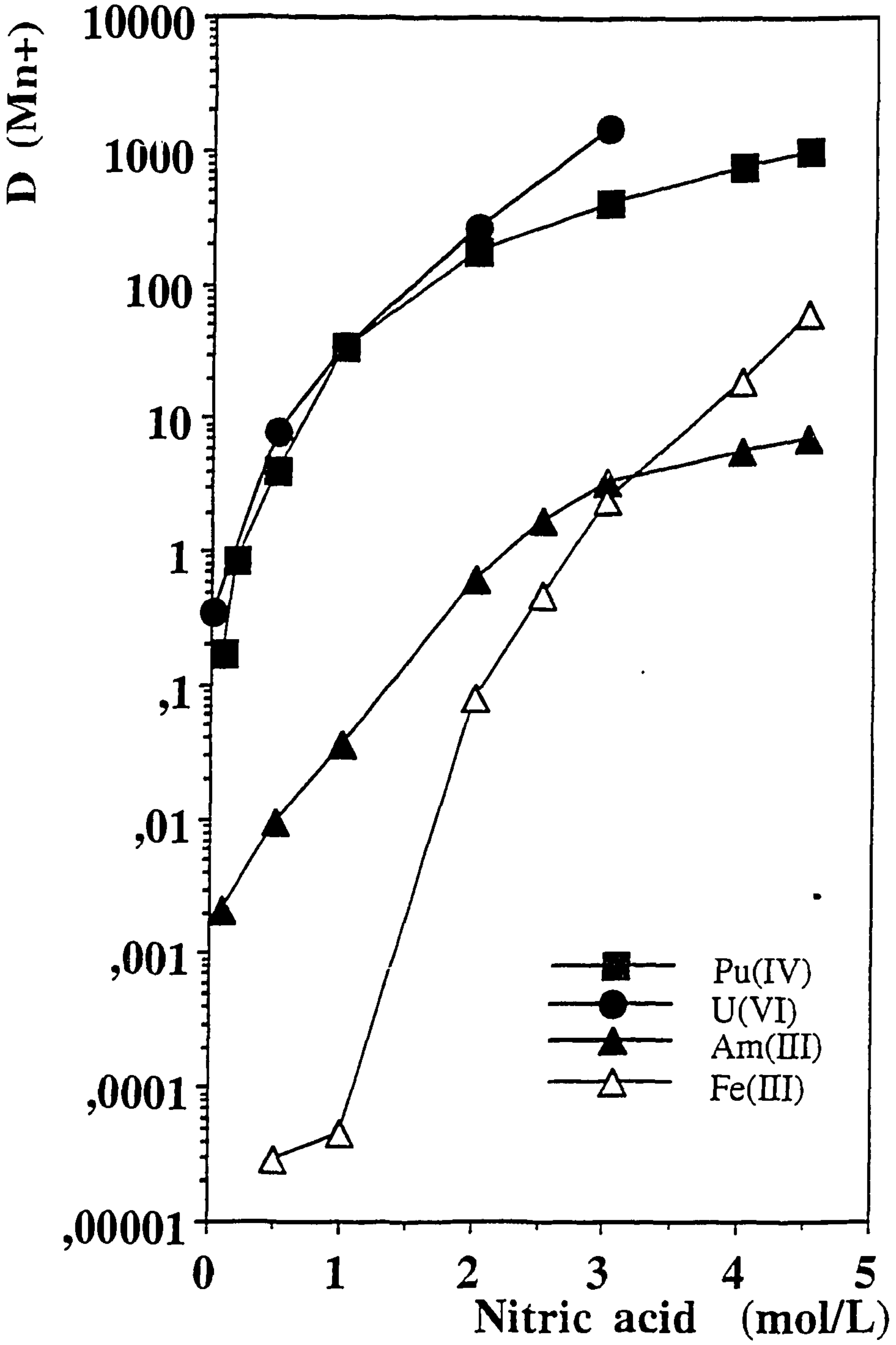

Figure 1. : DIAMEX. Extraction of Am(III), Pu(IV), U(VI) and Fe(III) nitrates by the DMDBTDMA (0.5 mol/L in TPH)

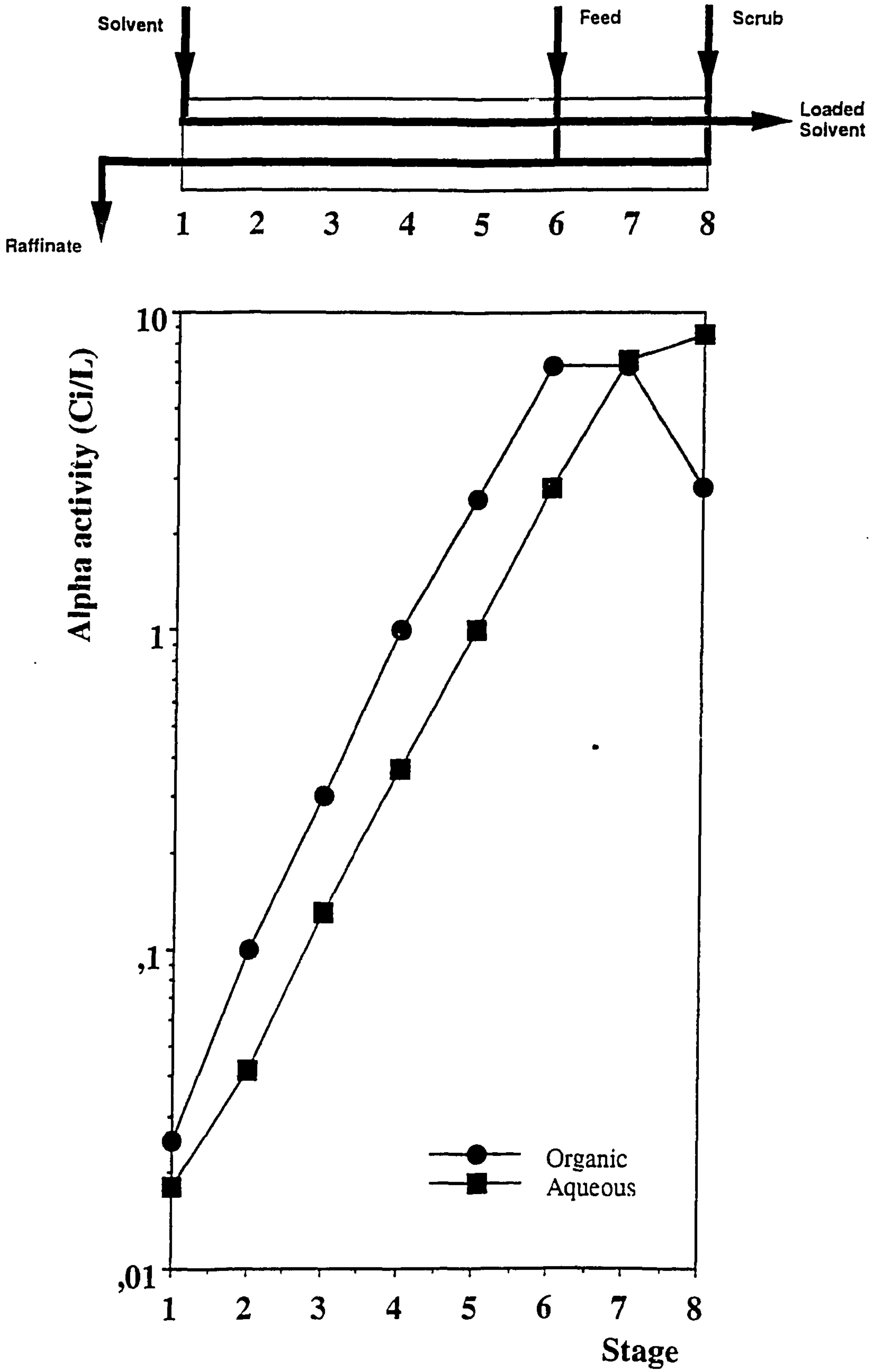

Figure 2. DIAMEX. Alpha activity profiles for the second hot test