

## CURRENT EUROPEAN RESEARCH ON THE SEPARATION OF ACTINIDES FROM HIGH-LEVEL RADIOACTIVE WASTES<sup>†</sup>

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Major part of the current European work on the development of a process for the separation of actinides from high-level radioactive wastes (HLLW) is performed within a European Community research programme. A flowsheet of such a process has been proposed, minimizing the amount of secondary wastes by using predominantly reagents composed only of carbon, hydrogen, oxygen and nitrogen. Actinides and fission lanthanides are to be extracted from the HLLW in the first cycle of the process by a completely incinerable N,N,N',N'-tetraalkylmalonamide extractant, such as N,N'dimethyl-N,N'-dibutyltetradecylmalonamide. In the second process cycle, Am(III) and Cm(III) are to be extracted selectively over fission lanthanides(III), using a soft-donor, i. e. a nitrogen or a sulfur donor extractant. Recent results of hot tests of malonamide extractants in counter-current experiments and achievements of the development of soft-donor extractants are described.

**Keywords:** partitioning of high-level radioactive waste, separation of actinides, solvent extraction of actinides, diamide extractants, soft-donor extractants

ヨーロッパにおける高レベル廃液からのアクチニド分離プロセスの開発は、現在主にECの研究プログラムの中で行われている。開発中の分離技術としては、2次廃棄物発生量を低減するために、炭素、水素、酸素、窒素原子で構成される試薬を用いた方法(CHONプロセス)が提案されている。アクチニドとランタニドは、第1サイクルにおいて完全に焼却可能なマロンアミド抽出剤により、高レベル廃液から抽出される。第2サイクルにおいては、窒素や硫黄原子等のソフトドナーを有する抽出剤により、Am(III)とCm(III)はランタニドから選択的に分離される。本稿では、マロンアミドを用いた向流抽出のホット試験およびソフトドナー抽出剤の開発に関する最近の結果を報告する。

**Keywords:** 高レベル放射性廃棄物の群分離、アクチニドの分離、アクチニドの溶媒抽出、ジアミド抽出剤、ソフトドナー抽出剤

### 1 INTRODUCTION

Separation of actinides from high-level radioactive liquid waste solutions (HLLW) and their subsequent transmutation to short-lived radionuclides (partition + transmutation, abbreviated P+T) is expected to facilitate the management of radioactive wastes. With some exceptions, the opinion is widely accepted in European countries. The actinide separation can only be achieved in a partitioning process, the costs and risks of which have to be compensated by benefits of the P+T option. If the actinides are to be separated from liquid wastes originated in the reprocessing of spent nuclear fuel by the Purex process, an aqueous partitioning process based on solvent extraction is the most appropriate procedure. This is well reasoned by experience gained in decades of work, reaching from laboratory research to industrial operation of processes of which the Purex process is to be mentioned first of all.

Special attention is paid to the partitioning of radioactive wastes in France, where a wide-spread nuclear fuel programme is carried out. The programme represents a closed fuel cycle, including fuel fabrication, irradiation, reprocessing and refabrication. Research on waste partitioning is performed within the ACTINEX project [1], which is a part of a broad SPIN (Separation and Incineration) programme [2]. Great Britain is another European country practising a closed fuel cycle policy, but the author of this review is not aware of any systematic research activity, in which the partitioning of high-level waste would be studied within the British nuclear fuel programme. A

partition process based on the application of dicarbollides has been developed in former Soviet Union [3,4]. Chemical fundamentals of the actinide separation in the course of the process are not known, and it neither is known whether the process is kept in operation and further developed.

A comprehensive and systematic work on the development of a solvent extraction partitioning process is currently performed within the specific programme "Nuclear Fission Safety 1994-1998" under a framework programme of European Community activities in the field of research and training for EURATOM. The work is concentrated in the project NEWPART (New Partitioning Techniques) [5]. As it can be expected with regard to the productiveness of the French nuclear programme, the project is coordinated by scientists of the French research center Valrhô at Marcoule (CEA). Participating are three universities, namely the University of Reading (Great Britain), Chalmers University of Göteborg (Sweden) and "Politecnico" University Milano (Italy). Further participating are the research centers Forschungszentrum Jülich and Forschungszentrum Karlsruhe (both in Germany) and ENEA Ispra (Italy). It should be noticed that the work of the British participation does not appear to be in any way connected with the British nuclear fuel programme. It also is worth of mentioning that research institutions of such countries participate in the project (Italy, Germany, Sweden) which do not follow their own closed cycle fuel programme. It is understandable that this review is concentrated on the work done in the scope of the NEWPART project.

The composition of HLLW solutions is reviewed in [6] and, with regard to particularities of the Purex process in the French plants at Cap Las Hague, in [7]. Simplified composition is given in Table 1. The separation of Np need not be

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Table 1. Simplified composition of HLLW after its release from the Purex process [6]. Burn-up 33 GWd/t, cooling time 150 d, volume 5000 l/t fuel. RE are rare earths, FP are fission products.

Actinides	g/l	M	Other FP	g/l	M
U	0.95	$4 \times 10^{-3}$	Cs	0.54	$2 \times 10^{-3}$
Pu	0.01	$4 \times 10^{-5}$	Rb	0.07	$8 \times 10^{-4}$
Np	<0.15	$<6 \times 10^{-4}$	Sr	0.18	$2 \times 10^{-3}$
Am	0.03	$1 \times 10^{-4}$	Ba	0.28	$2 \times 10^{-3}$
Cm	0.007	$3 \times 10^{-5}$	Zr	0.73	$8 \times 10^{-3}$
Am+Cm	0.037	$1.5 \times 10^{-4}$	Mo	0.69	$7 \times 10^{-3}$
RE FP	g/l	M	Te	0.11	$9 \times 10^{-4}$
La	0.25	$2 \times 10^{-3}$	Tc	0.16	$2 \times 10^{-3}$
Ce	0.58	$4 \times 10^{-3}$	Ru	0.45	$4 \times 10^{-3}$
Pr	0.24	$2 \times 10^{-3}$	Rh	0.08	$8 \times 10^{-4}$
Nd	0.78	$5 \times 10^{-3}$	Pd	0.26	$2 \times 10^{-3}$
Pm	0.01	$7 \times 10^{-5}$	Misc.	g/l	M
Sm	0.16	$1 \times 10^{-3}$	H <sub>3</sub> PO <sub>4</sub>	0.4	$4 \times 10^{-3}$
Eu	0.04	$3 \times 10^{-4}$	Na	1.6	$7 \times 10^{-2}$
Y	0.09	$1 \times 10^{-3}$	Fe	1.9	$3 \times 10^{-2}$
Total	2.15	0.015	Cr	0.1	$2 \times 10^{-3}$

included in the partitioning process in such particular cases, in which it leaves the Purex process in a separate stream.

## 2 SYMBOLS AND ABBREVIATIONS

Distribution ratios of Am(III) and Eu(III) will be denoted as  $D_{Am}$  and  $D_{Eu}$  respectively. The Am(III)/Eu(III) separation factor is defined as  $\alpha_{Am/Eu} = D_{Am}/D_{Eu}$ . Extractants and diluents will be abbreviated, or denoted by trade names as follows:

CMPO - octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide,

Cyanex 301 - di(2,4,4-trimethylpentyl)dithiophosphinic acid,

DMDBTDMA - N,N'-dibutyl-N,N'-dimethyltetradecylmalonamide,

DPTnP - 2,6-di(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine,

DBTzP - 2,6-di(3-butyl-1,2,4-triazol-5-yl)pyridine,

DMTzP - 2,6-di(3-methyl-1,2,4-triazol-5-yl)pyridine,

TBP - tributyl phosphate,

terPy - 2,2':6',2''-terpyridine,

TPH - „tetrapropyl hydrogène“, highly branched, commercially available French diluent, mainly consisting of 1,1,2,2,3,3,4,4-octamethylbutane,

TMPTZ - 2,4,6-tri(4-methyl-2-pyridyl)-1,3,5-triazine,

TPTZ - 2,4,6-tri(2-pyridyl)-1,3,5-triazine,

TtBPTZ - 2,4,6-tri(4-tert-butyl-2-pyridyl)-1,3,5-triazine,

### 3 DEVELOPMENT OF A PARTITIONING PROCESS

#### 3.1 GENERAL CONSIDERATIONS

The objectives of the project NEWPART, as given in [5], are to develop a partitioning process which would avoid difficulties encountered in previously suggested flowsheets. The first requirement is to minimize the generation of secondary waste. Thus, exclusively or predominantly such reagents should only be used which do not contain other elements than carbon, hydrogen, oxygen and nitrogen (so called CHON principle). Then the reagents can be completely incinerated and, after corresponding purification, the gases can be released into the atmosphere. Another requirement is to extract actinides from HLLW without reducing its content of nitric acid, because any acid removal can cause precipitation of solids.

Fig. 1 shows the flowsheet of a "European" partitioning process which is to be developed as insinuated in [5, 7]. The treatment of HLLW immediately after its release from the Purex process is desirable because, as reviewed in [6], precipitate forms in it during longer storage or even during concentra-

tion by evaporation. Zr(IV) and Mo(VI) tend to be coextracted with actinides in the first cycle of the process, irrespective of the extractant used. The coextraction of Zr(IV) and Mo(VI) has to be prevented, preferably by complexing the two elements in the feed stream. It has been suggested to complex Zr(IV) with ketomalonic acid and Mo(VI) with hydrogen peroxide [7]. It has also been shown [7] that oxalic acid, suggested to be used for complexing Zr(IV) in the TRUEX process [8], complexes both Zr(IV) and Mo(VI) quite satisfactorily.

It will be discussed below that bifunctional oxygen-donor extractants are used in the first extraction cycle, due to their high extraction ability. Such extractants possess no selectivity for actinides over fission lanthanides(III) and, inevitably, the latter are coextracted. They accompany Am(III) and Cm(III) in their strip by dilute nitric acid. The stripping of Pu(IV) and U(VI) is not presently studied, and the use of a complexing agent such as oxalic acid may plausibly be expected to be successful.

Since the mass of the fission lanthanides(III) is about 60

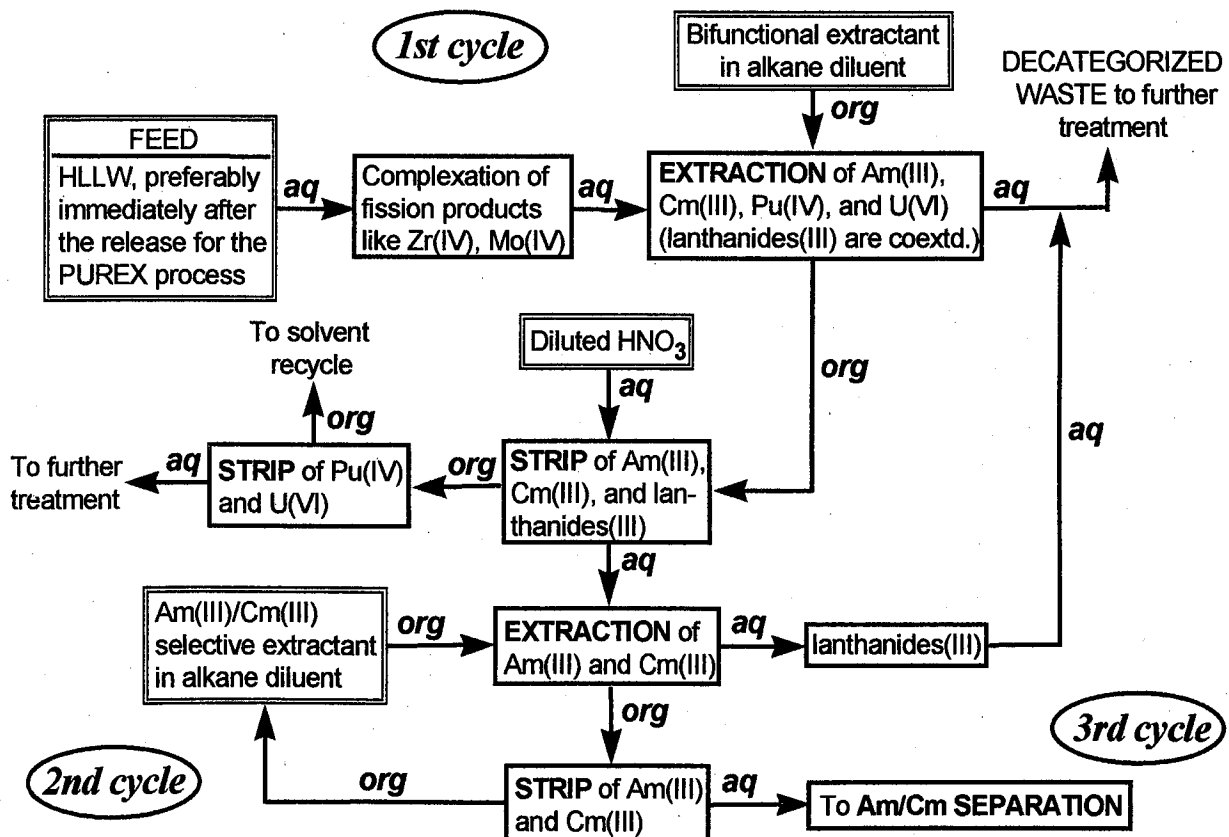


Fig. 1. Principles of the flowsheet of a European partitioning process

times as large as that of Am(III) and Cm(III), a transplutonium(III)/lanthanide(III) separation must be performed in the second extraction cycle. Selective extraction of the small mass of the transplutonium(III) over the lanthanides(III) is the preferred mode of the operation, and a possibility of extracting transplutonium(III) from acidic solutions ( $>0.05$  M  $\text{HNO}_3$ ) is considered a significant advantage. The desired selectivity can be achieved in using „soft“ donor extractants, i. e. those which bind the extracted metal ions through nitrogen or sulfur atoms. Finally, it can be expected that Am(III) has to be separated from Cm(III) [9] before the transmutation of the actinides. Study of this operation exceeds the scope of the NEWPART project, and published methods are planned to be used.

An alkane diluent should be used in all, or at least in the first two extraction cycles. This is reasoned by higher chemical and radiation stability of paraffinic diluents in comparison with e. g. aromatic ones. Good properties are exhibited by the highly branched French diluent TPH (“tetrapropyl hydrogène”), which is commercially available and mainly consists of highly branched dodecane, namely 1,1,2,2,3,3,4,4-octamethyl-butane. In comparison with e. g. n-paraffines, the branching enhances

the ability of the diluent to dissolve extractants of different types. Also the solubility of extracted complexes can be expected to be higher in TPH than in n-paraffines, and this essentially helps to avoid the formation of a third phase in extraction operations.

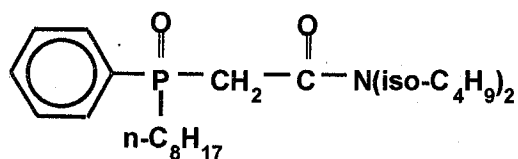
### 3.2 COEXTRACTION OF ACTINIDES AND FISSION LANTHANIDES

It is documented in [6] that bifunctional extractants are most advantageously used for the extraction of actinides in the first extraction cycle. This is due to the lower extractability of Am(III) and Cm(III) in comparison with Pu(IV), Np(VI) and U(VI). Monofunctional extractants extract the trivalent actinides under conditions which are in contradiction to principles specified above. So TBP extracts Am(III) and Eu(III) in the presence of large amounts of CHON incompatible salting-out agents like aluminium nitrate, and trialkylphosphine oxides extract the elements at reduced concentrations of nitric acid.

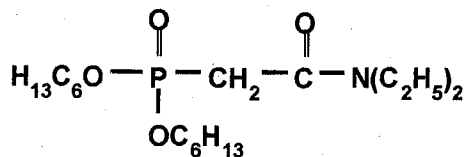
Various types of bifunctional extractants are gathered in Fig. 2. Main attention has worldwide been paid to carbamoyl phosphoryl compounds, of which the figure shows the most

#### CARBAMOYLPHOSPHORYL COMPOUNDS:

CMPO

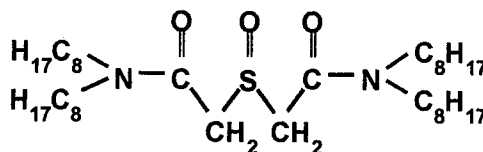


Dihexyl-N,N-diethylcarbamoylmethylphosphonate



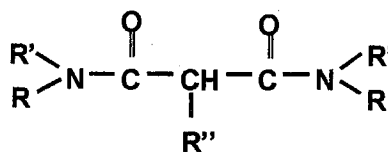
#### CARBAMOYLSULFOXIDE:

Di-N,N-dioctylcarbamoylmethylsulfoxide



#### MALONAMIDES:

General formula



Reference compound

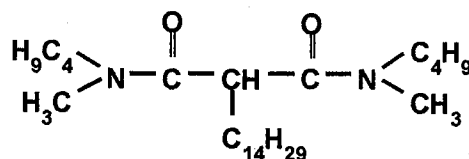


Fig. 2. Bifunctional extractants of various types.

frequent representatives (see [10] for a comparison of their extractant properties). Not only the extractants themselves are not CHON compatible but, to keep the solubility of extracted complexes high enough, in paraffinic diluents they can only be used in the presence of TBP as solvent modifier. Then the solvent can contain as much as  $\geq 1.4$  g-atom/l phosphorus, and this is in a serious conflict with the CHON principle. Moreover, CMPO (the most studied extractant of this class) seems to be too efficient. Hot counter-current experiments had shown that in the back extraction of Am(III) and Cm(III) by 0.05 M nitric acid the distribution ratios of the actinides(III) were not low enough in all stages of a battery of centrifugal extractants, and this caused a serious build-up in the battery [11].

Beside of having been little studied up to date, the dicarbonyl sulfoxide shown in Fig. 2 has the same disadvantages as CMPO. It is not CHON compatible and, as implied in the original source [12], it exhibits too high distribution ratios for actinides(III) at low  $\text{HNO}_3$  concentration and difficulties in stripping have to be expected.

It was decided to use CHON compatible malonamides (see Fig. 2) as bifunctional extractants in the first extraction cycle (giving the name DIAMEX to the process). The extractants were first reported in the 1980s by Musikas et al. and their ability to extract Am(III) has been demonstrated e. g. in [13] (see [6, 7] for references to further, more recent work). Since then the development of the extractants has been continued in France [7], with the aim to optimize properties such as the extraction efficiency for transplutonium(III) and low tendency to the third phase formation. Results of the development are summarized in [7] as follows: It is important that one of the substituents at each of the nitrogen atoms is small, namely a methyl group, to keep the carbonyl oxygen atoms accessible to the extracted metal ions. A butyl group has been established to be adequate as the other substituent at each of the nitrogen atoms. The tendency to form a third phase decreases with increasing length of the alkyl group at the malonic 2-position, and it is further suppressed if the alkyl group is replaced by a long 3-oxa or 4-oxaalkyl. The introduction of the oxalkyl substituents also enhances the extracting ability of the compounds. Of various malonamides,  $N,N'$ -dimethyl- $N,N'$ -dibutyltetradecylmalonamide (DMDBTDMA, see Fig.2) has been chosen as the reference compound, and its analogues containing an octadecyl or a 3-oxanonadecyl group instead of the tetradecyl group are suggested in [7] as the most promising candidates for further detailed investigations.

Generally, 0.5 M malonamides in TPH [7] or tert-butylbenzene [13] extract Am(III) and lanthanides(III) from  $>2$  M  $\text{HNO}_3$ , while efficient stripping is achieved with  $<1$  M  $\text{HNO}_3$ . So the distribution ratios in the extraction by 0.5 M

DMDBTDMA in TPH from real HLLW containing 4 M  $\text{HNO}_3$  are  $D_{\text{Am}} = 4.3$ ,  $D_{\text{Cm}} = 2.8$ ,  $D_{\text{Ce}} = 3.3$ ,  $D_{\text{Nd}} = 3.2$  and  $D_{\text{Eu}} = 1.7$ . The  $D_{\text{Zr}}$  value is suppressed from 35 to 0.9 by adding 0.05 M ketomalonic acid to the HLLW, and the coextraction of Mo(VI) is suppressed from  $D_{\text{Mo}} = 4.5$  to  $D_{\text{Mo}} = 0.3$  by adding 0.1 M hydrogen peroxide. Ru, Sb and Cs(I) are little extractable ( $D_{\text{Ru}} = 0.5$ ,  $D_{\text{Sb}} < 0.001$  and  $D_{\text{Cs}} < 0.001$ ) [7].

Three hot counter-current tests of DMDBTDMA with real HLLW were performed in laboratory scale mixer-settlers [7], with a flowsheet based on the above distribution data. Details of the flowsheet are given in Fig.3 and Table 2. The separation of Sb and Cs was very good ( $>99.8\%$  and  $>99.98\%$  respectively in each run). As seen in Table 3, improvement of the separation of some fission and corrosion products has to be achieved in future work. Stripping was tested in the second run only, and all extracted species but Ru could be stripped excellently. The fraction of Ru remaining in the solvent was 11%. The radiolytic stability of the solvent was satisfactory, if it was not aged in the loaded state. Worth of improvement is the hydraulics of the extraction operations.

Improved decontamination from Zr(IV) and Mo(VI) was demonstrated in a cold run with simulated HLLW [7], using a similar flowsheet as in the hot experiments. In this case the feed contained 3.5 M  $\text{HNO}_3$  + 0.1 M oxalic acid and the scrub contained 3.4 M  $\text{HNO}_3$  + 0.3 M oxalic acid. As little as  $<0.3\%$  Zr and  $<5\%$  Mo, but as much as  $\sim 73\%$  Fe(III) were coextracted with the actinide/lanthanide fraction. In spite of the coextraction of Fe(III), the ACTINEX process proved to be a promising procedure for the removal of actinides from high-level radioactive waste.

Further improvement of the extractant properties of diamides and, consequently, of the performance of the DIAMEX process can be achieved e. g. by changing the structure of the diamide molecule. Extensive work [7] has already been done in changing the size of the alkyl substituents at the nitrogen atoms and the constitution of the alkyl or oxalkyl group at the 2-position of malonamide. Also investigated have been  $N,N,N',N'$ -tetraalkylderivatives of diamides of 1,10-decanedioic to 1,14-tetradecanedioic acids [7]. Substituents other than alkyl groups have also been introduced into the malonamide molecule, and extractant properties of  $N,N'$ -dimethyl- $N,N'$ -diphenyltetradecylmalonamide and  $N,N'$ -dimethyl- $N,N'$ -dicyclohexyltetradecylmalonamide for actinides have been compared with those of  $N,N'$ -dimethyl- $N,N'$ -dibutyltetradecylmalonamide [14]. Last but not least, it has to be mentioned that the mechanism of the extraction of actinides by diamides has not yet been definitively elucidated. It just has been shown that it can be simple solvation of actinide nitrates by neutral molecules of diamides, ion-pair

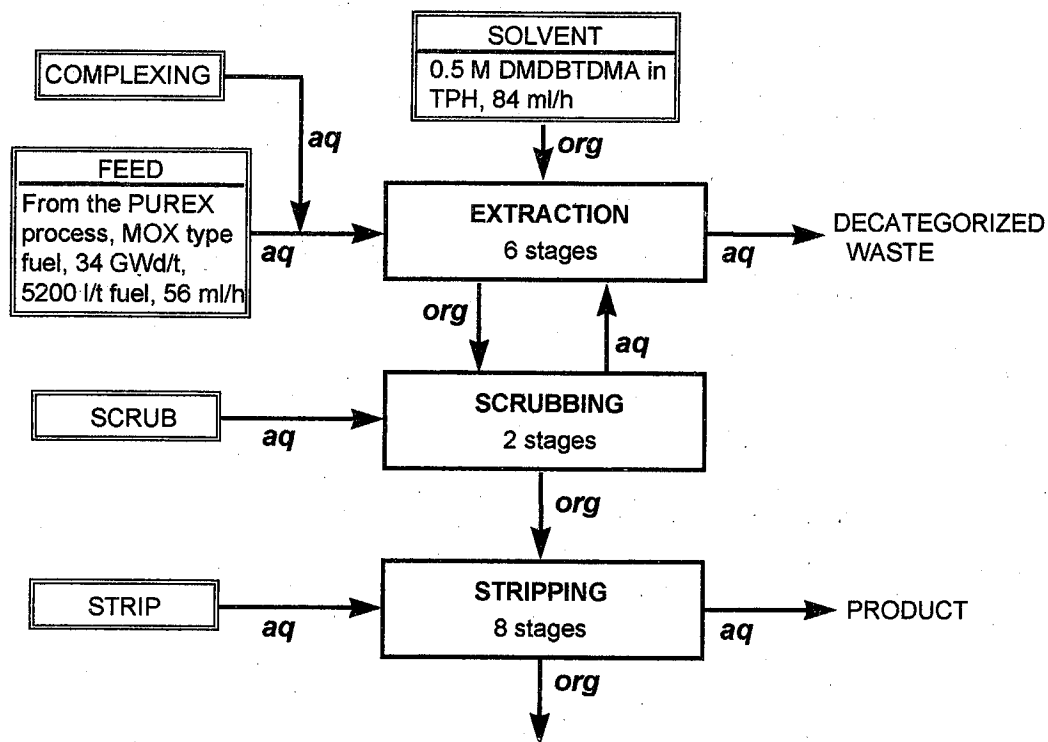


Fig. 3. Flowsheet of the hot test of the DiAMEX process [7]. See Table 2 for the composition of the complexing, scrub and strip solutions. DMBTDMA is N, N'-dimethyl-N, N'-dibutyltetradecylmalonamide.

Table 2. Composition and flow rates of the complexing, scrub and strip solutions in the flowsheet of the DIAMEX process, as given in Fig. 3. KMA is ketomalonic acid.

Test No.	Complexing	Scrub solution	Strip solution
1	none	2 M HNO <sub>3</sub> , 11.2 ml/h	none
2	5 M HNO <sub>3</sub> + 1 M KMA, 5.6 ml/h	2 M HNO <sub>3</sub> + 0.1 M KMA, 33.6 ml/h	0.5 M HNO <sub>3</sub> + 0.01 M Ca(II), 84 ml/h
3	5 M HNO <sub>3</sub> + 1 M KMA, 5.6 ml/h	2 M HNO <sub>3</sub> + 0.1 M KMA + 0.1 M H <sub>2</sub> O <sub>2</sub> , 33.6 ml/h	none

Table 3. Fractions of feed components transferred into the solvent stream after the extraction and scrub in hot tests of the DIAMEX process [7] (see flowsheet in Fig. 3).

Test No.	Total alpha	Am	Cm	Ce	Nd	Eu	Zr	Mo	Ru	Fe
1	99.89	99.91	99.88	100	99.9	100	9.8	99.6	54	86.4
2	99.66	99.95	99.60	99.5	99.4	100	0	73.4	50	66.2
3	99.44	99.52	99.44	99.4	99.2	100	47.2	57.4	44	59.8

formation by anionic nitrate complexes of actinides with protonated diamide molecules, or both mechanisms can act simultaneously, in dependence on the nitric acid concentration [7].

### 3.3 SEPARATION OF TRANSPLUTONIDES FROM FISSION LANTHANIDES

#### 3.3.1 GENERAL CONSIDERATIONS

Contrary to the coextraction of actinides and lanthanides in the DIAMEX process, the separation of the transplutonium(III) and lanthanide(III) groups is more or less in the state of basic research. Recently published work has been concentrated on the search of nitrogen-donor and sulfur-donor extractants. Reported results include distribution data illustrating the effect of the extractant structure and the nature of other components of the system studied on the extraction and separation efficiency, mostly obtained with Am(III) and Eu(III) as representatives of the transplutonium(III) and lanthanide(III) groups. Data on tests of extractants in counter-current experiments are scarce.

#### 3.3.2 EXTRACTION BY NITROGEN DONORS

It has been reported by Musikas (see e. g. [15]) as early as in the 1980s that 2,4,6-tri(2-pyridyl)-1,3,5-triazine (TPTZ,

see Fig.4) extracts transplutonium(III) selectively over lanthanides(III). Since TPTZ is a neutral molecule, lipophilic anions of an acid HA must be present in the system for the formation of an extractable complex of the type  $AmA_3 \cdot TPTZ$ . 2-Bromodecanoic and dinonylnaphthalenesulfonic acids are strong enough to make extraction at low pH values possible. Using the former in decanol or the latter in tert-butylbenzene together with TPTZ as synergistic extractant combinations, Am(III) and Cm(III) are extracted at pH 1 - 2 over Ce(III), Nd(III), Eu(III) or Gd(III) with a separation factor of  $\sim 10$  [15]. The applicability of TPTZ to the transplutonium(III)/lanthanide(III) separation has been demonstrated in counter-current experiments with feed solutions containing trace Am(III) and Eu(III) and variable amounts of Ce(III) together with 0.125 M  $HNO_3$ . The solvent was 0.03 M TPTZ + 0.05 M dinonylnaphthalenesulfonic acid in  $CCl_4$ , and 0.125 M  $HNO_3$  + 0.003 M TPTZ was used as a scrub solution. In dependence on the Ce(III) concentration, the fractions extracted in totally 16 stages (8 or 10 of them were a scrub section) were 99.5 - 99.8% Am, 2 - 10% Eu and 2 - 11% Ce [16].

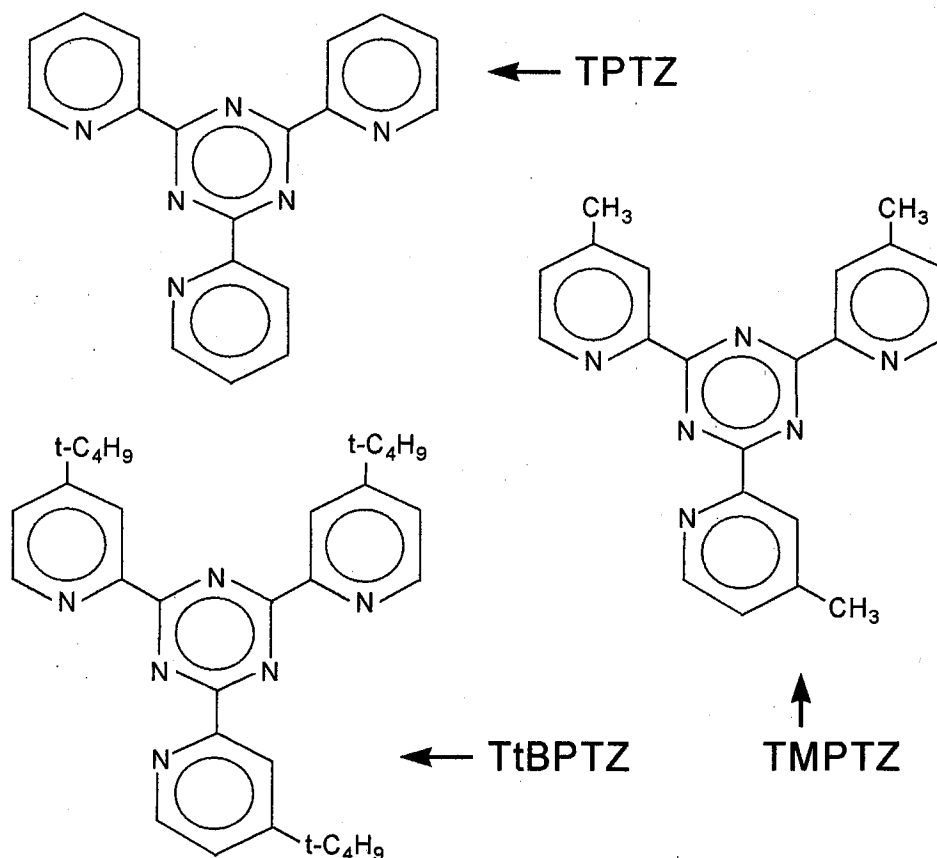


Fig. 4. Tripyridyltriazine extractants: 2,4,6-tri(2-pyridyl)-1,3,5-triazine (TPTZ), 2,4,6-tri(4-methyl-2-pyridyl)-1,3,5-triazine (TMPTZ) and 2,4,6-tri(4-tert-butyl-2-pyridyl)-1,3,5-triazine (TtBPTZ)

It has been very desirable to suppress the aqueous solubility of protonated forms of TPTZ, and the suppression has been achieved by introducing alkyl groups at the 4-position of the 2-pyridyl rings (see Fig.4). This structure change also improves the extraction efficiency and, with the extractants taken together with 2-bromodecanoic acid (HA) in TPH, the effectiveness of the extraction increases in the sequence TPTZ < 2,4,6-tri(4-methyl-2-pyridyl)-1,3,5-triazine (TMPTZ) < 2,4,6-tri(4-tert-butyl-2-pyridyl)-1,3,5-triazine (TtBPTZ) [7]. An illustration of the extraction of Am(III) and Eu(III) 2-bromodecanoates by TPTZ and TtBPTZ is given in Fig.5. It is seen there that logarithmic dependencies of the distribution ratios of Am(III) and Eu(III) on the hydrogen ion concentration are fairly consistent with straight lines of a slope -3, as it should be expected if complexes  $MA_3 \cdot B$  ( $B = N$ -donor extractant) are extracted. The Am(III)/Eu(III) separation factor is 9 - 13.

The efficiency of the extraction of Am(III) and Eu(III) 2-bromodecanoates is diluent sensitive, decreasing in the sequence TPH > toluene ~ 2-nitrophenyl octyl ether ~ tetrachloro-ethane > decanol [7]. This is illustrated by data in Table 4 for the TtBPTZ extractant. The data show that the separation efficiency is not essentially influenced by the diluent nature,

being somewhat lower with toluene and tetrachloroethane than with the other diluents. The effect of the nature of carboxylic acid on the extraction of Am(III) and Eu(III) carboxylates is shown in Table 5, also for TtBPTZ. As it is seen there, neither the extraction nor the separation efficiency is significantly influenced if 2-bromodecanoic acid is replaced by a CHON compatible cyanocarboxylic acid. The toluene diluent was taken for the experiments because not all of the carboxylic acids studied are well soluble in TPH.

Fig.5 also shows that 2,2':6',2''-terpyridine (terPy) is an essentially weaker extractant for Am(III) and Eu(III) 2-bromodecanoates than the tripyridyltriazines, while its separation efficiency for the Am(III)-Eu(III) pair is similar of that of TPTZ and TtBPTZ. The efficiency of the extraction but not that of the separation is enhanced, if the concentration ratio of terPy to 2-bromodecanoic acid is varied. Optimum results have been obtained at a ratio of 2/3, the total concentration of the extractants being 0.1 or 0.5 M [17]. As for the diluent effect, practically identical efficiency has been observed in the extraction of trace Am(III) and Eu(III) 2-bromodecanoates by terPy in TPH and tert-butylbenzene [17].

Table 4. Diluent effect on the extraction of trace Am(III) and Eu(III) 2-bromodecanoates by 2,4,6-tri(4-tert-butyl-2-pyridyl)-1,3,5-triazine (TtBPTZ). Organic phase 1 M 2-bromodecanoic acid + 0.02 M TtBPTZ, aqueous phase variable  $HNO_3$ , 25°C. Selected from data in Ref. [7].

Diluent	mol $HNO_3$ /l	$D_{Am}$	$D_{Eu}$	$\alpha_{Am/Eu}$
TPH	0.028	80	7.0	11.4
	0.053	13.6	1.0	13.6
	0.102	0.9	0.08	11.2
toluene	0.028	3.8	0.4	9.5
	0.053	0.4	0.09	4.4
	0.102	0.05	0.008	6.2
2-nitrophenyl octyl ether	0.028	4.3	0.3	14.3
	0.053	0.4	0.05	8.0
	0.102	0.02	0.002	10.0
1,1,2,2-tetrachloroethane	0.028	1.6	0.2	8.0
	0.077	0.04	0.007	5.7
	0.102	0.015	0.002	7.5
1-decanol	0.028	0.2	0.02	10.0
	0.053	0.03	0.002	15.0



Table 5. Effect of the carboxylic acid on the extraction of trace Am(III) and Eu(III) carboxylates by 2,4,6-tri(4-tert-butyl-2-pyridyl)-1,3,5-triazine (TtBPTZ). Organic phase 1 M carboxylic acid + 0.02 M TtBPTZ in toluene, aqueous phase variable  $\text{HNO}_3$ , 25°C. Selected from data in Ref. [7].

Carboxylic acid	mol $\text{HNO}_3$ /l	$D_{\text{Am}}$	$D_{\text{Eu}}$	$\alpha_{\text{Am/Eu}}$
2-bromodecanoic	0.028	3.9	0.4	9.8
	0.053	0.4	0.09	4.4
	0.102	0.05	0.008	6.2
2-cyanodecanoic	0.028	6.4	0.6	10.7
	0.078	0.2	0.03	6.7
	0.101	0.1	0.012	8.3
2-cyano-4-ethyloctanoic	0.031	7.7	0.7	11.0
	0.054	1.4	0.1	14.0
	0.103	0.1	0.011	9.1
2-cyano-4,6,6-trimethyl-heptanoic	0.030	6.4	0.6	10.7
	0.079	0.2	0.03	6.7
	0.102	0.09	0.013	6.9

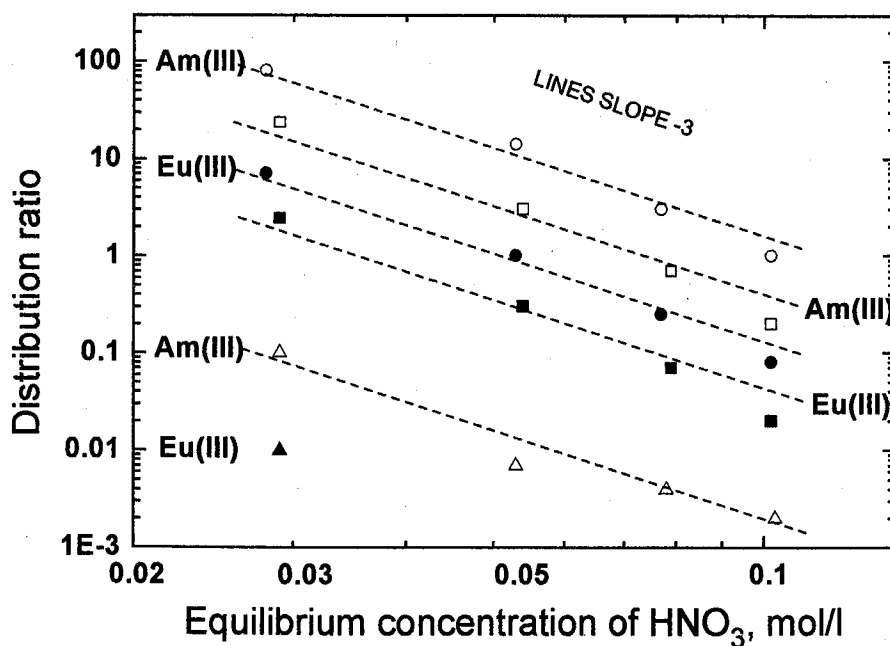


Fig. 5. Extraction of trace Am(III) and Eu(III) 2-bromodecanoates by 2,4,6-tri(4-tert-butyl-2-pyridyl)-1,3,5-triazine (TtBPTZ, circles), 2,4,6-tri(2-pyridyl)-1,3,5-triazine (TPTZ, squares) and 2,2':6',2''-terpyridine (terPy, triangles): Dependency of the distribution ratio on the equilibrium  $\text{HNO}_3$  concentration. Organic phase was 1 M 2-bromodecanoic acid + 0.02 M N-donor extractant in TPH, aqueous phase was variable  $\text{HNO}_3$ , 25°C (adapted from results in Ref. [7]).

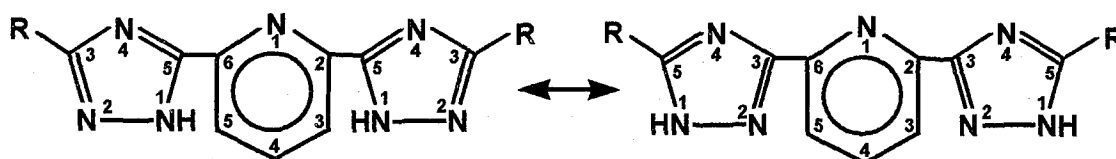
Substituted 2-pyridylbenzimidazoles are rather basic bidentate extractants and are able to extract Am(III) and Eu(III) thiocyanates at pH 4 - 5 with an Am(III)/Eu(III) separation factor of  $\leq 20$ . The extraction and separation efficiency is lower in the extraction of other Am(III) and Eu(III) salts like the nates, perchlorates and nitrates [18]. Substituted 3,5-dipyridyl-1,2,4-triazoles are potentially tridentate extractants, but act only as bidentate ones. Their extraction and separation effectiveness is somewhat higher than that of 2-pyridylbenzimidazoles, giving in the extraction of thiocyanates an Am(III)/Eu(III) separation factor of  $\leq 40$  at pH 4.2 [19]. Interesting is the ability of one compound of this class, namely 3-(2-pyridyl)-5-(4-tert-butyl-2-pyridyl)-1,2,4-triazole to act as an acidic extractant, releasing a  $H^+$  ion from the NH group of the triazole ring. The compound then yields an Am(III)/Eu(III) separation factor of  $\leq 60$ , indeed at a  $H^+$  concentration as low as pH 5.0 [19].

Very promising results have been obtained with 2,6-di(3-alkyl-1,2,4-triazol-5-yl)pyridines (see Fig. 6, structure A) and 2,6-di(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines (see Fig. 6, structure B) [20]. The former extracts Am(III) and Eu(III) as 2-bromohexanoates and Fig. 7 shows that the extraction and separation efficiency of the 2,6-di(3-alkyl-1,2,4-triazol-5-yl)pyridines is markedly increased when the alkyl being methyl is replaced by butyl. It should be noticed in Fig. 7 that the results for the butyl analogue (DBTzP) are valid for a higher concentration of nitric acid than those for the methyl analogue

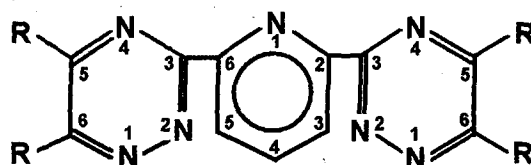
(DMTzP). The Am(III)/Eu(III) separation factor is high enough with DMTzP, namely 40 to 70, and it is as surprisingly high as 150 with DBTzP. The extractants of the ditriazolyl type are well lipophilic and appear to exhibit sufficient chemical stability. The only disadvantage of them is that they do not extract Am(III) and Eu(III) as nitrates.

2,6-Di(5,6-dialkyl-1,2,4-triazin-3-yl)pyridine with alkyl being methyl extracts Am(III) and Eu(III) 2-bromohexanoates with an enormous efficiency, giving  $D_{Am} > 1000$ ,  $D_{Eu} \sim 10$  and  $\alpha_{Am/Eu} \sim 140$  at 0.1 M  $HNO_3$  in the equilibrium aqueous phase [20]. However, the extractant, as well as its analogues with alkyl being e. g. propyl or butyl, decomposes overnight in the presence of bromohexanoic acid. This would be a serious drawback, if extractants of this class do not extract Am(III) and Eu(III) in a much more advantageous form, namely as nitrates. The ability to extract transplutonium(III) nitrates can be considered a great advantage, because nitrates are practically always present in process streams of separation processes in the nuclear fuel cycle.

The extraction of Am(III) and Eu(III) nitrates by 2,6-di(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (DPTnP) is illustrated by data in Table 6. The best results were obtained with modified TPH as the diluent. Notice that in modified xylene not only the extraction efficiency but also that of the separation is lower. Introduction of longer alkyl chains into the molecule of 2,6-di(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines suppresses the



Structure A, R = methyl or butyl



Structure B, R = methyl to butyl or isobutyl

Fig. 6. 2,6-Di(3-alkyl-1,2,4-triazol-5-yl)pyridines (structure A) and 2,6-di(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines (structure B)

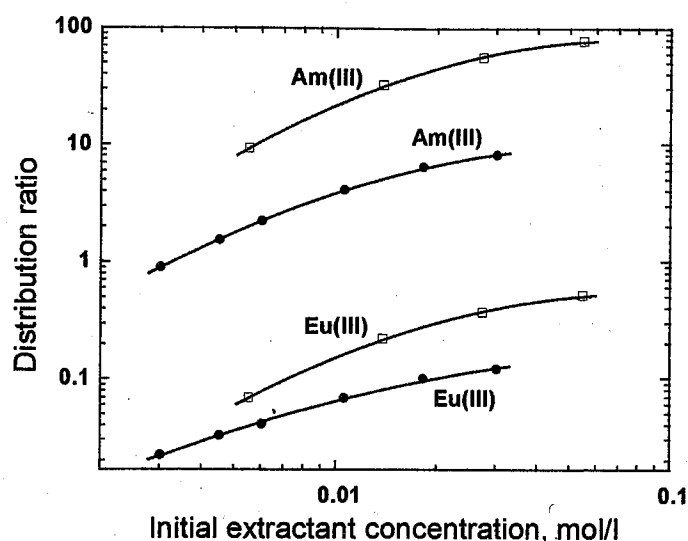


Fig. 7 Extraction of trace Am(III) and Eu(III) 2-bromohexanoates by 2,6-di(3-methyl-1,2,4-triazol-5-yl)pyridine (DMTzP, full circles) and 2,6-di(3-butyl-1,2,4-triazol-5-yl)pyridine (DBTzP, open squares). Organic phase was 1 M 2-bromohexanoic acid + variable DMTzP or DBTzP in TPH, aqueous phase was 0.05 M HNO<sub>3</sub> + 0.1 M NH<sub>4</sub>NO<sub>3</sub> with DMTzP and 0.1 M HNO<sub>3</sub> + 0.1 M NH<sub>4</sub>NO<sub>3</sub> with DBTzP. 22°C (adapted from results in Ref. [20]).

Table 6. Extraction of trace Am(III) and Eu(III) nitrates by 0.0344 M 2,6-di(5,6-di-propyl-1,2,4-triazin-3-yl)pyridine in modified hydrocarbon diluents from 1.90 M (H,NH<sub>4</sub>)NO<sub>3</sub>. Room temperature. Selected from data in Ref. [20].

Diluent/modifier (volume ratio)	Molarity of HNO <sub>3</sub>	D <sub>Am</sub>	D <sub>Eu</sub>	$\alpha_{Am/Eu}$
TPH/2-ethyl-1-hexanol (4/1)	0.30	45.3	0.316	143
	0.50	33.1	0.258	128
	0.90	22.6	0.173	131
TPH/butyraldehyde (4/1)	0.30	41.6	0.327	127
	0.50	49.4	0.353	140
	0.90	61.4	0.47	130
Xylene/1-butanol (7/3)	0.30	1.66	0.023	72
	0.50	1.15	0.0166	69
	0.90	0.68	0.0101	67

aqueous solubility of their protonated forms, but does not essentially change their extractant properties. As shown in [20], DPTnP and its diethyltriazinyl analogue little differ in their extraction and separation efficiency in the xylene/1-butanol diluent (the latter extractant is not sufficiently soluble in modified TPH), and small difference was also found between the extractant properties of DPTnP and its dibutyltriazinyl analogue in modified TPH. The compound with alkyl being isobutyl extracts Am(III) and Eu(III) nitrates more effectively, but yields the same Am(III)/Eu(III) separation factor as the compound with alkyl being n-butyl [20].

### 3.3.3 EXTRACTION BY SULFUR DONORS

It has been shown as early as in the 1980s [15] that di(2-ethylhexyl)dithiophosphoric acid in dodecane, combined with tributyl phosphate synergist, extracts trace Am(III) selectively over macro amounts of Eu(III) with a separation factor of  $>50$ . However, the separation effect becomes less significant with decreasing Eu(III) concentration and trace Am(III) is not at all separated from trace or small amounts of Eu(III) [21]. Later it has been reported [22] that a very pronounced selectivity for Am(III) over Eu(III) is exhibited by a related compound, di(2,4,4-trimethylpentyl)dithiophosphinic acid (see Fig.8), known under the trade mark name Cyanex 301. If thoroughly purified and used as a 0.5 M solution in kerosene, the compound gives an enormously high Am(III)/Eu(III) separation factor of  $\sim 6000$ .

It indeed has to be noticed that Cyanex 301 is applicable at pH 3 - 4, where the distribution ratio of Am(III) is sufficiently high. Since Cyanex 301 is an acidic extractant, the  $D_{Am}$  and  $D_{Eu}$  values decrease steeply with increasing concentration of hydrogen ions, and are too low at pH  $< 3$ . This can be seen as a disadvantage, and it also appears that the compound is not very stable in solutions. To overcome these drawbacks, aromatic dithiophosphinic acids have been synthesized and studied as extractants for the transplutonium(III)/lanthanide(III) separation [23]. Diphenyl-, di(chlorophenyl)- and di(fluorophenyl)-dithiophosphinic acids (see Fig. 8) alone in toluene do not extract Am(III) and Eu(III), giving  $D_{Am}$  and  $D_{Eu}$  values of  $< 0.001$ , but they exhibit a very good extraction and separation efficiency in the presence of trialkyl phosphates and trialkylphosphine oxides as synergists. The extractant properties of aromatic dithiophosphinic acids are illustrated in Fig. 9 for two of the above extractants and for tributyl phosphate as synergist. The extraction efficiency increases in the series diphenyldithiophosphinic acid  $<$  di(fluorophenyl)-dithiophosphinic acid  $<$  di(chlorophenyl)dithiophosphinic acid, while the separation efficiency decreases in this sequence [23]. To give some numerical values, at  $\geq 0.1$  HNO<sub>3</sub>, the value of  $\alpha_{Am/Eu} = 290, 60$  and  $31$  respectively are derived from data in

[23] for 0.5 M solutions of the three extractants in toluene containing 0.25 M TBP.

As further shown in [23], the separation efficiency increases with the concentration of the dithiophosphinic acid extractants, but decreases with increasing concentration of the TBP synergist. Dithiophosphinic acid and TBP concentrations of 0.5 M and 0.25 M respectively are recommended as an optimum compromise. The synergistic action of different phosphoryl compounds is illustrated by data in Table 7. See there that trihexyl phosphate is a much more powerful synergist than TBP, but it suppresses the selectivity for Am(III) over Eu(III). Trioctylphosphine oxide appears to be the optimum choice. A precipitate is formed during the phase contact with trioctyl and tri(2-ethylhexyl)phosphates present as synergists. Irradiation of the extractants to a dose of  $1 \times 10^5$  Gy does not significantly influence their extractant properties, but at  $7 \times 10^5$  Gy the distribution ratio of Am(III) slightly decreases while that of Eu(III) increases markedly [23].

## 4 CONCLUSIONS

The partitioning process, the development of which is surveyed in this article, can for several reasons be called a "European" partitioning process. The fact that the development work is performed within a European Community programme is not the only reason. Still more important reason is that principles have been induced into the design of the process, which are less rigorously regarded in analogous developments in other parts of the world. So the production of secondary wastes is stressed to be minimized by following the CHON principle as closely as possible. Completely incinerable diamide extractants, planned to be used in the first cycle of the process, have been introduced and systematically studied in a European country, namely in France. Transplutoniums are to be separated from fission lanthanides by selective extraction in trivalent state using a soft-donor extractant. Such extractants, bearing a nitrogen or sulfur donor atom, have also been developed to an essential part in European countries such as France and Germany.

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Table 7. Extraction of trace Am(III) and Eu(III) 0.5 M di(chlorophenyl)dithiophosphinic acid + 0.25 M synergist in toluene from diluted nitric acid. 21°C. Selected from data in Ref. [23].

Synergist	0.2 M HNO <sub>3</sub>			0.4 M HNO <sub>3</sub>		
	D <sub>Am</sub>	D <sub>Eu</sub>	$\alpha_{Am/Eu}$	D <sub>Am</sub>	D <sub>Eu</sub>	$\alpha_{Am/Eu}$
tributyl phosphate	2.13	0.068	31	0.19	0.0068	28
triethyl phosphate	25.5	21.2	1.2	3.25	3.31	0.9
triphenyl phosphate	0.0017	0.0002	8	-	-	-
tributylphosphine oxide	121	5.9	20.5	11.5	0.59	20
trioctylphosphine oxide	152	5.5	28	15.8	0.63	25

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