Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Diamides as Actinide Extractants for Various Waste Treatments

C. Cuillerdier[a]; C. Musikas[a]; L. Nigond[a]
[a] Commissariat à l'Energie Atomique DCC/DPR/SEMP/SECP, Fontenay-aux-Roses, France

To cite this Article Cuillerdier, C. , Musikas, C. and Nigond, L.(1993) 'Diamides as Actinide Extractants for Various Waste Treatments', Separation Science and Technology, 28: 1, 155 — 175
To link to this Article: DOI: 10.1080/01496399308019484
URL: http://dx.doi.org/10.1080/01496399308019484

SEPARATION SCIENCE AND TECHNOLOGY, 28(1-3), pp. 155-175 (1993)

DIAMIDES AS ACTINIDE EXTRACTANTS FOR VARIOUS WASTE TREATMENTS

C. Cuillerdier, C. Musikas, and L. Nigond
Commissariat à l'Energie Atomique DCC/DPR/SEMP/SECP
B.P. No. 6, 92265 Fontenay-aux-Roses
France

ABSTRACT

Substituted propanediamides were studied at Fontenay-aux-Roses for the declassification of nuclear liquid wastes by extraction of all the actinides. Their synthesis has been improved. By optimization of the formula, it is possible to use aliphatic diluents without third-phase formation in contact with nitric acid at 20°C. Addition of oxalic acid allows separation of iron and zirconium from americium and plutonium. In selected conditions, it appears that americium extraction is faster than iron extraction, which could lead to practical applications. Recent studies have shown that diamides can be used to remove the actinides from waste solutions in chloride medium coming from defense facilities. The current knowledge and the projects for using diamides as actinide extractants will be reviewed.

INTRODUCTION

Two main strategies are followed in the nuclear industry for handling spent nuclear fuel: either reprocessing with recovery of uranium and plutonium and storage of the wastes or direct storage of the spent fuel without reprocessing. Conventional reprocessing leads to the production of large amounts of effluents containing long-lived α actinides that have to be put in a solid matrix and stored in underground repositories. Better management of the wastes could decrease the cost and environmental impact of reprocessing. For instance, an improved method might consist of separation of the long-lived α actinides from fission products and deep storage of this reduced fraction of waste only.

In recent years, a new idea has occurred that consists of "advanced reprocessing" and "partitioning and transmutation." In this case, all the actinides are separated (not only the valuable ones like uranium and plutonium) and then burned in special reactors to be transmuted into shorter-half-lived radioisotopes. These two strategies are represented schematically in Figure 1.

An optimized management of the wastes needs the separation of α emitters such as Pu, Am, Np, and Cm and some fission products such as Tc from the bulk of fission and corrosion products. Solvent extraction is a good method for that purpose provided that the process does not create a large quantity of secondary wastes.

Many organophosphorus extractants have been used, but degradation products due to hydrolysis and radiolysis lead to the formation of precipitates or retention of actinides in the solvent. Moreover, the cleanup of the solvent for recycling often uses inorganic salt solutions, creating secondary wastes; and incineration of the degraded molecules produces radioactive P_2O_5.

A new concept for extractants is to make them totally incinerable, which minimizes production of secondary wastes. For several years, studies have been undertaken in Fontenay-aux-Roses with another sort of extractant: pentaalkylpropanediamides [$(RR'NCO)_2CHR''$ with R and R' alkyl and R" alkyl or oxyalkyl radicals]. Because of their chelating properties, these bifunctional molecules are able to extract all the actinides including the tervalent ones from acidic solutions. The aim of this communication is to present the basic results and new progress obtained with diamides and to show their applicability in waste treatment and in partitioning. However, diamides extract tervalent lanthanides with tervalent actinides, and the process has to be completed with other extractants to realize a total α/FP separation.

EXPERIMENTAL

The extractants used for these experiments are not commercially available, and they have been synthesized at IRCHA (Vert le Petit, France) by G. Thiollet according to (1) and (2), except $[(CH_3)_2NCO]_2CHC_{16}H_{33}$, which was synthesized by G. Tersac using the same method. Other commonly used chemicals are Merck or Prolabo analytical grade reagents without further purification. Radioactive metals are

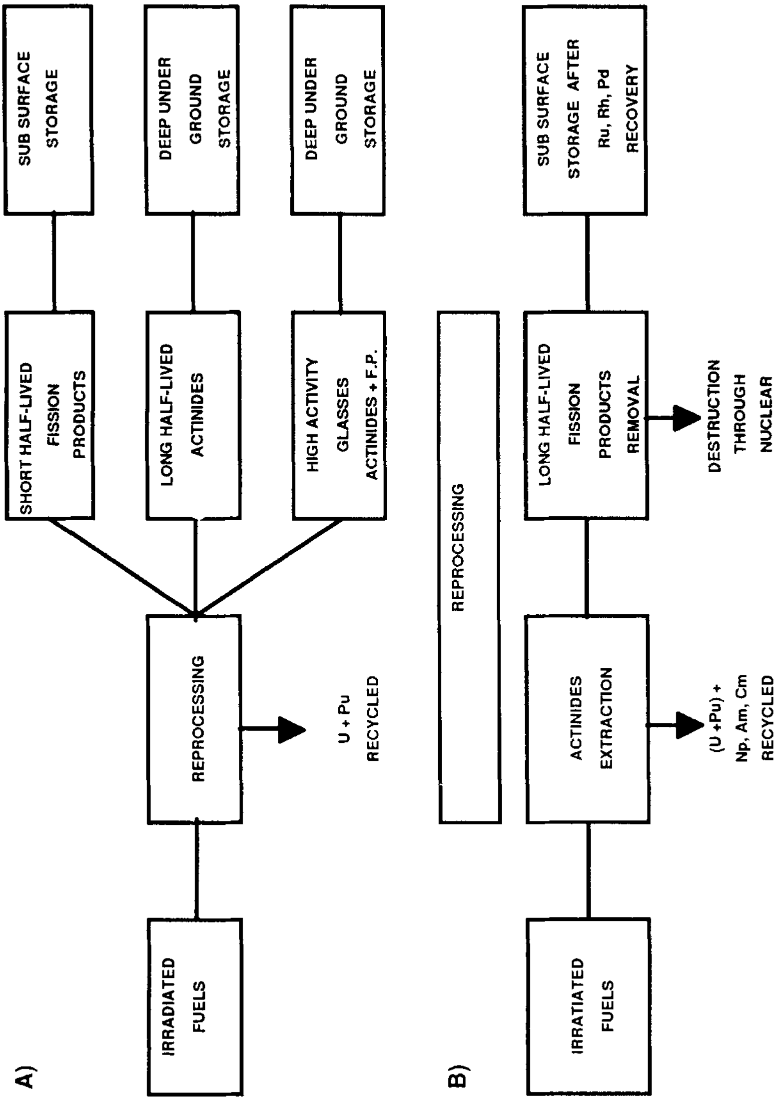

FIGURE 1. Existing (A) and possible (B) future back end of the nuclear fuel cycle.

obtained from Cogema (^{239}Pu), SPHA Fontenay-aux-Roses (^{242}Cm, ^{239}Np, ^{241}Am) or ORIS Industrie Saclay ^{99}Tc, ^{152}Eu). For all the experiments, cations are tracers except when the concentration of the metal is given.

Distribution coefficients are measured by contacting solvent previously equilibrated with an aqueous phase at the same acidity, with an aqueous phase containing the metal (equal volumes are normally used and experiments performed at room temperature). Test tubes are agitated with a "Vortex" agitator for about 5 min. After centrifugation and separation, each phase is analyzed, mainly by radiometric (α or γ spectrometry) methods; γ spectrometry is used for ^{241}Am, ^{152}Eu, ^{59}Fe, and ^{239}Np, α spectrometry is used for ^{239}Pu. Some other methods are sometimes needed, such as potentiometry in nonaqueous medium [described in (3)] or NMR to measure the degradation of the solvent.

RESULTS

Optimization of the Extractant Formula

The first studies undertaken with diamides (1-5) have shown that the distribution coefficient of americium was highly dependent on the nature of R, R', and R"; the main conclusions were that for unsubstituted malonamides, the best choice was R methyl and R' butyl or octyl (butyl being preferred for economic reasons). Further enhancement of D_{Am} was obtained by branching a long alkyl or oxyalkyl radical on the central carbon. With the type of molecules described in (3), it was possible to realize a good separation of tervalent actinides from a real waste concentrate. However, it is not possible to say that optimization is completely achieved. For instance, a molecule was synthesized by G. Tersac with the formula R = R' = CH_3 and R' = $C_{16}H_{33}$. This diamide is a solid product; unfortunately, it is very weakly soluble in hydrogenated tetrapropylene (TPH), which is the diluent used in French nuclear plants. However, it has a greater extracting power for Am^{3+} compared to R' = CH_3, R = C_4H_9, and R" = $C_{14}H_{29}$ in benzene. With an aqueous concentration of nitric acid of 2.5 M and 0.5 M diamide in the organic phase (O/A = 1 and t= 25°C), D_{Am} is 1.38 and 0.24, respectively, after 0.5 min of contact between the two phases.

TABLE 1. INFLUENCE OF THE STRUCTURE OF THE EXTRACTANT ON THIRD-PHASE FORMATION

(Aqueous HNO_3 in M when the third phase occurs)

Extractant $(RR'NCO)_2CHR''$ 0.5 M in TPH, t = 25°C

R"	R' = CH_3	R' = C_2H_5
C_2H_4-O-C_2H_4-O-C_6H_{13}	0.41	
C_2H_4-O-C_6H_{13}	0.90	2.25
C_2H_4-O-C_2H_4-O-C_8H_{17}	0.97	
C_2H_4-O-C_8H_{17}	1.7	
C_2H_4-O-CH(C_2H_5)-CH_2-CH$(CH_3)_3$	2.0	3.9
$C_{12}H_{25}$	3.5	
$C_{14}H_{29}$	4.7	
C_2H_4-O-$C_{12}H_{25}$	4.8	

A problem remained which was the necessity of using an aromatic diluent to prevent a third-phase formation when the solvent is contacted with aqueous concentrated HNO_3 solutions. Experiments were then undertaken to find an extractant usable in TPH. Reported in Table 1 are the values of aqueous HNO_3 concentrations when a third phase occurs as a function of the solvent formula. As can be seen in Table 1, it is favorable to increase the length of R' and R" and to have a branched radical R". But two oxygens in R", despite their positive influence on the distribution coefficient of Am^{3+}, decrease the solubility of the acidic complex in the aliphatic diluent and give third-phase formation at a lower acid concentration in the aqueous phase. For the last three examples (R" = $C_{12}H_{25}$, $C_{14}H_{29}$, or C_2H_4O-$C_{12}H_{25}$, respectively), it is possible to use an aliphatic diluent in a sufficiently large range of HNO_3 concentration to obtain a good D_{Am}. These data concern third phases occurring in contact with HNO_3 when cations are tracers; when the solvent loading increases, a third phase can occur due to the diamide-metal complexes.

For industrial applications, the solubility of the extractant in the aqueous phase is an important factor to be considered. Generally, ether oxygen in the substituent of the diamides tends to increase the values of aqueous solubilities. Distribution of the diamide between the diluent and the aqueous phase is measured by potentiometric titration. Only substituted malonamides are practically usable. Effectively, when R" = H, aqueous solubility can be very important for the amides with short N substitutes; for instance, with R′ = CH_3 and R = C_4H_9 or with R′ = C_2H_5 and R = C_4H_9, solubility reaches 0.25 M. For substituted diamides, values of solubility in the aqueous phase are between 1.1 x 10^{-4} M and 2 x 10^{-3} M.

At this point, it appears that some compromise has to be found concerning the extractant formula. Two oxygen in R" increase extractive properties, but they increase the aqueous solubility of the diamide and enhance third-phase formation; R = methyl is better for D_{Am} in spite of the decreased solubility in TPH.

Optimization of the Diluent

It is interesting to note that Am^{3+} distribution coefficients are greater in TPH than tert-butylbenzene (for the same acidity and solvent concentration), as can be seen in Table 2. This phenomenon makes it practical to work with a lower aqueous HNO_3 concentration, which decreases extractant degradation due to hydrolysis (see later). Values of distribution coefficients for some diamides in TPH are represented in Figure 2 as a function of HNO_3 concentration.

It is possible to use diluents other than TPH. For instance, decahydronaphtalene (decaline) or tetrachloroethylene with a diamide having a long R", such as $C_{14}H_{29}$. However, this is not necessarily useful because of values of D_{Am} are generally lower (see Table 2).

Complexes of diamides with HNO_3 are much more soluble in aromatic diluents than aliphatic ones. For instance, with the diamide $[C_4H_9(CH_3)NCO]_2CH\text{-}C_2H_4\text{-}O\text{-}C_6H_{13}$ diluted to 0.5 M, third-phase formation occurs for 0.9 M HNO_3 in TPH and at 9 M HNO_3 when the extractant is diluted in tert-butylbenzene.

Distribution of the diamide between the diluent and the aqueous phase is in favor of aromatic diluents, thus lowering its solubility in the aqueous phase. When nitric acid concentration increases, the solubility of the extractant increases too.

TABLE 2. INFLUENCE OF THE DILUENT ON D_{Am}

Extractant No. 1 $[CH_3(C_4H_9)NCO]_2$-CH-$C_{14}H_{29}$
Extractant No. 2 $[C_4H_9)C_2H_5NCO]_2$-CH-C_2H_4O-C_6H_{13}
O/A = 1, t = 25°C

Diluent	(Diamide) M	(HNO_3) M	D_{Am}
C_2Cl_4	No. 1	3	0.28
	0.487	4	0.81
		5	1.5
		6	1.2
Decaline	No. 1	3	0.81
	0.487	4	2.2
		5	3.5
		6	2.9
TPH	No. 1	2	0.61
	0.5	3	3.28
		4	5.65
		4.5	7.2
TPH	No. 2	1	0.035
	0.5	2	0.75
$tBuC_6H_5$	No. 2	1	0.012
	0.5	2	0.11

At this point of the extractant development, it is not possible to say that the system formula of the extractant-diluent is completely optimized, but current studies are mainly carried out with diamides such as

$[CH_3(C_4H_9)NCO]_2CH$-$C_{12}H_{25}$
$[CH_3(C_4H_9)NCO]_2CH$-$C_{14}H_{29}$, or
$[CH_3(C_4H_9)NCO]_2CH$-C_2H_4-O-$C_{12}H_{25}$,

which are usable in TPH for practical applications.

Extraction and Separation of Iron

Iron is frequently found in nuclear waste solutions. Its concentration can reach 0.5 M in concentrates of high-level wastes. It is then absolutely necessary to

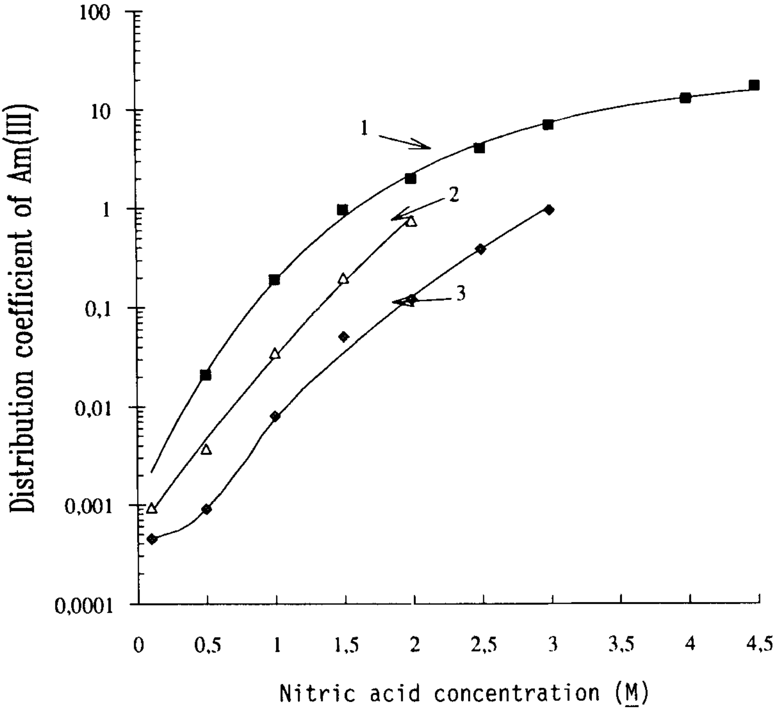

FIGURE 2. Influence of acidity on americium extraction.
Extractant $(RR'NCO)_2CHR''$ 0.5 M in TPH
1: $R = C_4H_9$ $R' = CH_3$ $R'' = C_2H_4\text{-O-}C_{12}H_{25}$
2: $R = C_4H_9$ $R' = C_2H_5$ $R'' = C_2H_4\text{-O-}C_6H_{13}$
3: $R = C_4H_9$ $R' = C_2H_5$ $R'' = C_2H_4\text{-O-}C_8H_{17}$

separate most of this cation, or the saturation of the extractant with iron leads to an important decrease of the distribution coefficients of americium. Unfortunately, iron follows americium during the extraction and back extraction stages of the process (Figure 3). Moreover, occurrence of iron during reductive back extraction creates Fe^{2+}, which can reduce neptunium to Np(IV), which remains in the organic phase.

The presence of oxalic acid allows a good separation between Am and Fe. The studies were then carried out on this method with plutonium and zirconium in the same solution. The main results are given in Tables 3 and 4 for cations in trace

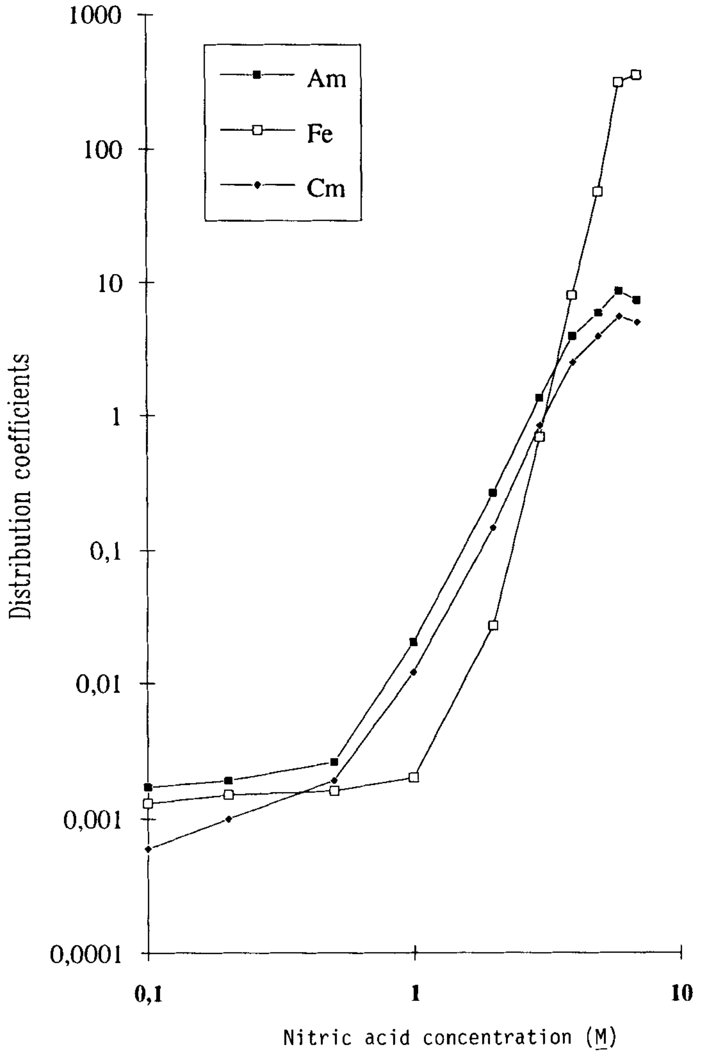

FIGURE 3. Distribution coefficients of Am^{3+}, Cm^{3+}, and Fe^{3+} as a function of nitric acid concentration.
Extractant $[(CH_3)C_4H_9NCO]_2CH-C_2H_4-O-C_6H_{13}$ 0.5 M in tertbutylbenzene O/A = 1, t = 25°C.

TABLE 3. SEPARATION OF Am AND Pu FROM Fe AND Zr WITH OXALIC ACID

Extractant $[CH_3(C_4H_9)NCO]_2\text{-}CH\text{-}C_2H_4\text{-}O\text{-}C_6H_{13}$ 0.5 M in tert-butylbenzene,
O/A = 1, t = 25°C

(HNO_3)	$(H_2C_2O_4)$	D_{Am}	D_{Pu}	D_{Fe}	D_{Zr}
2	0.05	0.275	1.44	0.003	0.004
2	0.1	0.205	0.405	0.003	0.004
2	0.2	0.185	0.167	0.002	0.006
2	0.5	0.151	0.136	0.0005	0.002
3	0.05	1.306	13.33	0.136	0.024
3	0.1	1.17	5.29	0.062	0.014
3	0.2	1.12	5.8	0.033	0.008
3	0.5	0.962	1.4	0.011	0.005

concentration and for concentrations of Fe and Zr representative of real ones. It was already known that Fe and Zr could be separated by $H_2C_2O_4$, but it is interesting that plutonium can still be extracted despite the complexing power of the oxalate ion. Moreover, oxalic acid itself is not extracted by the diamides (3).

Kinetic Separation of Iron

As can be observed in Table 5 and Figure 4, extraction of Am(III) is faster than iron extraction. This phenomenon, however, takes place only with diamides having an aliphatic R" (without oxygen atom). Compare Figure 4a and 4b. Besides the nature of the extractant, this phenomenon is enhanced by:

- concentration of the diamide in the organic phase (Figure 4c and 4d).
- acidity in the aqueous phase (Figure 4b and 4c), but for great acidities, D_{Fe} becomes more important than D_{Am} after 10 min.
- nature of the diluent: experiments in benzene showed that equilibria are more quickly reached in this diluent than in TPH for the same diamide concentration and acidity.

TABLE 4. SEPARATION OF Am AND Pu FROM Fe AND Zr WITH OXALIC ACID

Extractant $[CH_3(C_4H_9)NCO]_2$-CH-C_2H_4-O-C_6H_{13} 0.5 M tert-butylbenzene, O/A = 1, t = 25°C

HNO_3 M	$[H_2C_2O_4]$ M	Fe g/L	Zr g/L	D_{Am}	D_{Pu}	D_{Fe}	D_{Zr}
2	0.5	0.2	0.2	0.172	0.06	0.001	0.002
2	0.5	0.6	0.6	0.112	0.111	0.001	0.002
2	0.5	1	1	0.100	0.121	0.001	0.007
3	0.5	0.2	0.2	0.642	1.161	0.011	0.0165
3	0.5	0.6	0.6	0.658	1.148	0.012	0.0005
3	0.5	1	1	0.726	1.638	0.019	0.003
4	0.5	0.2	0.2	2.291	7.51	0.170	0.0015
4	0.5	0.6	0.6	2.023	6.48	0.170	0.013
4	0.5	1	1	1.702	7.8	0.206	0.009
3	0.5	2	1	0.617	4.46	0.0197	0.010
3	0.5	5	1	0.734	7.23	0.0396	0.0013
3	0.5	10	1	0.722	7.63	0.094	0.0002
3	0.5	12	1	0.767	11.15	0.128	0.0002
3	0.7	12	1	0.653	11.20	0.067	0.005
3	0.7	15	1	0.646	9.69	0.097	0.0003
3	0.8	15	1	0.630	11.67	0.085	0.0002
4	0.8	15	1	2.97	7.81	0.225	0.0002
4	1	15	1	2.87	5.67	0.204	0.002

- nature of the emulsion: in concentrated nitrate solutions simulating real waste concentrates, it has been noticed that the difference in the extraction kinetics of Am and Fe occurred only when the emulsion was of the type "continuous aqueous phase." When a "continuous organic phase" emulsion is created, iron extraction is quicker than previously. This fact is not observed for reverse extraction.

- iron concentration: in all these experiments, metals are tracers and solvent loading is low. The extraction kinetics are slower as the iron concentration increases; however, a third phase is formed as [Fe] reaches 0.1 M at equilibrium.

TABLE 5. SEPARATION OF Am/Fe BY A KINETIC EFFECT

Conditions: O/A = 1, t = 25°C, diluent TPH

Extractant $[CH_3(C_4H_9)NCO]_2$-CH-$C_{14}H_{29}$

Time (min)	Conditions								
	$[HNO_3]$ 2.5 M $[Diam]$ 0.5 M			$[HNO_3]$ 4 M $[Diam]$ 0.5 M			$[HNO_3]$ 3 M $[Diam]$ 0.767 M		
	D_{Am}	D_{Fe}	SF	D_{Am}	D_{Fe}	SF	D_{Am}	D_{Fe}	SF
0.25	1.7	0.039	27	7.5	0.075	100	7.8	0.077	101
0.5	2.0	0.075	27	9.4	0.14	67	7.9	0.13	61
1	2.2	0.16	14	8.8	0.29	30	8.0	0.18	44
2	2.2	0.28	8.6	7.1	0.54	13	7.7	0.27	28
3	2.2	0.34	6.5	6.8	0.94	7.2	7.9	0.37	21
5	2.0	0.47	4.4	7.6	2.4	3.2	8.0	0.55	14
10	1.7	0.52	3.2	6.1	6.1	1	7.6	1.1	7.0
20	1.6	0.49	3.2	7.0	14.9	0.47	7.5	2.1	3.6
30				6.8	18.2	0.37	7.0	3.0	2.3
40				6.8	18.2	0.37	7.1	3.9	1.8
50							6.9	4.6	1.5
60							6.3	4.4	1.4

In a practical sense, it is possible to extract americium very quickly from concentrated iron solutions if the critical concentration of iron in organic phase is still not reached.

The mechanism of iron extraction is not completely elucidated at the present time. We postulate the formation of a complex in the organic phase that involves an acid molecule according to the equilibrium ("or" means in organic phase):

$$x(Diam)_{or}\ Fe^{3+} + 3NO_3^- + HNO_3 \longleftrightarrow [Fe(NO_3)_4H(Diam)x]_{or} .$$

There are some promising possibilities for practical separations utilizing kinetic effects, but many questions remain to understand all the phenomena.

Optimization of the Synthesis of the Molecule

As described more extensively in (2), the synthesis of the diamides was realized in three main steps. The tetraalkylpropanediamide was first obtained, then the

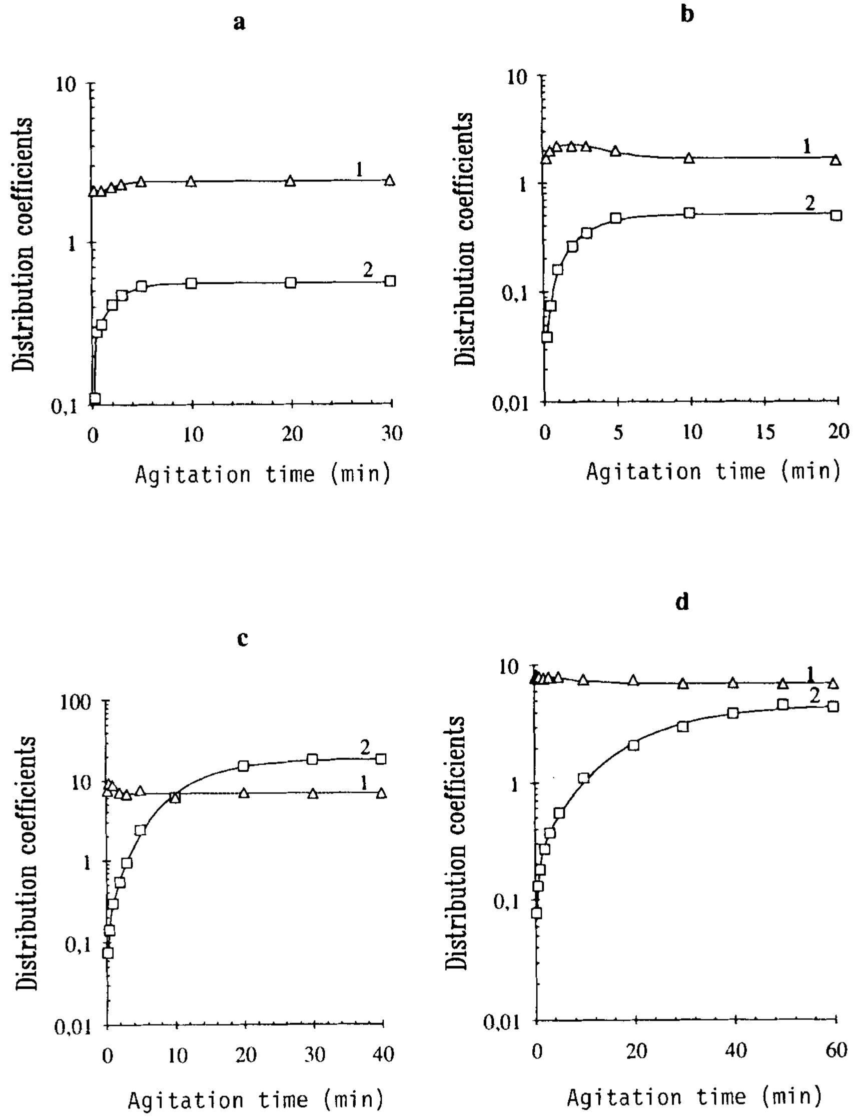

FIGURE 4. Kinetics of americium and iron extraction.
Curve 1: D_{Am} Curve 2: D_{Fe} $R = C_4H_9$ $R' = CH_3$
a: diamide 0.5 M in TPH $R'' = C_2H_4\text{-}O\text{-}C_{12}H_{25}$ HNO_3 2 M
b: diamide 0.5 M in TPH $R'' = C_{14}H_{29}$ HNO_3 2.5 M
c: diamide 0.5 M in TPH $R'' = C_{14}H_{29}$ HNO_3 4 M
d: diamide 0.75 M in TPH $R'' = C_{14}H_{29}$ HNO_3 2.5 M

TABLE 6. DISTRIBUTION COEFFICIENTS OF PLUTONIUM IN DEGRADED DIAMIDES

Conditions: extraction from 2 M HNO_3; back extraction with 0.2 M hydroxylamine in 0.1 M HNO_3 at 45° C; diluent TPH except point noted* where dodecane is used.

R′	R″	[Diam] M	DPu EX.	DPu B. EX.	% Degraded Solvent
C_2H_5	C_2H_4-O-C_6H_{13}	0.5	2.4	0.053	2
CH_3	C_2H_4-O-C_6H_{13}	0.5	13.6	0.081	4.4
CH_3	$C_{12}H_{25}$	0.5	43.8	0.0094	10
CH_3	$C_{12}H_{25}$	1.0*	76.2	0.3	6

bromide of R" is realized when not commercially available. Then, branching of R" was made with the help of butyl-lithium; this step is difficult to realize in industry.

An improvement was obtained by using for this step a phase-transfer reaction (which can take place at normal pressure and not very high temperature) using a quaternary ammonium salt as catalyst. This catalyst acts as a surfactant, so it is necessary to purify the extractant on an adsorbent to eliminate all the surfactant molecules remaining. Then, phase disengagement normally occurs.

Degradation of the Diamides with Long Alkyl R"

As has already been published (3), degradation of the diamides under hydrolysis is a complex phenomenon. NMR studies have shown that other diamides, monoamides, secondary amines, carboxylic acids, and sometimes alcohol are formed. Experiments conducted to compare diamides having either an alkyl or an oxyalkyl R" radical showed that, though the mechanisms are different, resistance to hydrolysis is roughly the same.

It is important to note that extraction and back extraction of plutonium remain possible in degraded solvents, as can be seen in Table 6.

Recent experiments have shown that for 50 d of hydrolysis (HNO_3 3 M, O/A = 13 at 25° C, constantly agitated), diamide diluted at 1 M in TPH was degraded at 8.2% (extractant: $[C_4H_9(CH_3)NCO]_2CHC_{14}H_{29}$). Diluent has an important influence; for instance, for the same diamide diluted 0.25 M in benzene, degradation was found to be 5.8% for 45 d. However, it is important to notice that in some concentrates of wastes, acidity is lower leading to a decreased hydrolysis.

USE OF DIAMIDES FOR WASTE TREATMENT

Nitric Acid Medium

For the purpose of waste declassification, all alpha-emitters must be removed to obtain products that can be stored in near-surface repositories.

Test tube experiments have shown that all the actinides are well extracted. Specifically, tervalent Am(III) and Cm(III) and hexa- and tetra-valent actinides are highly extracted. Plutonium polymers are completely extracted and can be stripped with a reducing or complexing medium [HF or $H_2C_2O_4$ for old (>6 months) polymers]. Concerning neptunium, it is interesting to note that Np is extracted even when it occurs in the pentavalent state because oxidation or disproportionation displaces the extraction equilibrium in concentrated HNO_3. Back extraction is easy for americium and curium in a weak acid medium, and a reducing solution like hydroxylamine nitrate (0.2 M) in diluent HNO_3 is needed, but sufficient, for Pu(IV), Pu(VI), or Np(VI); when neptunium occurs as Np(IV) in the organic phase, a complexing agent, such as $H_2C_2O_4$ or HF, has to be used. Uranium (VI) is easily washed with very dilute HNO_3.

Recent results have shown that Zr and Fe can be separated from Am and Pu by the addition of oxalic acid; moreover, differences between the extraction kinetics of americium and iron could lead to practical applications. Ruthenium is not extracted; some problems remain with Tc.

A bench-scale experiment was carried out with real waste concentrate coming from the pulsed-column facility of Fontenay-aux-Roses [more details are published in (3) or (6)] using the diamide

$$[C_4H_9(CH_3)NCO]_2CH\text{-}C_2H_4\text{-}O\text{-}C_6H_{13}$$

TABLE 7. COMPOSITION OF THE WASTE SOLUTION USED FOR THE MIXER-SETTLER EXPERIMENT

Element	Content	Element	Content
H^+	5 M	Fe	500 mg/L
$[NO_3^-]$	5.5 M	P_{Total}	270 mg/L
Pu	110 mg/L	$^{237\text{-}239}Np$	50 mg/L
Am	0.91 mg/L	^{152}Eu	traces
U	5.9 g/L	α activity	50 mCi/L
Tc	134 mg/L		

TABLE 8. DECONTAMINATION FACTORS OBTAINED IN THE BATTERIES

Element	DF Extraction	DF Stripping
Am	1.26×10^4	800
Eu	6.7×10^3	250
α_{tot}	1.1×10^4	125
Pu	10^5	274
Np	144	400
U	>1000	
Fe	>1000	

diluted to 0.5 M in tert-butylbenzene. The composition of the waste solution is given in Table 7 and decontamination factors in Table 8 (in the extraction stage, DF means the decontamination factor of the waste; and for the stripping stage, DF means the decontamination factor of the loaded solvent). Two mixer-settler batteries were used: the first one for extraction (10 stages in 5 M HNO_3) and scrub to decrease acidity in the solvent (2 stages), the second one for stripping with a reducing solution at 45° C (12 stages). The scheme is given in Figure 5.

This experiment has shown the feasibility of the process to extract all the alpha emitters with diamide to declassify nuclear waste solutions. Improvements could be obtained by using another diluent (TPH for instance), using a more lipophilic diamide, and by optimizing iron extraction in a more complex scheme.

Chloride Medium

Most of the waste solutions provided in the nuclear industry are in nitric acid; however, some pyrochemical process used for the production or the purification of defense plutonium, create effluents in chloride medium (mainly mixtures of HCl and concentrated salts such as NaCl, KCl, $MgCl_2$, and $CaCl_2$). As it is more extensively described in (7), diamides can be used for extraction of actinides from chloride medium. Plutonium (IV) and (VI), Am(III), Np(IV) and (VI), and U(VI) can be extracted completely. It is possible to back extract Pu(IV), Pu(VI), and Np(VI) with a reducing solution (ascorbic acid or hydroxylamine chloride in dilute HCl); Am(III), U(VI), or Np(IV) can be washed with diluted acid. Separation of plutonium from other elements, such as americium, is easy. By using a monoamide for the first stage, it is possible to extract large amounts of plutonium without extraction of americium. It is then possible to realize a process like "PUREX-TRUEX," described in the literature (8), with completely incinerable extractants.

USE OF DIAMIDES IN THE FRAME OF PARTITIONING AND TRANSMUTATION

In the concept of partitioning and transmutation, diamides can be easily used as a first step in the process; they effectively extract all the actinides concerned. Unfortunately, they extract all the lanthanides too. A separation of these two groups

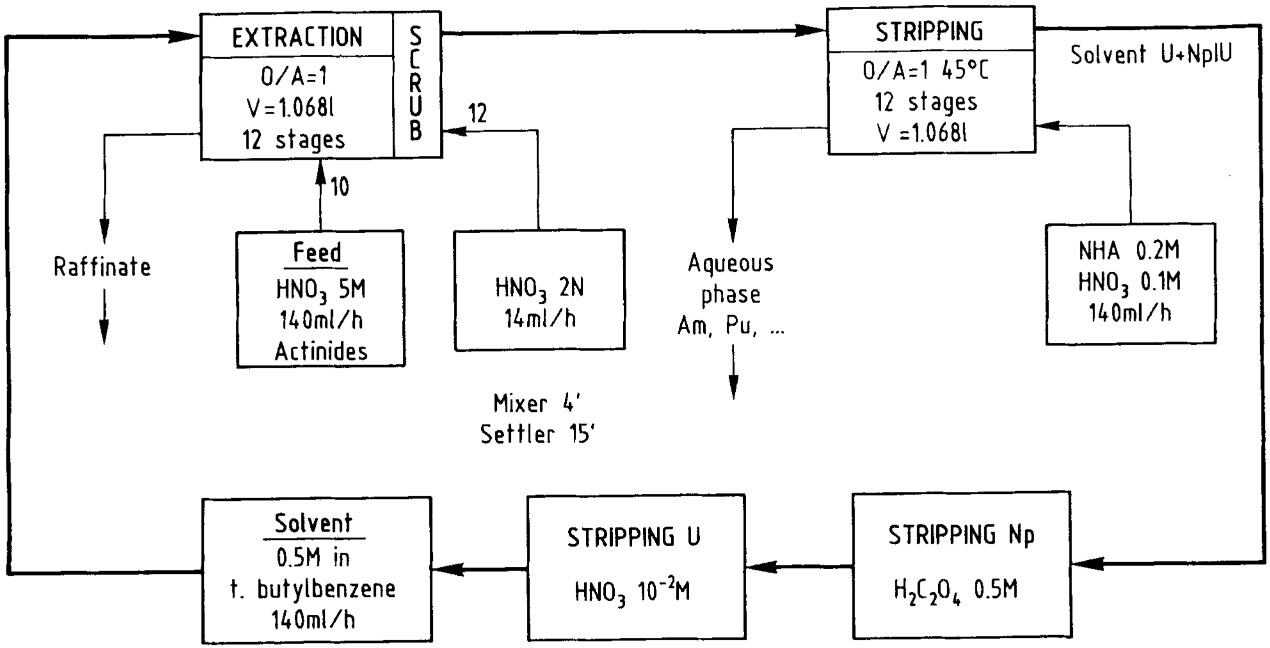

FIGURE 5. Scheme of the mixer-settler experiment for the treatment of waste in nitric medium.

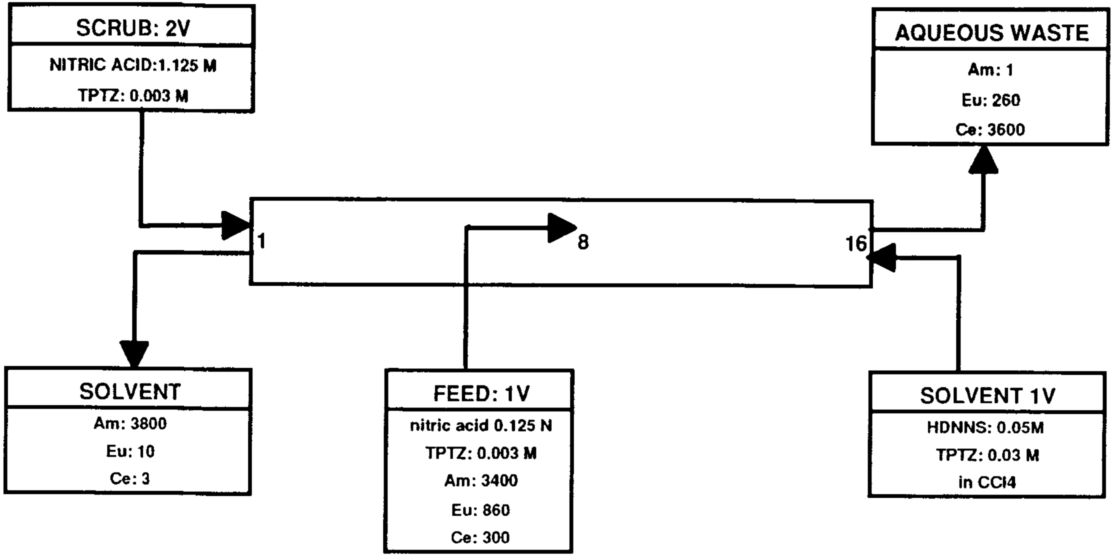

FIGURE 6. Scheme and results of the mixer-settler experiment for separation of americium from lanthanides.

of cations is then necessary. Practically, it is a different problem because they have very similar chemical properties. Two strategies can then be followed: either add a complexing agent directly at the first step of the process to extract only the actinides, or add a second step specially devoted to lanthanide-actinide separation.

For this last operation, some experiments have been carried out using tris 2-pyridyl 1,3,5 triazine (TPTZ) mixed with dinonylnaphtalenesulfonic acid (HDNNS). Soft donor ligands have been found to be selective for actinide complexation (9). TPTZ is a nitrogen donor, which complexes actinides better than lanthanides in the organic phase. However, it has to be used with an acid acting as a cationic exchanger to neutralize the charge of the tervalent cations (for instance HDNNS).

Results of a mixer-settler experiment have shown that it is feasible to separate americium from the lanthanides (10); the scheme of this experiment is given in Figure 6. Studies are now being undertaken to improve the system by changing the cation exchanger, for instance, by using α-bromocapric acid or others.

CONCLUSIONS

Pentaalkylpropanediamides can be used for the treatment of several types of waste solutions. In nitric acid, these extractants can remove all of the α emitters from high-activity liquid wastes giving "non TRU" solutions which can be stored in near-surface repositories.

The use of aliphatic diluents like TPH facilitates the utilization of diamides in nuclear reprocessing. Moreover, progress obtained in the separation of iron from alpha emitters increases the interest of these solvents for the treatment of concentrates of high-activity wastes.

Utilization of diamides is possible in chloride medium to treat effluents coming from military plants (in this case, TPH is usable too). Concerning waste treatment, it is very important to notice that these extractants are completely incinerable, hence creating no additional wastes.

For the partitioning and transmutation concept, diamides can be used with other molecules (for instance TPTZ) to separate lanthanides from actinides.

Recent progress realized in the synthesis and purification of the extractants makes industrialization of the production easier.

REFERENCES

1. G. Thiollet, L. Lafosse, C. Musikas, and P. Hoel, Nouveaux propanediamides et leurs procédés de préparation, French Patent FR 2 585 700 (1985).

2. G. Thiollet and C. Musikas, Solvent Extr. Ion Exch. 7, 813 (1989).

3. C. Cuillerdier, C. Musikas, P. Hoel, L. Nigond, and X. Vitart, Sep. Sci. Technol. 26(9), 1229 (1991).

4. H. Hubert and C. Musikas, Procédé de récupération des actinides et/ou des lanthanides présents à l' état trivalent dans une solution aqueuse acide, French Patent FR 2 537 326 (1982).

5. C. Musikas, P. Hoel, and G. Thiollet, Procédé de récupération des actinides et/ou des lanthanides par extraction dans un solvant organique contenant un propane diamide, French Patent FR 2, 585, 692 (1985).

6. C. Cuillerdier, C, Musikas, and P. Hotel, "New extractants for the treatment of nuclear wastes solutions," I. Chem. E. Symp. Series No. 119, Extraction 90, Institution of Chemical Engineers Rugby, U.K., p. 47 (1990).

7. C. Cuillerdier and C. Musikas, "Extraction of actinides from a chloride medium using pentaalkylpropanediamides," submitted to Sep. Sci. Technol. (1992).

8. L. Reichley-Yinger and G. F. Vandegrift, Sep. Sci. Technol. 23 (12&13), 1409 (1988).

9. C. Musikas, Proceedings of the International Symposium on Actinides-Lanthanides Separations, Honolulu, Hawaii, December 16-22, 1984, G. R. Choppin, J. D. Navratil, W. W. Schulz, Eds., World Scientific, Philadelphia, 1985, p. 19.

10. C. Musikas, X. Vitart, J. Y. Pasquiou, and P. Hoel, Chemical Separations, C. Judson King, Ed., Litarvan Literature, Denver, Vol. II, 1986, p. 359.