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EXTRACTION OF ACTINIDES FROM A CHLORIDE MEDIUM USING PENTAALKYLPROPANEDIAMIDES

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ABSTRACT

Pyrometallurgical processes for the purification of plutonium for defense create waste solutions containing actinides, mainly americium, in chloride medium. Studies have been undertaken to study the extraction of actinides in a chloride medium (hydrochloric acid mixed with concentrated salts such as LiCl, $CaCl_2$, $MgCl_2$, KCl) using pentaalkylpropanediamides as extractants. Plutonium(IV) is very easily extracted, but Am(III) needs a salting-out agent such as LiCl. Back extraction of trivalent cations is easy in HCl <5 M. Plutonium(IV) and (VI) can be stripped by reduction either with ascorbic acid or hydroxylammonium salts in a weak-acid medium. Several diluents can be used (aromatic, chlorinated, or even aliphatic) with addition of decanol to prevent third-phase formation. In conclusion, diamides can be used for declassification of various wastes, they are potentially completely incinerable, and, as the synthesis has been optimized, they appear to be promising extractants.

INTRODUCTION

Pyrochemical processes used for the preparation or the purification of plutonium for defense needs create effluents containing actinides such as ^{239}Pu or ^{241}Am in a chloride medium (mixture of HCl and concentrated salts); for example, the processes developed at Los Alamos and Rocky Flats (1,2):

- "DOR" process (direct oxide reduction), which consists of a direct reduction of PuO_2 by metallic calcium in molten $CaCl_2$ at 800°C;
- "MSE" process (molten salt extraction), which allows extraction of ^{241}Am from a mixture of molten NaCl and KCl; and

- "ER" process (electrorefining process), which is an electrorefining of plutonium at 740° C in the mixture of molten salts: NaCl, KCl, $PuCl_3$, $MgCl_2$.

In the United States, the "PUREX-TRUEX" process has been adopted for the treatment of effluents in chloride media (3). This process has two main stages:

1. extraction of Pu(IV) by TBP diluted in C_2Cl_4 (25% TBP), and
2. extraction of ^{241}Am by 0.5 M CMPO in C_2Cl_2.

(CMPO = octylphenyl-N,N-diisobutylcarbamoylmethylphosphineoxide.) These two solvents, however, are not completely incinerable and generate new wastes. Diamide extractants (formula: $(RR'NCO)_2CHR''$ with R and R′ alkyl and R" oxyalkyl radicals) have been studied for several years in Fontenay-aux-Roses and have shown potential for the treatment of effluents containing actinides in nitric acid solutions (4,5,6). The purpose of this communication is to show the possibility of treating aqueous chloride effluents with diamides.

EXPERIMENTAL

The diamide used for these studies has been synthesized at IRCHA (Vert le Petit France) by G. Thiollet according to the method described in (7). Its formula is $(C_4H_9CH_3NCO)_2CHC_2H_4OC_6H_{13}$. Its purity has been checked by several methods such as ^{13}C NMR and pH metric titration in a nonaqueous medium (diamides can be titrated in acetic anhydride with $HClO_4$ diluted in acetic acid using a glass electrode). The diluent is mainly tert-butylbenzene, but several other diluents have been tested. With this extractant, aliphatic diluents cannot be used; among the aromatic diluents, tert-butylbenzene, selected in the past as the trilaurylamine diluent for the Pu purification, has been chosen again because of its good chemical stability. All the chemicals are commercial products (Prolabo, Fluka, Carlo Erba). Radioisotopes are supplied either by Cogema (Pu), SPHA Fontenay-aux-Roses (^{241}Am, ^{237}Np, ^{233}U), or ORIS ^{59}Fe ^{152}Eu.

Experiments were conducted by contacting equal volumes of aqueous and organic phases which were then agitated for 10 min with a "Vortex" agitator. After centrifugation and separation, each phase was analyzed. The organic phase is normally preequilibrated with HCl before use. The distribution coefficient of an element is the ratio between organic and aqueous concentrations of this element. Analysis of metallic cations was made by α or γ radiometry (for ^{239}Pu, ^{233}U, ^{241}Am, ^{59}Fe, ^{152}Eu); neptunium was titrated by spectrophotometry, which allows checking of the oxidation state of the cation. The plutonium solutions used contained no polymer, and the oxidation state was adjusted chemically just before the extraction experiments.

RESULTS

Extraction and Back Extraction of Hydrochloric Acid and Actinides

Extraction of HCl, Pu, and Am has been studied in concentrated LiCl, $MgCl_2$, $CaCl_2$, $AlCl_3$, and HCl, or their mixtures, for practical reasons. To compare extraction coefficients, it is necessary to calculate activity coefficients a_{Cl^-} (which is the mean activity) in the different media. Two main difficulties are met concerning calculations of activity coefficients. First, electrolytes are concentrated, and activity coefficients are not published for such high ionic strengths and cannot be calculated simply. Secondly, solutions of interest are composed of mixtures of electrolytes. The method described in (8) and (9) has been adopted using Bromley's formulas. To extrapolate activity coefficients at high ionic strengths for individual salts, Meisner's method has been used. Densities of the solutions were measured to use molal scales.

Hydrochloric acid is not very extensively extracted (less than nitric acid at the same concentration); in highly salting out media, the distribution coefficient can reach 0.89. At high concentration of acid, a third phase occurs which can be suppressed with decanol (10% in organic phase). Decanol is used to increase the solubility of the diamide-acid complexes, but it decreases the distribution coefficients of the cations. The extractant concentration is generally 0.5 M for practical reasons (viscosity, phase disengagement times...), but higher concentrations are possible. Results are reported in Table 1.

Americium extraction is the most limiting case; several media have been studied: mixtures of HCl with LiCl, $MgCl_2$, $CaCl_2$, or $AlCl_3$. All the results are reported in Table 2, Table 3, and Figure 1. One can notice that it is always possible to obtain $D_{Am} > 1$ in all the chloride salts studied, except $AlCl_3$. On Figure 1, it

TABLE 1. EXTRACTION OF HCl FROM WATER AND CONCENTRATED LiCl

Conditions: extractant 0.5 M in tert-butylbenzene,
O/A = 1, t = 25°C
In test tubes designated with *, 10% decanol is added

[HCl] M	[LiCl] M	a_{Cl^-}	D_{HCl}
0.25	0	0.19	0.0028
0.5	0	0.38	0.018
2	0	2.153	0.038
3	0	4.46	0.052
6*	0	29.4	0.064
7*	0	50.9	0.082
8*	0	90.3	0.140
3	9	436	0.66
3	10	689	0.89
0.5	9	195	0.083
0.5	10	316	0.33

appears that all the distribution coefficients belong to the same straight line when plotted as a function of chloride activity (slope ~6), except points obtained in concentrated LiCl; but it is difficult to conclude a particular behavior because of the lack of precision of activity coefficients in concentrated media.

However, higher distribution ratios at high HCl concentration suggest that species such as $AmCl_6(H.Diam)_3$ are formed; this hypothesis has to be confirmed with other experiments. It is possible to extract Am(III) from weak-acid medium if chloride activity is sufficient, but it is impossible to extract in concentrated HCl alone: D_{Am}

TABLE 2. EXTRACTION OF Am(III) AND Pu(IV) FROM AQUEOUS HCl AND HCl-LiCl MIXTURES

Conditions: extractant 0.5 M in tert-butylbenzene, O/A = 1, t = 25°C

[HCl] M	[Salt] M	a_{Cl^-}	Decanol (%)	$D_{Am(III)}$	$D_{Pu(IV)}$
5	0	15.76	0	0.024	29.7
7	0	50.96	10	1.12	2.52
8	0	90.33	10	0.87	7.38
0.5	LiCl 7	61.55	0	0.066	50.0
0.5	8	112.6	0	0.325	58.7
0.5	9	194.9	0	2.7	69.0
0.5	10	316	0	14.67	55.6
4	8	689	0	3.92	55
5	3	89.9	0	3.28	
3	4	50.05	0	0.061	128
3	5	83.65	0	0.99	72
3	6	155.88	0	3.93	46
3	8	436	0	10.53	46.6
3	9	689	0	9.95	23.8
3	10	1042	0	9.43	43

is >1 only when [HCl] is >7 M, and in that case a third phase occurs. It can be suppressed with decanol addition, but D_{Am} decreases when the percentage of decanol increases. This is due to the competition of Am chloride complexes with HCl for the coordination sites of diamides. Back extraction of Am(III) is very easy in diluted medium.

TABLE 3. EXTRACTION OF Am(III) and Pu(IV) FROM AQUEOUS HCl-$CaCl_2$, HCl-$AlCl_3$, AND HCl-$MgCl_2$ MIXTURES

Extractant 0.5 M in tert-butylbenzene, O/A = 1, t = 25°C

[HCl] M	[Salt] M	a_{Cl^-}	Decanol (%)	$D_{Am(III)}$	$D_{Pu(IV)}$
0.5	$CaCl_2$ 4.76	32.03	0	0.314	36
0.5	5.31	37.05	0	7.79	54
0.5	5.85	76.6	0	13.70	47
3	2.77	38.9	0	1.80	44
3	3.57	53.7	7	3.1	57
3	4.33	70.8	7	3.72	60
0.5	$AlCl_3$ 1	10.25	0	0.001	13.3
0.5	2	20.9	0	0.0145	39
0.5	2.5	28.53	0	0.055	15.7
3	2	29.35	13	0.377	
0.5	$MgCl_2$ 3	16.12	0	0.019	59.7
0.5	4	25.96	0	0.351	73.2
0.5	5	40.57	0	16.79	63.3
3	2	27.78	0	0.043	46
3	3	46.74	0	5.18	56.6

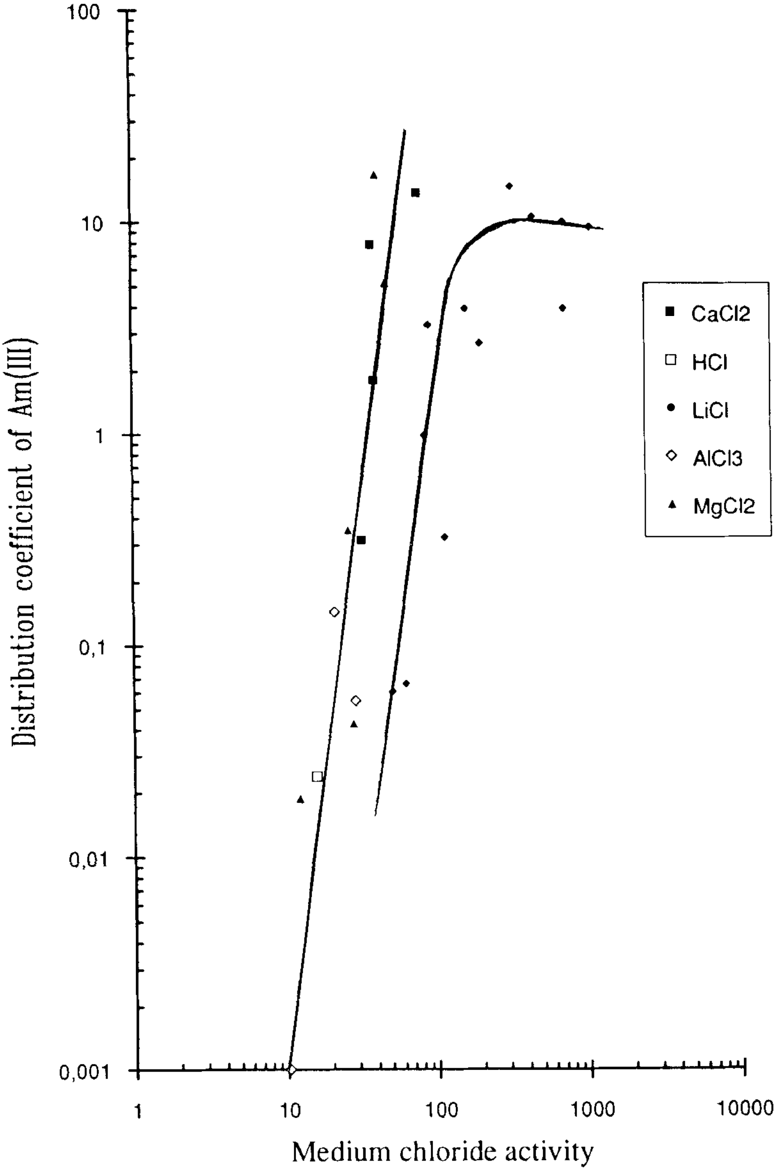

FIGURE 1. Distribution coefficients of Am(III) in chloride solutions as a function of chloride activity.

TABLE 4. DISTRIBUTION COEFFICIENTS OF Np(IV) AND Np(VI) IN CHLORIDE MEDIUM

Extractant 0.5 M, O/A = 1, t = 25°C

[HCl] M	[LiCl] M	$D_{Np(VI)}$	$D_{Np(IV)}$
0.5	8	24.5	23.5
0.5	9	244	96.9
0.5	10	385	93
3	8	584	288
3	9	834	192
3	10	745	224

Extraction of plutonium has been studied in the conditions where americium is also extracted; possibilities of back extraction of Pu(IV) and (VI) and separation from Am have been researched. Pu(IV) is completely extracted when Am is extracted (see Tables 2 and 3); it is easy to separately wash Am by choosing a medium with a sufficiently low chloride activity (e.g., HCl <5 M). Back extraction of Pu(IV) is done with a reducing solution: either hydroxylamine chloride (0.1 M) or ascorbic acid (0.1 M) in diluted HCl (0.2 M). Pu(VI) has a similar behavior with higher distribution coefficients than those of Pu(IV). It can be stripped with the same reducing media (D_{PuVI} >500 for LiCl 8 M and HCl from 0.5 to 4 M).

Neptunium(IV) and (VI) are highly extracted (see Table 4). They can be back extracted, respectively, by a very diluted medium or the same reducing solution as Pu(IV).

Uranium is completely extracted under the same conditions (D_{UVI} >1000 in, respectively, HCl 0.5 to 3 M for LiCl 8, 9, or 10 M); it can be back extracted with a very dilute HCl solution (HCl <0.5 M but better at 0.01 M).

TABLE 5. EXTRACTION OF IRON IN CHLORIDE MEDIUM BY DIAMIDE

Extractant 0.5 M, O/A = 1, t = 25°C

[HCl] M	[LiCl] M	D_{Fe}
0.5	8	3200
0.5	9	460
0.5	10	640
3	8	390
3	9	310
3	10	396
0.1	0	0.008
1	0	0.08
2	0	2.5
5	0	71.6

TABLE 6. EXTRACTION OF ACTINIDES BY A MONOAMIDE IN CHLORIDE MEDIUM

Extractant 0.5 M $CH_3\text{-}C(CH_3)_2\text{-}CH_2\text{-}CO\text{-}N(CH_2\text{-}CH(C_2H_5)\text{-}C_4H_9)_2$
in tert-butylbenzene, O/A = 1, t = 25°C

[HCl] M	[CaCl$_2$] M	[MgCl$_2$] M	[KCl] M	[NaCl] M	D_{Am}	D_{Pu}
4.98	2.2				0.021	371
5.14	1.8				0.025	209
5.61		0.30	0.2	0.19	0.014	423
5.12		0.85	0.3	0.1	0.013	578
1.26		2.7	0.31	0.3	0.01	19.72

TABLE 7. INFLUENCE OF THE DILUENT ON AMERICIUM EXTRACTION

Conditions: O/A = 1, t = 25°C

Diluent	[HCl] M	[LiCl] M	Decanol %	D_{Am}
$C_{10}H_{18}$	0.5	8	9.3	1.66
(Decaline)	0.5	9	10.6	12.50
	0.5	10	10.6	57.5
	3	8	10.6	20.57
	3	9	10	8.75
	3	10	13.3	7.13
	4	8	12	4.35
	5	8	12	1.14
CCl_4	3	8	0	6.74
	4	8	0	2.55
	5	8	0	0.80
C_2Cl_4	3	8	0	13.31
	3	9	0	5.29
	3	10	0	3.13
	4	8	0	2.65
	5	8	0	0.55

Extraction of Lanthanides and Iron

Tervalent lanthanide cations are extracted in the same conditions as americium as it is observed in nitric acid. (Experiments were mainly realized with ^{152}Eu as tracer.)

Iron is highly extracted, and it cannot be separated with oxalic acid with the same method as in nitric medium (4). Some results are given in Table 5.

Extraction of Large Amounts of Plutonium

Some effluents contain large concentrations of plutonium that must be, for that purpose, recycled. The PUREX-TRUEX process is used in chloride medium with a first step being extraction of Pu(IV) with TBP (3). According to our concept of using completely incinerable extractants, it is better to use either diamides or even monoamides, which can be considered as a substitute to TBP in the PUREX process. Under these conditions, Am(III) is not extracted and Pu(IV) can be extracted to a great extent (42 g/L); some results are given in Table 6 using solutions having the same composition as those considered in (10).

Influence of the Diluent

The diluent used in these studies was mainly tert-butylbenzene. As it is described in a nitric medium (6), optimization of the formula of the diamide enables the use of TPH as a diluent; but the molecule used here is not the best one for this purpose. Cis-trans decaline and chlorinated diluents (CCl_4 and $CCl_2{=}CCl_2$) can be convenient too, but they show no special interest. Some values of D_{Am} are reported in Table 7 with these diluents.

Degradation of the Diamide in Chloride Medium

As in nitric acid, the most important parameters that influence the degradation of the extractant are concentration of HCl and temperature. Degradation is not important in weak acid solutions (e.g., HCl 0.5 M) where it is always possible to extract Am(III) in a salting-out medium.

CONCLUSIONS

In this short communication, it has been shown that diamides can be considered as promising extractants to treat the wastes coming from military plants. It is possible to effectively extract Am(III) and Pu(IV), and their separation is easily accomplished. Back extraction of plutonium is easy using a reducing solution.

Wastes containing large concentrations of plutonium require a first stage using a monoamide extractant, which leads to an extraction of plutonium only with recycling. These two molecules are completely incinerable and do not create new wastes. The formulas can be optimized; the examples given here just show the feasibility of the actinide separation.

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