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EXTRACTION OF ACTINIDES FROM 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 chloride medium (hydrochloric acid mixed with concentrated salts such as LiCl, CaCl₂, MgCl₂, KCl) using pentaalkylpropanediamides as extractants. Plutonium (IV) is very easily extracted, Am (III) needs a salting out agent such as LiCl. Back extraction of trivalent cations is easy in HCl <5M. Plutonium(IV) and (VI) can be stripped by reduction either with ascorbic acid or hydroxylammonium salts in 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 various wastes declassification, 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 ²³⁹Pu

or ²⁴¹Am in chloride medium (mixture of HCl and concentrated salts); for instance the processes developed at Los Alamos and Rocky Flats (1), (2):

- "DOR" process (direct oxide reduction) which consists of a direct reduction of PuO₂ by metallic calcium in molten CaCl₂ at 800°C,

- "MSE" process (molten salts extraction) which allows extraction of ²⁴¹Am from a mixture of molten NaCl and KCl,

- "ER" process (electrorefining process) which is an electrorefining of plutonium at 740°C in the mixture of molten salts: NaCl, KCl, PuCl₃, MgCl₂.

In the USA the "PUREX-TRUOX" process has been adopted for the treatment of effluents in chloride medium (3). This process has two main stages :

- 1- extraction of Pu(IV) by TBP diluted in C₂Cl₄ (25%TBP)
- 2- extraction of ²⁴¹Am by 0.5M CMPO in C₂Cl₂

(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 their interest 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. Thiollot according to the method described in (7). Its formula is: (C₄H₉CH₂NCO)₂CHC₂H₄OC₆H₁₃ . Its purity has been checked by several methods such as ¹³C NMR and pH metric titration in non-aqueous medium, (diamides can be titrated in acetic anhydride with HClO₄ diluted in acetic acid using a glass electrode). 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 triaurylamine 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) or by 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 minutes with a "Vortex" agitator. After centrifugation and separation, each phase was analysed. The organic phase is normally preequilibrated with HCl before use. Distribution coefficient of an element is the ratio between organic and aqueous concentration 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 to check the oxydation state of the cation. The plutonium solutions used contained no polymer, the oxydation 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 have been studied in concentrated LiCl, MgCl_2 , CaCl_2 , AlCl_3 , 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, activity coefficients are not published for so 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, 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.

TABLE 1. EXTRACTION OF HCl FROM WATER AND CONCENTRATED LiCl.

Conditions: extractant 0.5M 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

Americium extraction is the most limiting case, several media have been studied: mixtures of HCl with LiCl, MgCl₂, CaCl₂ or AlCl₃. All the results are

reported in Table ., Table 3 and Figure 1. One can notice that it is always possible to obtain $D_{Am} > 1$ in all the chlorides salts studied, except $AlCl_3$. On Figure1, it appears that all the distribution coefficients belong to the same straight line when plotted as a function of chloride activity (slope roughly 6) except points obtained in concentrated $LiCl$; but it is difficult to conclude to a particular behavior because of the lack of precision of activity coefficients in concentrated media.

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

Conditions: extractant 0.5M 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	<u>LiCl</u> 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

TABLE 3. EXTRACTION OF Am(III) AND Pu(IV) FROM AQUEOUS HCl-CaCl₂, HCl-AlCl₃, AND HCl-MgCl₂ MIXTURES.

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

[HCl] M	[Salt] M	aCl ⁻	Decanol %	D _{Am(III)}	D _{Pu(IV)}
0.5	<u>CaCl₂</u> 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	<u>AlCl₃</u> 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	<u>MgCl₂</u> 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

However, higher distribution ratios at high HCl concentration suggest that species such as AmCl₆(H.Diam)₃ are formed; this hypothesis has to be confirmed with other experiments. It is possible to extract americium (III) from weak acid medium if chloride activity is sufficient but it is impossible to extract in concentrated HCl alone: D_{Am} is greater than one only when [HCl] is greater than 7M 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.

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 Table2 and Table3), it is easy to separately wash Am by choosing a medium with a sufficiently low chloride activity ($\text{HCl} < 5\text{M}$ for instance). Back extraction of Pu(IV) is done with a reducing solution: either hydroxylamine chloride (0.1M) or ascorbic acid (0.1M) in diluted HCl (0.2M). Pu(VI) has a similar behavior with higher distribution coefficients than those of Pu(IV). It can be stripped with the same reducing media, ($D_{\text{PuVI}} > 500$ for LiCl 8M and HCl from 0.5 to 4M).

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

Extractant 0.5 M , O/A=1, $t=25^\circ\text{C}$.

[HCl] M	[LiCl] M	$D_{\text{Np(VI)}}$	$D_{\text{Np(IV)}}$
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

Neptunium (IV) and (VI) are highly extracted (see Table4). 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 ($D_{\text{U(VI)}} > 1000$ in, respectively, HCl 0.5 to 3M for LiCl $8,9$ or 10M); it can be back extracted with a very dilute HCl solution ($\text{HCl} < 0.5\text{M}$ but better 0.01M).

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 realised 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.

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

Extraction of Large Amounts of Plutonium.

Some effluents contain large concentrations of plutonium which must be, for that purpose, recycled. PUREX -TRUEX process is used in chloride medium with a first step of 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 (42g/l); some results are given in Table 6 using solutions having the same composition as those considered in (10).

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

Extractant 0.5 M CH₃-C(CH₃)₂-CH₂-CO-N(CH₂-CH(C₂H₅)-C₄H₉)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

Influence of the Diluent.

The diluent used in these studies was mainly tert-butylbenzene. As it is described in 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 (CCl₄ and CCl₂=CCl₂) 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 which influence the degradation of the extractant are concentration of HCl and temperature. Degradation is not important in weak acid solutions (for instance HCl 0.5M) where it is always possible to extract Am(III) in a salting out medium.

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 (decaline)	0.5	8	9.3	1.66
	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 ₂ Cl 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

CONCLUSION.

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 effectively to extract Am(III) and Pu(IV) and their separation is easy. Back extraction of Pu 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 Pu only with recycling. These two molecules are completely incinerable and don't create new wastes. The formulas can be optimized, the examples given here just show the feasibility of the actinides separation.

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CAPTION OF THE FIGURE

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

