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ABSTRACT

In the frame of the French radioactive waste management Acts of December 1991 and June 2006, minor actinide separation processes have been developed to significantly decrease the radiotoxicity of the ultimate waste produced by the nuclear industry.

For actinide/lanthanide separation, several routes are possible, either with two cycles using two different solvents (generally DIAMEX for the first one, and SANEX for the second one), or with a single cycle and the same solvent during the whole process. The DIAMEX-SANEX concept described in this paper is a sort of intermediate between these two strategies: the organic phase consists of a cationic exchanger and the N,N'-dimethyl-N,N'-dioctylhexylethoxymalonamide, (DMDOHEMA), which play different role in distinct key stages of the process. The main idea of this process is to split the organic phase in two solvents: one containing the DMDOHEMA, the other the acidic extractant. So this latter doesn't interact with DMDOHEMA during the first extraction step.

This paper describes some results obtained with di-n-hexyl phosphoric acid (HDHP), which fulfils the required criteria for the process. For instance, this reagent can easily extract lanthanides from a weak acidic aqueous solution, and it can be stripped selectively from DMDOHEMA, thanks to a basic solution.

I. INTRODUCTION

The CEA has undertaken researches on the partitioning of long-lived radionuclides found in a PUREX raffinate. Among these nuclides, the more radiotoxic ones are the actinides such as americium, curium and neptunium. The last one can be separated with a modified PUREX process. The separation of the others requires specific processes, which can recover americium and curium from a concentrated nitric medium containing many fission products, such as lanthanides. The DIAMEX-SANEX process studied by CEA consists in operating separation with only one partition cycle, directly from a PUREX raffinate, by the selective back-extraction of actinides(III), after their co-extraction along with lanthanides and yttrium (Refs. 1, 2). The solvent contains an acidic extractant in addition to the malonamide used in DIAMEX (Ref 3).

First paragraphs explain the principle of the process and the required criteria the extractant has to fulfill.

Moreover, we discuss about studies on the extractant separation step, especially on the choice of the aqueous phase. Three carboxylic acids, partially neutralized by four "CHON" bases, have been tested. The aim is to separate the two extractants in an aqueous medium at a pH above 4 and below 7 to avoid the operating conditions of the actinide stripping or those of the solvent treatment. Some batch experiments have been carried out in order to validate the total recovery of HDHP from an organic phase into an other.

II. PRINCIPLE OF THE DIAMEX-SANEX PROCESS

II.A Principle

DIAMEX-SANEX is a liquid-liquid extraction process, based on DIAMEX (Refs. 1, 2), which recovers actinides(III) (americium and curium) in one single liquid-liquid extraction cycle, directly from a PUREX raffinate. After their co-extraction with lanthanides by DMDOHEMA, actinides are selectively back-extracted thanks to a polyaminocarboxylate aqueous reagent. The latter is an effective chelating agent for actinides(III) pro-

viding the pH exceeds 2. At this acidity, DMDOHEMA can not extract An(III) without salting-out agents, which have negative effects on waste management. In order to avoid this drawback, DIAMEX solvent is supplemented by an acidic extractant, to ensure effective extraction at low acidity (Ref. 3). Scientific feasibility step of this process was demonstrated in 2001 with diethylhexylphosphoric acid (HDEHP) (Ref. 2). However, to improve the flowsheet and avoid the presence of the acidic extractant in the extraction step, an extractant splitting step has been implemented, after the stripping of the lanthanides. Thus, molybdenum, zirconium and iron are not extracted by the acidic extractant at the first stage.

This DIAMEX-SANEX process consists of (Fig. 1):

- A co-extraction of actinides and lanthanides thanks to DMDOHEMA in HTP and aqueous reagents, such as oxalic acid and HEDTA (like in the DIAMEX process, Ref. 2),
- An actinide stripping with selective aqueous reagents at pH>2, the acidic extractant being added at this step to keep lanthanides in the organic phase,
- A stripping of the lanthanides,
- A splitting of the two extractants, DMDOHEMA, being recycled in the first step and the acidic extractant in the second one.

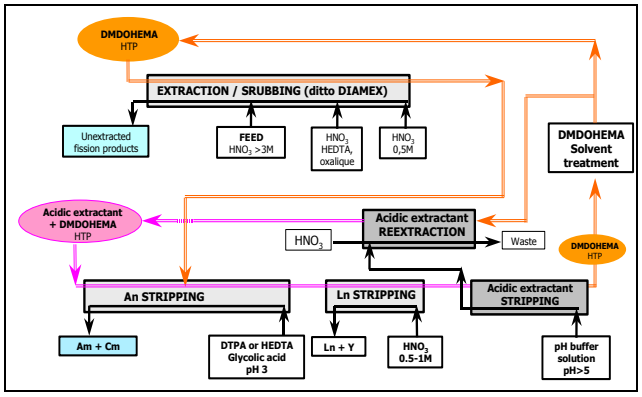


Fig. 1. General flowsheet of the DIAMEX-SANEX process

II.B. Selection criteria for the acidic extractant

HDHP has been chosen because it fulfills the following criteria: ·

- Its distribution ratio is higher than 20 in the actinide stripping operation conditions (pH~3), in order to minimize HDHP loss in the aqueous phase outflow (lipophilic property),
- It can be easily withdrawn from an organic phase, containing DMDOHEMA 0.65 M, thanks to an aqueous phase at a pH higher than 4. We aim to strip 60%-70% of HDHP in the aqueous phase after one contact (extractant separation)
- HDHP can maintain the lanthanides during the actinide separation step ($D_{Ln} > 0.2$). Furthermore, separation factors between actinides (Am(III), Cm(III)) and lanthanides are higher than 9, to minimizie stages number in the process flowsheet,
- HDHP displays good hydrolytic and radiolytic stabilities, higher than those of DMDOHEMA,
- This molecule does not induce precipitates or gels in process operating conditions.

Since a lot of DMDOHEMA degradation products are acidic, the solvent treatment is also carried out in a basic medium. Thus, in order to recover HDHP without other acidic compounds, the extractant separation should occur in a weak acidic medium (pH value ranging from 4 to 7)

In this paper, we give and comment the main results concerning the two first criteria.

III. PARTITION OF HDHP IN An, Ln STRIPPING STEPS

[HDHP] determination by titration

A known volume of organic phase was equilibrated at room temperature (22°C) with a 5 fold larger volume of aqueous solution. After centrifugation, a precise volume of the aqueous phase was withdrawn and equilibrated with a 8 fold smaller volume of HTP phase. HDHP concentrations in the two organic phases were analysed by acid-base titration, after having been acidified with 0.1-0.5 M nitric acid to reprotonate the HDHP. In case of HDHP – DMDOHEMA mixtures, it was necessary to strip the organic nitric acid with water, otherwise it was difficult to distinguish between HDHP and nitric acid by titration.

The distribution ratio of HDHP can be written as:

$$D_{HDHP} = \frac{\overline{[HDHP]}}{[HDHP]}$$

If HDHP is not too much stripped in the aqueous phase, for instance $D_{HDHP} \geq 30$, its partition ratio can be written as:

$$D_{HDHP} = 8\frac{\overline{[HDHP]}_{1st\,contact}}{\overline{[HDHP]}_{2nd\,contact}}$$

In the others cases, its partition ratio can be written as:

$$D_{HDHP} = 5 \frac{\overline{[HDHP]}_{1stcontact}}{\overline{[HDHP]}_{initial} - \overline{[HDHP]}_{1stcontact}}$$

[HDHP] determination by extraction

To determine the distribution ratio by this method, it is necessary to know first the dependencies for the extraction of ^{152}Eu and ^{241}Am traces amounts, under similar operating conditions (HDHP concentrations, temperature, mixing time, aqueous solution). The method consists in mixing the same organic phase successively with aqueous phases, changed after each contact. Thus, every parameter is unchanged for each extraction, except the concentration of HDHP in the organic phase. Am and Eu distribution ratios decrease with HDHP organic concentration. Providing a few acidic extractant is stripped in the aqueous phases, it is possible to calculate its concentration after each extraction, knowing HDHP dependency law, distribution ratio values and initial extractant concentration.

During actinide/lanthanide separation (pH 2-4) and lanthanide stripping ([HNO_3]>1mol/L), HDHP dissolution in the aqueous phases should be as low as possible. Results are gathered in table I. In the case of extraction procedure, values given are averages of two or three measurements.

TABLE I. HDHP partition coefficient between DMDOHEMA/HTP and DTPA/glycolic solutions

	No or few organic cations			With organic Ln	
Final PH	Titration	^{241}Am extraction	^{152}Eu extraction	Titration	^{152}Eu extraction
3.9	10^1				
3.5	$3.\ 10^1$	$2.\ 10^1$	$2.\ 10^1$	5	6
3.0	10^2	10^2	$6\ 10^1$	8	9
2.5	$2.\ 10^2$			8	

Organic solutions: [HDHP]=0.15M + [DMDOHEMA]=0.6M in HTP, spiked with ^{241}Am + ^{152}Eu, with or without rare earths (0.025M in total)
Aqueous solutions: [DTPA]=0.03M +[glycolic acid]=1M, pH fitted with NaOH.

As expected, theses results show a decrease in HDHP partition coefficients as the pH increases. The higher the acidity is, the more the proton of the acidic extractant becomes labile, and thus, the more polar and hydrophilic this molecule becomes. Therefore, to avoid too much HDHP partition in the aqueous phase, it is better to keep the pH under 3.5. Lanthanides in biphasic system drastically decrease the partition coefficient of HDHP. This phenomenon can be explained by an greater dissolution of Ln-$HDHP^{n+}$ complexes in the aqueous phase.

Since the aqueous outflow of the actinide stripping step would contain only few lanthanides, majority of them remaining in the organic phase, the HDHP partition coefficient should exceed 20 in the last stage. Thus, this extractant is lipophilic enough to design a process flowsheet, providing a "HDHP scrubbing" is implemented thanks to the recycling of part of the DMDOHEMA organic flow.

V. HDHP / DMDOHEMA SEPARATION

As observed before, increase in pH of aqueous solutions is better to decrease the partition ratio of HDHP. Nevertheless, if this solution is too basic(pH close to that of solvent treatment), acidic degradation products of DMDOHEMA can follow HDHP in the aqueous phase. Moreover, pH control in this step is important because HDHP stripping leads to a decrease in pH and therefore to an increase in HDHP partition. This phenomenon is connected with the acid conversion into its conjugated base.

In order to keep the pH into a correct operating zone, it is better to use a pH buffer solution. Three acids have been selected:

- tartaric acid (pK_{A1}=4.4, pK_{A2}=3.0 with a null ionic strength, Ref. 7),
- glycolic acid (pK_A=3.8 with a null ionic strength, Ref. 7),
- citric acid (pK_{A1}=6.4, pK_{A2}=4.8, pK_{A3}=3.1 with a null ionic strength, Ref. 7),

The pK_A values of citric acid fit the targeted operating conditions (4<pH<7): the closer the pK_A value to the pH is, the stronger the buffering effect is. Therefore, to stabilize the pH value, citric acid would be less concentrated than the two other carboxylic acids. But, on the other hand, studies about acid destruction are in favor of tartaric acid or glycolic acid. Organic mineralization by hydrogen peroxide has led to a rapid and total destruction of these 3 acids, Ref. 8. However, acetic acid, a stable reagent, can be produced from the degradation of citric acid and should be completely destroyed thanks to more hydrogen peroxide added.

Because of its assumed lipotropic characteristic, tetramethylammonium hydroxide (TMAOH) was used as base solution to compare these three carboxylic acids.

V.A. Tartaric acid

Performances obtained with citric and tartaric acids were comparable under same operating conditions. The more concentrated tartaric acid is, or the lower the pH decreases, the shorter the settling time is. At 1M of tartaric acid, a third phase could appear in some cases and HDHP distribution ratio did not decrease. A pH between 4.2 and 5.8 seemed to be suitable to strip more than 99.9% of HDHP into the aqueous phase. However, third phase formation is prohibited since it could modify hydrodynamics in the process. Therefore, in order to approach operating conditions of a multistage test, several successive extractions were carried out, renewing the organic phase. So the aqueous phase was enriched with HDHP, as first stages in process. As for the previous experiment, a third phase appeared for pH values closed to 4.3. Strangely, this third phase disappeared after an other equilibrium with fresh organic solution, whereas HDHP aqueous concentration was slightly the same as the previous equilibrium. An other experiment showed that a lower concentration of HDHP in the organic phase led to the same third phase formation. Moreover, this latter occurred more rapidly, then disappeared after the third extraction. The origin of this phenomenon was not clear but did not seem linked to the solubility of HDHP in tartaric/TMAOH medium. Therefore, this aqueous system could not be chosen for the process, in spite of its good extractant separation performances.

V.B. Glycolic acid

Results obtained with glycolic acid showed that, with the same TMAOH concentration and doubled acid concentration, glycolic acid led to performances comparable to those of the tartaric acid. For instance, HDHP partition ratios were similar to that obtained with 0.6M of glycolic acid or 0.3M of tartaric acid. This is the consequence of the fact that there is only one acidic function in glycolic acid instead of two for tartaric acid. To reach pH=5, the two functions have to be neutralized according to the pK_A (see values in paragraph V.A.). Hydrodynamics was quite similar between the 2 systems. Settling time decreased as the pH values decreased and the concentrations of the aqueous reagents increased. A third phase appeared with 2M of glycolic acid, instead of 1M of tartaric acid.

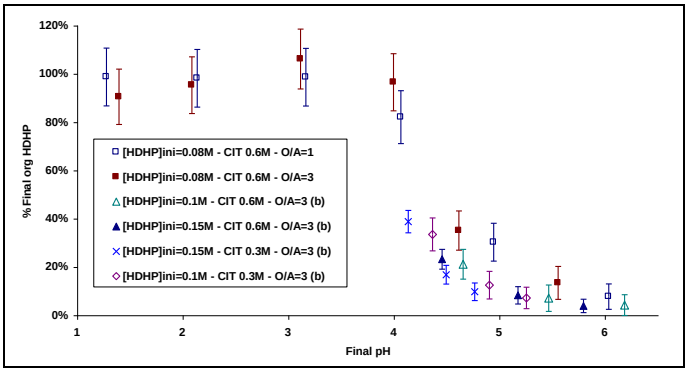
This aqueous system could not be selected owing to this third phase formation and the double concentration of glycolic acid as compared to tartaric acid necessary to obtain the same performances.

V.C. Citric acid

Fig. 2. shows the impact of pH on HDHP stripping, with various organic HDHP concentrations and citric acid concentrations.

In view of uncertainty, plots on Fig. 2 follow the same trend. HDHP or citric acid concentrations influence only the pH after extraction. This one decreases for high HDHP concentrations (increase in acid stripped in aqueous phase) and low citric acid concentrations (weaker pH buffer). The diminution of pH decreases the dissociation of the acid, which becomes less polar, and thus less hydrophilic.

HDHP stripping was effective for pH values higher than its pK_A close to 3.6. This result is logical since this acid, which is lipophic in its neutral form, can only be soluble in the aqueous phase when it becomes its conjugated base, *i.e.* pH higher than pK_A.



CIT = citric acid, O/A = organic to aqueous volume ratios.
% final org HDHP = ratio between organic HDHP concentrations before and after extraction.
Bar lines represent uncertainty on results.
(b) = second experiment carried out.
Organic solutions: $[HDHP]_{ini}$=0.083-0.15M + [DMDOHEMA]=0.6M in HTP
Aqueous solutions: [citric acid]=0.3-0.6M, pH fitted with TMAOH.
Extraction in tubes during 10 min at room temperature,
O/A=3 : aqueous volume = 0.3mL = organic volume = 0.9 mL
O/A=1 : aqueous volume = organic volume = 0.9 mL

Fig. 2. Effect of citric acid, HDHP and TMAOH concentrations on HDHP stripping in the aqueous phase

Other experiments showed that a citric acid concentration of 0.6 M led to third phase formations for pH>6 and pH<4.7. This phenomenon was not observed with 0.3M of citric acid, except for a pH below 4.1. Therefore, an initial pH, which is high enough, and an on-line addition of base, should prevent third phase appearance. Moreover, in the frame of the same experiments, no third phase was detected when HDHP was at 0.03M in the initial organic phase. In the process, the major stripping of HDHP would occur in the first stage of extractant separation step, where about 80-

90% of HDHP would be stripped in the aqueous phase. Thus, organic HDHP concentration into the other stages would be below 0.03M, which is enough to avoid third phase formation.

Settling times increased with pH. An experiment in a Becher vessel, to control emulsion of the biphasic system, showed that continuous organic mode (addition of aqueous droplets in organic emulsion) led to a faster settling time than continuous aqueous mode (addition of organic droplets in aqueous emulsion): in the first case, natural settling occurred after 7 minutes whereas, vigorous centrifugation was necessary in the other mode. This hydrodynamic feature requires specific contactors to carry out this extractant separation step.

Few experiments were carried out to study "CHON" bases other than TMAOH. To avoid addition of mineral cations in the waste production, the selected reagents contained only C, H, O and N atoms: tetrabutylammonium hydroxide (TBAOH), hydrazine base (HYD), ammonium carbonate (AC). Results are given in Table II.

Among the tested bases, TMAOH and TBAOH were the most effective for the stripping of HDHP. This phenomenon can be explained by alkyl- functions on these reagents, making the aqueous phase more "organic", allowing more interactions with the alkyl chains of HDHP. This explanation is however not sufficient since TMAOH was more efficient than TBAOH: only 68% of HDHP were stripped with TBAOH instead of 89% in the case of TMAOH, in spite of a higher final pH. This can be linked to a partial extraction of tetrabutylammonium ion (TBA) in the organic phase, detected by acid-base titration. With organic phases containing only DMDOHEMA 0.65M in HTP equilibrated with solutions of citric acid neutralized at pH 6 by TBAOH or TMAOH, no TBA or TMA were detected by titration under same operating conditions. That means that TBA seems to be extracted by complexation with HDHP.

TBAOH is not interesting for the process since it is not easier to destroy this reagent than TMAOH.

Hydrazine base and ammonium carbonate showed very poor HDHP stripping performances, even under caustic conditions. An other experiment with ethylene diamine led to similar results.

TMAOH appeared to be the only interesting reagent to separate HDHP from DMDOHEMA, thanks to a buffer solution at pH<8, in order not to be in the caustic conditions DIAMEX solvent treatment.

TABLE II. Performances obtained with citric acid / TMAOH and other "CHON" bases

	[HDHP] ini (mol/L)	Base	pH ini	pH fin	Vorg ini (mL)	Vaq ini (mL)	O/A ini	Vorg fin (mL)	Vaq fin (mL)	O/A fin	[HDHP]org fin (mol/L)	% HDHP org fin
Citric acid 0.6M	0.07	**TMAOH**	5.9	4.9	0.9	0.3	**3**	0.9	0.3	**3**	0.008	**11%**
	0.07	**TBAOH**	6.0	5.4	0.9	0.3	**3**	0.9	0.3	**3**	0.024	**32%**
Citric acid 0.3M	0.14	**TMAOH**	5.0	3.9	0.6	0.6	**1**	0.6	0.6	**1**	0.040	**28%**
	0.14	**HYD**	5.1	4.7	0.6	0.6	**1**	0.6	0.6	**1**	0.13	**94%**
Citric acid 0.3M	0.15	**TMAOH**	6.0	4.1	0.9	0.3	**3**	0.8	0.4	**2**	0.059	**34%**
	0.15	**AC**	9.0	8.8	0.9	0.3	**3**	0.9	0.3	**3**	0.13	**85%**
	0.15	**AC**	10	9.8	0.9	0.3	**3**	0.9	0.3	**3**	0.12	**81%**
	0.051	**AC**	9.0	9.0	0.9	0.3	**3**	0.9	0.3	**3**	0.039	**77%**
	0.051	**AC**	10	9.9	0.9	0.3	**3**	0.9	0.3	**3**	0.030	**59%**

pH ini = initial pH, pH fin = final pH, Vorg = organic volume,
Vaq = aqueous volume ini=initial, fin=final.
% final org HDHP = ratio between organic HDHP concentrations before and after extraction
TMAOH = tetramethylammonium hydroxide
TBAOH = tetrabutylammonium hydroxide
HYD = hydrazine base, AC = ammonium carbonate
Organic solutions: $[HDHP]_{ini}$=0.05-0.15M + [DMDOHEMA]=0.6M in HTP
Aqueous solution: [citric acid]=0.3-0.6M, pH fitted with a "CHON" base
Extraction in tubes during 10 min at room temperature,
O/A=3 : aqueous volume = 0.3mL = organic volume = 0.9 mL
O/A=1 : aqueous volume = organic volume = 0.9 mL

V.D. Composition of the aqueous solution

According to previous paragraphs, the more favourable aqueous phase to separate HDHP from DMDOHEMA was: [citric acid]=0.3M at pH 6-7 fitted with tetramethylammonium hydroxide.

Even if this solution presented some drawbacks, in particular because TMAOH was hard to destroy completely, it had nevertheless the required characteristics to separate the two extractants:

- 80-90% of HDHP could be stripped into the aqueous phase after only one stage,
- operating pH was below 7,
- this solution was buffering the pH enough to reach separation with organic to aqueous flow ratios of 3 and a HDHP concentration below 0.2M.

VI. HDHP STRIPPING THEN REEXTRACTION

The aim here was to check if HDHP extractant was quantitatively stripped, and then reextracted in the operating conditions chosen for the process. Moreover, this study allowed us to measure the amount of DMDOHEMA which follows HDHP.

The experiment consisted in equilibrating 3 times an organic phase containing HDHP 0.1 mol/L and

DMDOHEMA 0.6 mol/L in HTP, with a citric acid aqueous solution (pH 6 fitted with TMAOH), successively. This aqueous phase was renewed after each extraction. Consequently, the organic phase contained less and less HDHP. After that, the aqueous phase from the first stripping was acidified and equilibrated with the organic phase of the third stripping, in order to recover HDHP in an organic solution.

After two extractions, HDHP concentration in the organic phase was below the detection limit of titration. Since the pH value changed after the third extraction, that meant that very few HDHP was stripped again. This was not a clue that no HDHP remained in organic solution but we could assume that more than 95% of HDHP had been stripped. This result was good enough for the process.

With this protocol, two stages were necessary to quantitatively reextract HDHP in the organic phase.

No significant amounts of DMDOHEMA were detected by titration during stripping and reextraction. The mass balance on malonamide showed that less than 1% of this extractant follows HDHP.

Other experiments with rather the same protocol and nominal citric acid concentration (0.3 M instead of 0.6 M), led to the same results. With a higher concentration of acid in the reextraction step, HDHP could be quantitatively recovered in one stage.

VI. CONCLUSION

This short paper shows that, with specific aqueous phase, an organic extractant could be separated from DMDOHEMA, which is a key step of the DIAMEX-SANEX process. Thus, each extractant could be injected selectively into the process step where this reagent plays a key role.

Among all the di-alkyl-phosphoric acids synthesized in CEA, the di-*n*-hexyl phosphoric acid (HDHP) proved to be the extractant, which followed the criteria necessary for SANEX process with extractant separation. The experiments described in this article show that HDHP is lipophilic enough to limit stripping in an aqueous phase used to recover the actinides(III) (pH 2-4). Moreover, studies have shown that HDHP / DMDOHEMA separation could be carried out thanks to an aqueous phase containing citric acid, TMAOH at pH 5-6. Extractants are separated under less basic aqueous solution than those used for solvent treatment.

Some batch experiments have validated the stripping, and then, the reextraction of HDHP in an organic phase. The extractant separation step has to be carried out in contactors dedicated to emulsive biphasic system, since settling time is rather long.

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