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The separation of extractants implemented in the DIAMEX-SANEX process

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Abstract – DIAMEX-SANEX is a process developed at the CEA to recover selectively the actinides(III) after a COEXTM or a PUREX process, in order to significantly decrease the radiotoxicity of the ultimate waste produced by the nuclear industry. This liquid-liquid extraction process is based on the DIAMEX process, using a malonamide supplemented by an acidic extractant. Besides an actinide extraction step and a lanthanide stripping step are implemented an actinide(III) stripping step and an extractant splitting step. The latter is carried out to avoid interactions between these two extractants during the first co-extraction step of the actinides and the lanthanides. This paper gives some results obtained with di-n-hexyl phosphoric acid (HDHP), which fulfils the required criteria for process development. Batch experiments or cold counter-current tests showed that it is possible to separate this extractant from DMDOHEMA. HDHP can moreover maintain the lanthanides(III) in the organic phase when the actinides(III) are back extracted from the organic phase..

INTRODUCTION

The CEA has undertaken researches on the partitioning of long-lived radionuclides present in PUREX raffinates. The more radiotoxic among them are the actinides, such as americium, curium, and neptunium. The latter can be separated by modifying the PUREX process. However, the separation of the two others requires specific processes, which can recover americium and curium from concentrated nitric media, containing many fission products, such as the lanthanides. The DIAMEX-SANEX process developed by the CEA Marcoule tackles the separation of actinides(III) from lanthanides(III) in one single partitioning cycle, directly from a PUREX raffinate, through the selective back-extraction of the actinides(III), after their co-extraction along with the lanthanides and yttrium [1], [2]. The solvent contains an acidic extractant and the malonamide developed for the DIAMEX process: N,N'-dimethyl-N,N'-dioctylhexylethoxy malonamide named DMDOHEMA [3]. The principle of the process will first be explained and the required criteria the extractant has to fulfill will then be set out in the paragraph below. The studies currently carried out at the CEA Marcoule on di-n-hexyl phosphoric acid (HDHP) to optimize the extractant separation step (especially the formulation of the aqueous

phases) will also be described. The goal is to separate the two extractants, by the selective dissolution of HDHP into an aqueous medium which is different from those implemented either in the actinide stripping step or in the solvent treatment step.

PRINCIPLE OF THE DIAMEX-SANEX PROCESS

DIAMEX-SANEX is a liquid-liquid extraction process, based on the DIAMEX process [1],[2], which recovers actinides(III) (americium and curium) in one single cycle, directly from a PUREX raffinate. After having been co-extracted with the lanthanides(III) by the DMDOHEMA (like in the DIAMEX process), the trivalent actinides are selectively stripped thanks to a polyaminocarboxylate aqueous reagent. The latter is an effective chelating agent for actinides(III) providing the pH exceeds 2. However, at this acidity, DMDOHEMA is unable to keep the trivalent lanthanides in the organic phase without salting-out agents, which would have negative effects on the management of the final waste. In order to avoid this drawback, the DIAMEX solvent is supplemented by an acidic extractant, to ensure effective extraction of the lanthanides at low acidity [3].

The scientific feasibility of this process was demonstrated in 2001 with di-(ethyl-2-hexyl)-phosphoric acid (HDEHP) [4]. However, to simplify the flowsheet and avoid the presence of the phosphorus acidic extractant at the extraction step (which induces the concomitant extraction of molybdenum, zirconium and iron), an extractant splitting step is put in the process flow-sheet, after the stripping of the lanthanides. The DIAMEX-SANEX process thus consists of (Fig. 1):

- the co-extraction of actinides(III) and lanthanides(III) by DMDOHEMA (in Hydrogenated Tetra Propylene, HTP, like in the DIAMEX process, [2]),
- the selective stripping of the actinides(III) by suitable aqueous reagents ($\text{pH} > 2$), the acidic phosphorus extractant being added at this stage to keep the trivalent lanthanides in the organic phase,
- the stripping of the lanthanides(III),
- the splitting of the two extractants, DMDOHEMA being recycled in the first "loop" of the process flow-sheet and the acidic extractant in the second one.

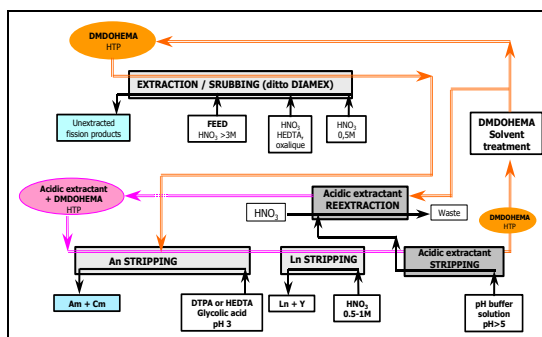


Fig. 1. DIAMEX-SANEX process general flow-sheet

CRITERIA FOR THE PHOSPHORUS ACIDIC EXTRACTANT SELECTION

The distribution ratio of the phosphorus acidic extractant should exceed 20 at the actinide stripping step, in order to minimize its losses in the aqueous phase outflow. The phosphorus acidic extractant should maintain the lanthanides in the organic phase during the actinide selective stripping ($D_{Ln} > 0.2$). Furthermore, separation factors between actinides and lanthanides should

be high to minimize the number of stages required. The phosphorus acidic extractant should not form precipitates or gels while operating the process, and should be easily stripped from an organic phase containing DMDOHEMA in a suitable aqueous solution (up to 60%-70% recovery yield in one contact). Finally, it should display good hydrolytic and radiolytic stabilities.

HDHP was chosen because it fulfills all these criteria. The partition ratios of HDHP (measured either by titration or liquid-liquid extraction methods) between a DIAMEX-like solvent and the complexing solution used for the selective stripping of actinides(III) are high, although decreasing as the pH increases. The lower the acidity of the aqueous solution, the more labile the proton of the phosphorus acid, and thus, the more polar and hydrophilic the latter is. Therefore, to avoid big losses of HDHP in the aqueous phase, it is better to keep the pH below 3.5. Lanthanides drastically decrease the partition coefficient of HDHP. This phenomenon can be explained by a greater dissolution of the Ln-HDHP^{n+} complexes in the aqueous phase. However, since the aqueous outflow of the actinide stripping step should contain only few lanthanides (majority of them remaining in the organic phase), the HDHP partition coefficient should exceed 20 in the last stage of the process.

BATCH EXPERIMENTS

As observed previously, a pH increase of the aqueous solution favors the dissolution of HDHP in the latter. However, if the solution is too basic (i.e.: pH close to that of the solvent treatment), the acidic degradation products of DMDOHEMA will follow HDHP. Moreover, the pH control is important in this step, because the dissolution of HDHP induces a decrease of the pH, which reduces the partition of HDHP from the organic to the aqueous phase.

In order to keep the pH in a suitable operating zone, it is better to use a buffering solution. This explains the choice of citric acid as the carboxylic acid: the targeted operating conditions ($4 < \text{pH} < 7$) of the extractant splitting step fits in with the three pK_A of citric acid ($\text{pK}_{A1}=6.4$, $\text{pK}_{A2}=4.8$, $\text{pK}_{A3}=3.1$ with a null ionic strength [5]). The closer to the pH the pK_A values are, the stronger the buffering effect of the aqueous solution. On the other hand, studies show

carboxylic acid destruction by hydrogen peroxide is rapid [6], but acetic acid, a stable reagent that can be produced from the degradation of citric acid, requires much more hydrogen peroxide.

Good performances (*i.e.*: more than 99.9% of HDHP stripped into the aqueous phase) were obtained with citric acid, when the pH, fitted with a suitable base, was higher than five. This pH has decreased more, for high initial HDHP concentrations, because of the increase of the amount of HDHP stripped in the aqueous phase. Moreover, for low initial citric acid concentrations, pH value decreased owing to the weaker buffering effect. HDHP stripping is nevertheless effective for pH values greater than 3.6 (the pK_A of HDHP).

Other experiments showed that some third phase formation could occur according to the concentration of citric acid. With an appropriate concentration value, no third phase was detected whatever pH and HDHP concentration in the initial organic phase. In the process, the major stripping of HDHP will occur in the first stage of the extractant separation step, where about 80-90% of HDHP will be stripped in the aqueous phase. Thus, the organic concentration of HDHP in the other stages will be smaller than 0.03M. Therefore, the aqueous phase selected for the splitting of HDHP and DMDOHEMA contains citric acid and a base, and its initial pH value has been set at more than 5. The objective is to maintain the aqueous solution at a pH below 7 in order to prevent the stripping of acidic degradation products, occurring during, for example solvent regeneration.

An experiment carried out in a specific Beaker 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 implies that specific contactors be used to carry out the extractant separation step.

COUNTER CURRENT EXPERIMENTS

The aim was to check if HDHP could be quantitatively stripped, and then extracted again in centrifugal contactors. Since the settling time of the biphasic system is very slow during

HDHP stripping step, specific centrifugal contactors are required. Only four of them were sufficient to withdraw more than 99% of the injected HDHP in the first stage. Potentiometric measurements showed that less than 1% of the initial DMDOHEMA followed HDHP during its stripping. The aqueous outflow of this step was acidified in order to form a second light phase which went out the centrifugal contactor without any organic phase injected. After this stage, remaining traces of HDHP were re-extracted thanks to a part of the organic flow coming from the extractant splitting step. From this experiment, more than 95% of HDHP initially in the solvent were stripped after 2 extractions, and more than 90% of HDHP dissolved in the aqueous phase were recovered in the organic phase with only one extraction stage. Less than 1% of DMDOHEMA followed HDHP during its stripping.

CONCLUSION

This paper shows that, with specific aqueous phases, a phosphorus acidic extractant can be separated from DMDOHEMA, which simplifies the DIAMEX-SANEX process. Among all the di-alkyl-phosphoric acids synthesized at the CEA Marcoule, the di-*n*-hexyl phosphoric acid (HDHP) proved to be the extractant which follows the requirements for process implementation: HDHP is lipophilic enough to limit its losses in the aqueous phase used to selectively recover the actinides(III) (pH 2-4). HDHP / DMDOHEMA separation can be carried out thanks to an aqueous phase containing citric acid at pH 5-6. Extractants are separated under less basic aqueous conditions than those used for the DMDOHEMA treatment.

Some batch experiments and a counter current trial have validated the stripping, and then, the reextraction of HDHP in the 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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