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Actinide Partitioning by HDEHP Solvent Extraction. A Verification of the Process Scheme by Countercurrent Experiments in Hot Cells

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Introduction

Three HAW partitioning processes have been investigated on a laboratory scale at the JRC-Ispra Establishment (CEC) [1–7]. Their purpose was to demonstrate the chemical feasibility of actinide separation from HAW in order to reduce the potential long-term hazard of vitrified HAW. To verify on a larger fully-active scale the flow-sheets of two of these processes based on liquid-liquid extraction, a fruitful collaboration was established between the JRC (Ispra Establishment) and the CEA (CEN-Fontenay aux Roses, France). In this frame and on the basis of indications resulting from the previous laboratory investigations at the JRC, continuous countercurrent experiments with mixer-settler (M-S) batteries were performed in the hot cells of CENFAR laboratories.

The present paper deals with the verification of option 1 of the HDEHP process flow sheet and illustrates related experimental results. The objectives to be attained by such an experiment were the following:

to verify on a larger hot scale the overall feasibility of the actinide separation from HAW;

to test HAW denitration under well-controlled process conditions (formic acid reactivity) and to verify actinide behaviour during denitration;

to verify the hydraulic behaviour during continuous countercurrent extraction and back-extraction cycle with M-S batteries;

to check extraction and back-extraction yields of actinides attainable by M-S experiments.

Experimental

The process step sequence applied for the verification of the HDEHP 1 process is illustrated in Fig. 1 and includes the following steps:

1) Denitration of the HAW raffinate by HCOOH up to a final pH of about 2, with the HAW raffinate added to the boiling HCOOH.

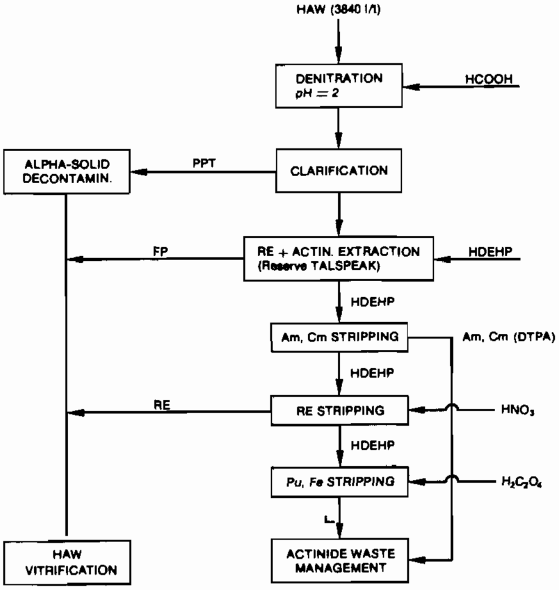

Fig. 1. General scheme of the *HDEHP* 1 process for actinide separation from HAW.

2) Filtration, washing by HCOOH and digestion of denitration precipitates (the latter step only for analytical purposes).

3) Countercurrent extraction of actinides (U, Pu, Np, Am, Cm) and RE by a 0.3 *M* HDEHP-0.2 TBP solution in n-dodecane (named "HDEHP solvent") using a M-S battery.

A fully active HAW raffinate (42 litres, 3840 l/t) was prepared at the CENFAR hot laboratories by dissolving about 11 kg of irradiated uranium (32544 MWd/t U, about 5.5 years cooling) and then by separating U and Pu by a TBP Purex-type extraction cycle. The fully active HAW was denitrated in the cell of the "Petrus" shielded enclosure according to the following operational procedure:

i) introduction in the reaction vessel (dissolver) of the 26.6 formic acid (14 litres) and heating to 80 °C;

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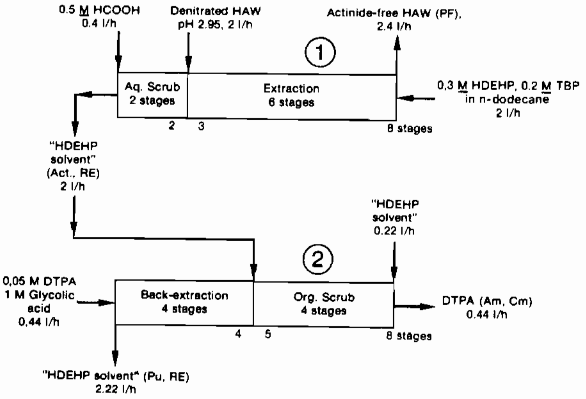
ii) addition (41/h) of the HAW raffinate (42 litres, 4.35 *M* HNO_3) with a gradual heating increase so as to attain the boiling point of the mixture;

iii) after the HAW addition was completed, boiling under reflux of the solution so as to reach a pH of about 2.

The denitration was carried out be operating under a relative over pressure of 100 mm H_2O and with a $HCOOH/HNO_3$ molar ratio of 2.2. After cooling, the denitrated HAW solution was filtered on two "millipore" filters (5 and 0.5 microns); a black solid residue of about 100 ml was separated on each filter. The filtered solution (brown) did not show any precipitate after one month storage. The solid residue was treated under boiling reflux twice with about 4.5 litres of 0.5 *M* HCOOH and then the resulting solutions after sampling for analysis were joined to the denitrated HAW in order to remove Pu. In order to determine the actinide fraction still present after the formic acid washes, the solid residue was then digested with 2 litres of a 8 *M* HNO_3, 0.1 HF solution. After 8 hours of treatment under boiling reflux, the solution was filtered.

Two M-S batteries with 8 stages per unit were used for countercurrent experiments. Six extractions and two aqueous scrub stages followed by four back-extractions and four organic scrub stages were utilized, respectively for actinide + RE extraction and Am, Cm back-extraction cycles according to the following scheme:



Scheme 1.

4) Countercurrent back-extraction of Am and Cm from loaded solvent by a 1 *M* glycolic acid-0.05 *M* DTPA solution at pH 3, again by a M-S battery.

5) Batchwise back-extraction of RE by 5 *M* HNO_3 and Pu (Np, U) by a 1 *M* glycolic acid-0.05 *M* DTPA solution from loaded solvent.

6) Exhausted solvent treatments (alkaline clean up, acidic reconversion and make up of extractant if necessary) in view of its recycle. Experiments on a test tube level were performed for all the above operations and for the subsequent verification of the extraction capacity of the regenerated solvent.

Sequential batch treatments were performed on the actinide-free 'HDEHP solvent', resulting from the foregoing countercurrent extraction and back-extraction cycles with the aim of removing RE, Pu, U and radiolytic degradation products. 5 *M* HNO_3 and a 0.8 *M* $H_2C_2O_4$ solution were used for back-extracting RE and Pu (at 50 °C), respectively.

An alkaline solution, 4 *M* NaOH and 0.5 *M* Na_2CO_3 and 1 *M* nitric acid were used for the clean-up and acid reconversion of the exhausted 'HDEHP solvent'.

Results

An average reaction stoichiometry of 1.65 (moles of HCCOH consumed per mole of HNO_3) was calculated by the acidity balance which was well consistent with results obtained at Ispra [7]. After denitration it was difficult to establish a very close Pu mass balance, due to the very slight contribution (<0.2%) of Pu-239 and Pu-240 to total alpha-emissions.

As it can be calculated from data reported in Table I, the actinide sorbed on the denitration precipitate was about 6.6%, 0.5% and 0.45% of Pu, Am and Cm amounts inititally present in the HAW.

By two HCOOH washes (see Table I) about 5% of the residual Pu and 0.4% and 0.35% of Am and Cm initially present in the HAW (*i.e.* about 75%, 85% and 77% of Pu, Am and Cm sorbed on the denitration precipitate) was removed from the precipitate. After these washings the residual Pu and Am still present in the precipitate represented about 1.6% of the Pu and 0.1% of the Am, Cm amounts initially present

TABLE I. % Distribution of Actinides in Various Streams Generated by Denitration and Washing of Denitration Precipitates.

Stream	Volume (litres)	Pu 239–40	Am 241–43	Cm 242–44
Acidic HAW, 4.35 *M* HNO_3	42	100	100	100
Denitrated HAW, 1 *M* HCOOH, pH 2.2	48	~93.4	>99	>99
1st PPT wash, 0.5 *M* HCOOH	4.2	~4.1	~0.33	~0.3
2nd PPT wash, 0.5 *M* HCOOH	4.2	~0.8	~0.05	~0.05
3rd PPT wash, 8 *M* HNO_3, 0.1 *M* HF	2.0	~1.6	~0.11	~0.09
PPT (after HNO_3–HF wash)		<0.2	<0.2	<0.2

in the HAW solution (*i.e.* 0.68% and 100% of Pu and Am present in the spent fuel). The above results concerning Pu are in good agreement with results previously obtained at Ispra laboratories [7]; the retention of Am appears on the contrary to be lower. The digestion of the denitration precipitate with nitric-hydrofluoric acid allowed to further reduce Pu and Am, Cm losses to less than 0.2% of their amounts initially present in the HAW solution. The main constituents of the denitration precipitate determined by emission spectroscopy were Pd, Ru, Rh, Zr, Sn, Fe, Al, Si and Mo (probably as phosphomolybdate). Antimony was detected by gamma-spectrometry in the nitric-hydrofluoric acid solution.

The results attained by continuous countercurrent extraction and back-extraction operations are shown in Table II, and can be summarized as follows:

- More than 99.4% of Pu, Am and Cm ($DF\alpha$ tot $> 10^2$) initially present in the input HAW was separated by a countercurrent M-S extraction cycle using HDEHP. This was the result achieved at the end of the extraction cycle and was based on actinide measurements (total alpha-counting) on the solvent and HAW effluents cumulated at the outputs of the battery. A still higher overall actinide extraction yield (>99.9%, hence $DF\alpha$ tot $>10^3$) was measured by total alpha-counting when, for control purposes, millilitre aliquots of solvent and HAW effluents were sampled from the respective output settlers, during the running of the battery at equilibrium.
- Back-extraction yields of about 99.75% were attained for Am and Cm with a concentration factor of 4.5.
- The separated trivalent actinides contained less than 1% of the RE amount initially present in the HAW. Separation factors of 150 and more than 1000 were attained for Eu and Ce respectively.
- No detectable Pu was present in the glycolic acid solution used for stripping trivalent actinides.
- The hydraulic behaviours of countercurrent extraction and back-extraction cycles were satisfactory, the formation of reduced volumes of interphacial cruds having produced a negligible effect on them.

The results obtained from batch operations such as back-extraction of RE, Pu and solvent regeneration can be summarized as follows:

- Rare earths FP such as Ce-144 and Eu-154 were completely back-extracted ($D_A{}^0 < 10^{-3}$) from the loaded solvent.
- Pu stripping from loaded solvent was operated on the basis of an experimental $D_A{}^0$ value of about 1.4×10^{-2}.
- A $D_A{}^0$ value of 70 was measured for Am, Cm when the regenerated solvent was reused. This value is very near to that attained using fresh solvent.

Conclusions

The verification experiment on a larger fully active scale has proven the feasibility of the HDEHP 1 process scheme. Its performances in terms of overall actinide removal by countercurrent operations with M-S batteries and their hydraulic behaviours were satisfactory. A DF of more than 10^2 has conservatively been indicated but the possibility of attaining DF of more than 10^3 was demonstrated.

The HAW denitration is indeed the most critical process step. However, the final actinide losses to the denitration precipitate appears to be even on larger process scale still acceptable. This is mainly due to the formic acid washes which allowed us to reduce these losses.

It was confirmed that a slight overpressure ensuring the presence in solution of reaction catalyzers is an essential requirement in order to attain an effective HAW denitration.

The obtained results also indicated those steps of the process scheme where further investigations are needed, namely:

- the back-extraction of trivalent actinides to minimize the presence of Sr;
- the back-extraction of Pu(Np) to find less critical operating conditions;
- the alkaline clean-up of solvent to minimize the volumes of salt waste.

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TABLE II. % Distribution of Actinides in Various Streams of the HDEHP 1 Process.

Stream	Pu	Am, Cm	Eu	Ce
Denitration precipitate	1.6–1.7	0.1–0.2	~0.1	~0.1
Am, Cm back-extraction		>98.95	~0.6	
Am, Cm free-solvent	>97.7	<0.25	>98.7	>99.3
Partitioned HAW	<0.6	<0.6	<0.6	<0.6
HAW dec. factor	$>10^2$	$>10^2$		
RE/actinide separation factor			150	10^3

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