SEPARATION OF MINOR ACTINIDES FROM GENUINE HLLW USING THE DIAMEX PROCESS

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Abstract

In the present work a counter-current extraction experiment, MA separation from real high-level PUREX raffinate, is reported. HLLW feed, obtained from small scale PUREX reprocessing of commercial LWR fuel (45.2 GWd/tM) in a centrifugal extractor battery, was used without further treatment for the DIAMEX process which was carried out in the same 16-stage centrifugal extractor set-up.

With up to six extraction stages, feed decontamination factors above 400 for lanthanides and above 1 000 for minor actinides were reached. Co-extraction of Mo and Zr was efficiently prevented using oxalic scrubbing. The back-extraction proved to be very efficient, yielding in four stages more than 99.9% recovery of MA and lanthanides. Co-extracted Tc, Ru and Pd were less efficiently stripped

Introduction

The potential harmfulness of the wastes generated by reprocessing are primarily due to the presence of minor actinides, MA, and they are of special concern regarding separation and transmutation.

Two step processes are at present considered necessary combining i) a separation of lanthanides and actinides from high acidity HLLW, ii) a separation of actinides from lanthanides at lower acidity. Several extraction processes have been investigated for use in the first step, the best known being the TRUEX process based on CMPO, n-octyl(phenyl) N,N diisobutyl carbamoylmethylphosphine oxide [1]. The TRPO process developed in China utilises a trialkyl (C6-C8) phosphine oxide extractant [2]. DIDPA, diisodecyl phosphoric acid, extracts actinides from feed solutions from 0.5 M nitric acid and offers thereby also the potential to be used in a one-stage process [3,4]. Of these three the TRPO process is the best compromise between extraction and back-extraction and CMPO is the only one capable to extract from a high acidity feed. However, due to a strong complexation, the CMPO shows accumulation in the back-extraction section of a continuous multistage process [5].

The French DIAMEX process uses at present dimethyl-dibutyl-tetradecyl malonamide, (DMBDTDMA) as reference molecule [6] in a completely combustible solvent (CHON principle). Similar to CMPO, actinides and lanthanides are extracted from a high acidity PUREX raffinate (3-4 M HNO_3). Batch experiments have indicated [5] that also the back-extraction is very efficient, similar to TRPO.

In the present work, the DIAMEX process has been tested in continuous counter-current extraction experiments, using a centrifugal extractor battery installed in a hot cell. The feed was a genuine HLLW obtained from small scale PUREX reprocessing of commercial LWR fuel (45.2 GWd/tM).

The high radiation dose delivered, especially from alpha decay, as well as the complex chemical composition with respect to the speciation of a large number of elements, necessitates the verification of the process using a genuine HLLW solution.

Experimental

Fuel

The characteristics of the fuel are given in Table 1.

Table 1. **Characteristics of the reprocessed fuel**

Pellet characteristics

Density:	94.3-95.0 %TD
Grain size:	6.5-7.0 μm
^{235}U enrichment:	3.2 %
Diameter:	9.11 mm
He fill gas pressure:	2.21 MPa
Cladding material:	Zry 4

Average burn-up:	45.2 GW/tM
Average cycle power	
Cycle 1:	35.8 kW/m
Cycle 2	28.8 kW/m
Cycle 3	23.9 kW/m

Chemicals

All reagents and chemicals were of analytical grade. Tributylphosphate >99%, TBP, used without further treatment, and dodecane >99% were obtained from MERCK (Germany). The nitric acid solutions were prepared either from dilution of concentrated nitric acid or from Titrisol ampoules. MQ grade water (18 MΩ/cm) was used for all dilutions.

The diamide, DMDBTDMA, of ca. 98% purity and TPH were obtained from PANCHIM (France). It was diluted with pentane and purified in an Alumina-B (ICN Biomedicals, grade super I) filled column. The pentane was removed by vacuum evaporation and the pure DMDBTDMA (2.1 M) was diluted into TPH (hydrogenated tetrapropene) to an approximate concentration of 0.5 M. The exact concentration was determined by titration using perchloric acid in acetic anhydride media.

Equipment and Procedures

The centrifugal extractor equipment installed in the hot cells is described elsewhere [2]. For the present study, it was extended from 12 to 16 stages, divided into four batteries with four extractors each. Two different sampling techniques were used. When the system had reached steady-state conditions (ca. 1.5 h), samples were taken on-line from each stage. At the end of the experiment, usually three hours after introducing the feed, the centrifuges and pumps were switched off simultaneously and samples were taken from the mixing chambers (wells). In addition, the feed and all collected fractions were sampled.

All concentrations in the aqueous samples were determined by a quadrupole ICP-MS (Perkin-Elmer, ELAN250). Samples taken from the organic phase were back-extracted twice with 0.1 M HNO_3 prior to the analysis. The acidity profile was determined for the aqueous phase by titration.

PUREX process

The PUREX process flow-sheet is shown in Figure 1. The feed for the PUREX process was produced by dissolving 60 g of fuel (see Table 1) in 300 mL 4 M HNO_3.

Figure 1. **Flow-sheet for the PUREX process**
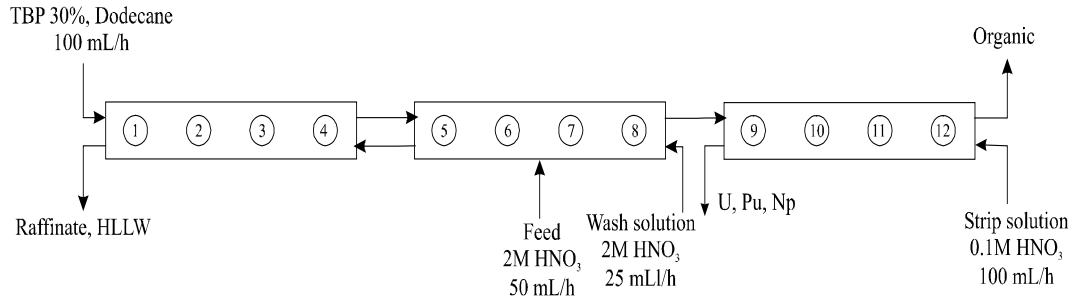
In total, 11 on-line samples were taken from the aqueous phase together with samples from the collected aqueous and organic effluents.

The decontamination factor of this process is defined by the equation (1):

$$DF = \frac{[M]_{Feed}}{[M]_{Raffinate}} \Theta \quad (1)$$

Θ is flow rate ratio between the raffinate and the feed.

DIAMEX process

The feed for the DIAMEX process is the HLLW fraction collected from the PUREX process. Before use the acidity was adjusted to 3.5 and 0.3 M in nitric acid and oxalic acid, respectively, avoiding significant dilution. Oxalic acid was added to prevent the extraction of Zr and Mo.

For the DIAMEX process the flow-sheet was optimised on the basis of data obtained from a cold test with a simulated lanthanide solution. The flow ratio in the extraction and in the back-extraction (with 0.1 M HNO_3) were 1.8 and 2.1 respectively. Figure 2 shows the profiles from this experiment in comparison to those calculated by means of the PAREX code [7].

Figure 2. **Experimental and calculated (PAREX code) results from the cold test**
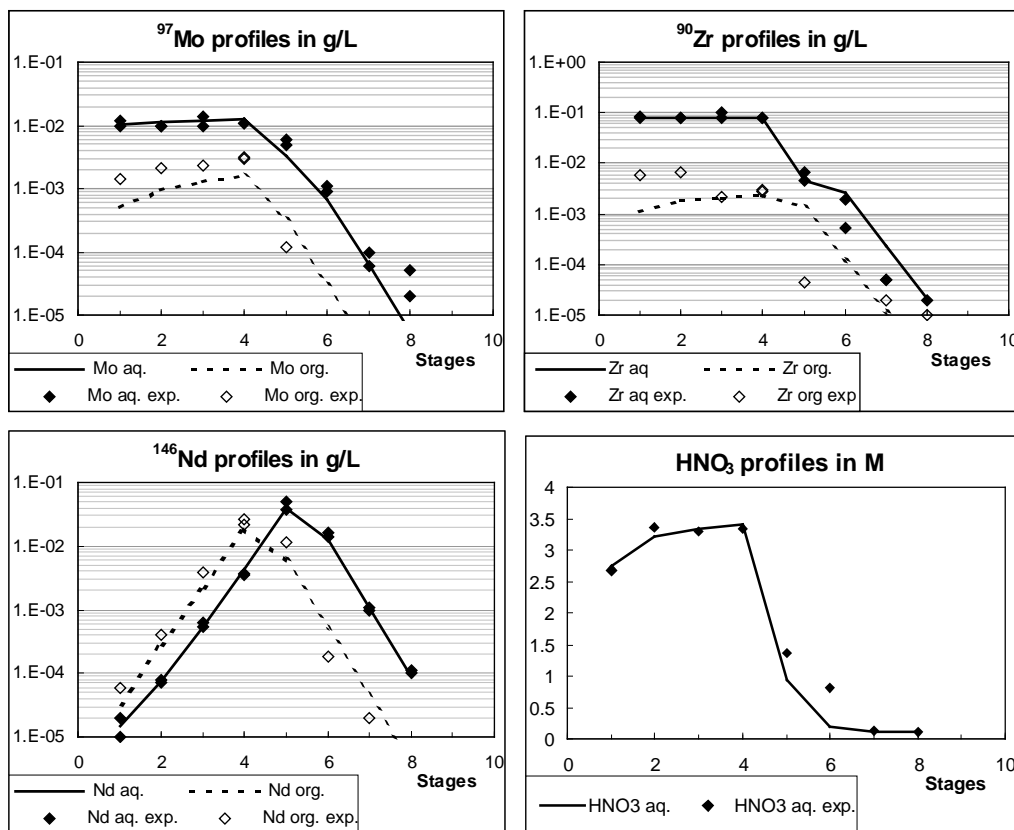
It can be seen that the experimental concentration profiles are fairly well simulated. On the basis of this result, an optimised flow-sheet for a 16 stage counter-current process was designed (Figure 3).

Figure 3. **Flow sheet used in the DIAMEX hot-test**
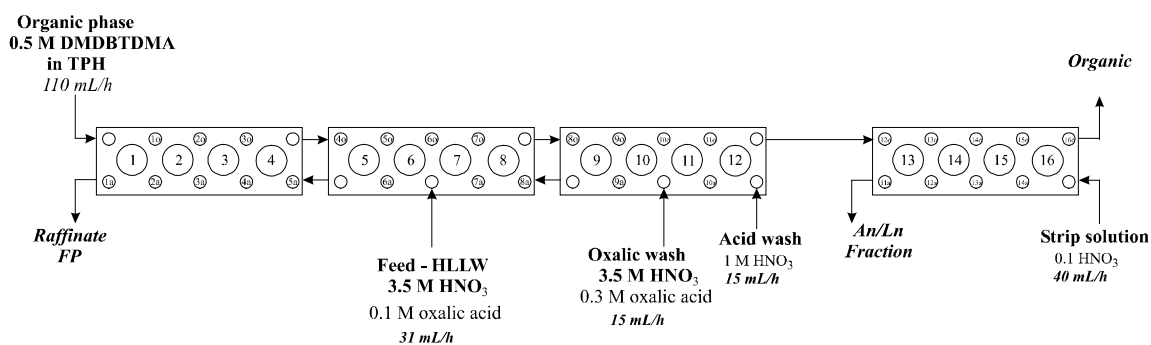
The decontamination factor for this process is defined in the equation (1).

Titration and ICP-MS analyses of the aqueous well samples were performed. All out-going fractions were analysed including the solvent. On-line samples from stages 4a, 6a, 8a and 12o (a=aqueous, o=organic) were taken for comparison to the well samples. A good agreement was found in most cases, indicating that well samples taken after the experiment were also in extraction equilibrium conditions.

Results and discussion

PUREX

U and Pu were efficiently extracted in six stages, with decontamination factors (see eq. 1) of 10 [5] and 10 [3], respectively. Np was also extracted to about 70%. Of the fission products, only Tc was to some extent co-extracted. The composition of the feed and raffinate solutions for the PUREX process are tabulated in Table 2. It should be pointed out that the HLLW is diluted by a factor 2/3 versus the feed.

Table 2. **Concentrations (μg/g) in the PUREX experiment**

Isotope	Feed	HLLW	Isotope	Feed	HLLW
^{85}Rb	33	30	^{139}La	210	169
^{87}Rb	60	58	^{140}Ce	215	169
^{88}Sr	89	92	^{141}Pr	243	188
^{89}Y	111	101	^{143}Nd	126	97
^{91}Zr	128	112	^{144}Nd	256	193
^{92}Zr	136	117	^{145}Nd	118	90
^{93}Zr	146	126	^{146}Nd	130	99
^{94}Zr	154	134	^{151}Sm	2	1
^{95}Mo	102	96	^{152}Sm	19	14
^{97}Mo	104	94	^{153}Eu	22	16
^{98}Mo	108	99	^{156}Gd	23	17
^{99}Tc	101	57	^{158}Gd	5	4
^{101}Ru	52	47	^{234}U	26	0
^{102}Ru	55	49	^{235}U	704	0
^{103}Rh	32	29	^{236}U	631	0
^{105}Pd	44	38	^{237}Np	222	62
^{106}Pd	42	36	^{238}U	130-543	2
^{107}Pd	24	21	^{238}Pu	38	0
^{108}Pd	16	14	^{239}Pu	673	1
^{111}Cd	2	2	^{240}Pu	364	1
^{112}Cd	2	1	^{241}Am	94	91
^{114}Cd	1	1	^{242}Pu	116	0
^{130}Te	10	8	^{243}Am	24	21
^{133}Cs	168	135	^{244}Cm	6	5
^{135}Cs	45	35			
^{138}Ba	229	179	Acidity (M)	1.98	1.94

DIAMEX

Figure 4 shows the aqueous concentration profiles (in µg nuclide per g of solution) obtained for the minor actinides, and for some lanthanides. All minor actinides (Am, Cm and also Np) are efficiently extracted, similar to the lanthanides. The back-extraction of actinides and lanthanides is even more efficient, except for Np. The profiles for the lanthanides indicate a decreasing extraction with the element number.

In Figure 5 the profiles for some relevant fission products are shown. The oxalic scrubbing efficiently reduces co-extraction of Zr and Mo. The reduced acidity in the two acid wash stages has also a good scrubbing effect on these elements. In the scrubbing section the aqueous concentration of Zr and Mo decreases by several orders of magnitude with an almost complete wash-out.

Tc and Pd, and also to some extent Ru, are co-extracted and scrubbing is not efficient in this case. In the back-extraction section the Pd and Ru profiles indicate a slow back-extraction, and the efficiency could probably be increased using more stages. The Tc profile in the back-extraction section indicates an accumulation in the organic phase.

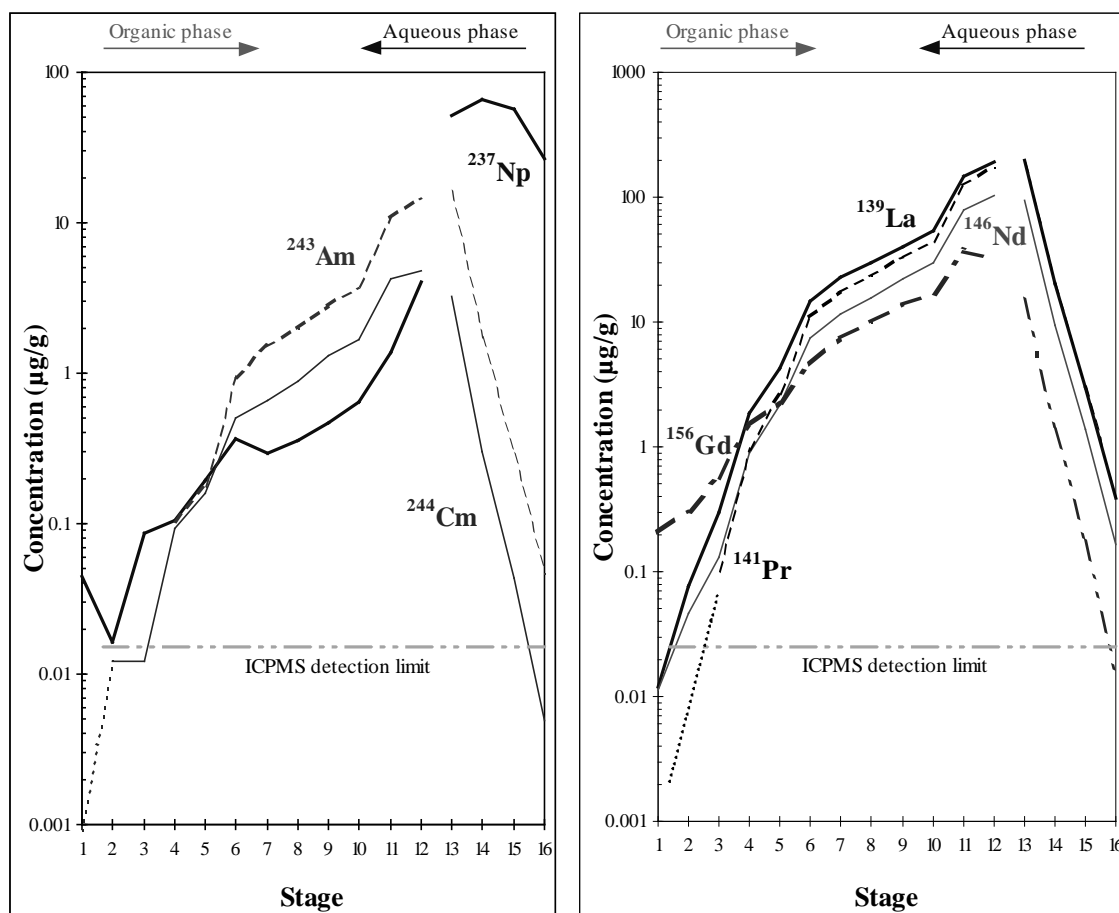Figure 4. **Actinide and lanthanide concentration profiles in the DIAMEX process**

Figure 5. **Concentration profiles for the light fission products in the DIAMEX process**
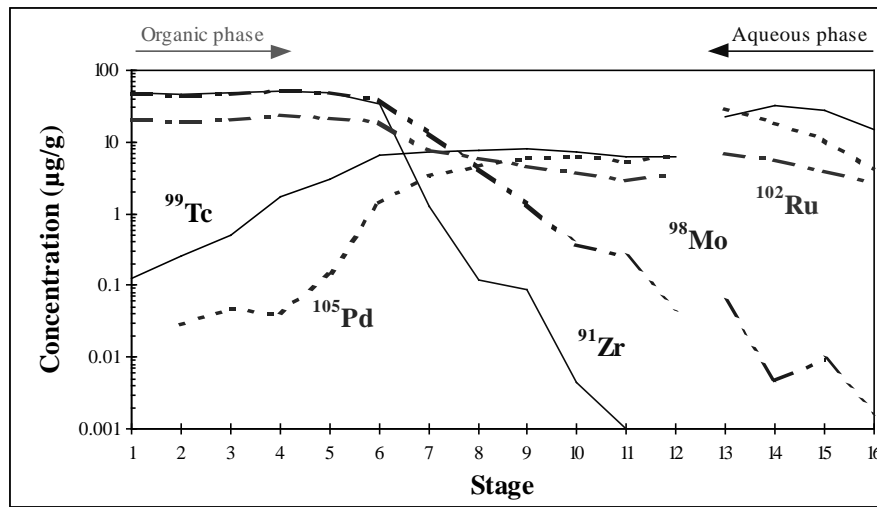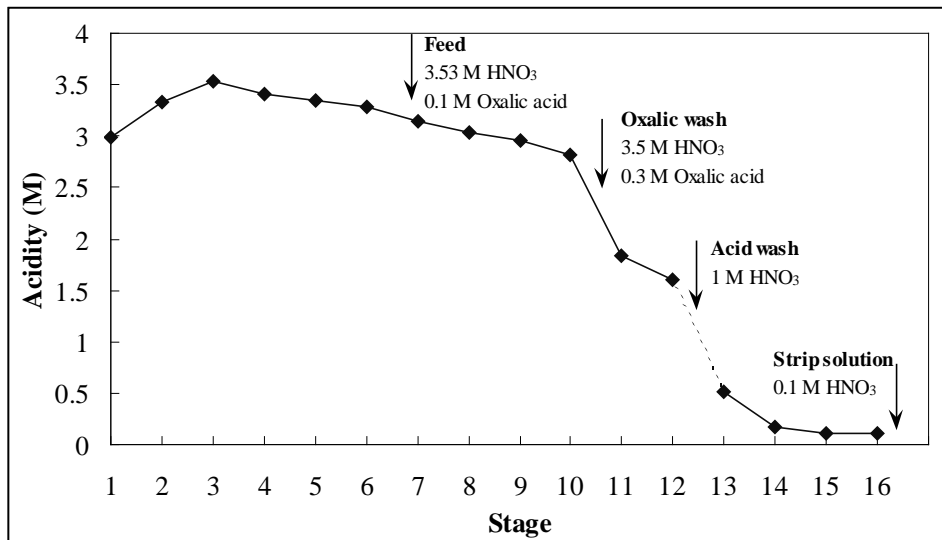

Figure 6 shows the acidity profile in the aqueous phase of the extractor battery. A slight co-extraction of HNO_3 is observed in the extraction and scrubbing section with a minimum at stage 3.

Figure 6. **Nitric acid concentration profile in the DIAMEX test**

The acidity in the lanthanide/actinide fraction is 0.5 M HNO_3. This is an acidity that allows a subsequent lanthanide-actinide separation process without or little adjustment of the feed. Table 3 shows the decontamination factors of the feed for the major isotopes analysed, calculated with eq. 1.

Table 3. **Decontamination factors (DF) achieved in the DIAMEX process (Feed/Raffinate)**

Isotope	DF	Isotope	DF
^{91}Zr	3.7	^{146}Nd	609
^{98}Mo	3.8	^{152}Sm	426
^{99}Tc	462	^{153}Eu	438
^{101}Ru	4.9	^{156}Gd	189
^{105}Pd	610	^{237}Np	1020
^{139}La	650	^{243}Am	1000
^{140}Ce	815	^{244}Cm	1167
^{141}Pr	835		

MA elements show higher DF values compared to lanthanides. In the lanthanide series DF values vary with the element number with a maximum for Ce and Pr, see also Figure 4. This result can be explained by a different stability of the extracted complexes. From the analyses of aqueous and organic effluents, a recovery of more than 99.9% of Am and Cm in the process was calculated.

Table 4 shows the decontamination factors of the "loaded" organic phase. The DF's of the lanthanides and Am are more than 22 000 which indicate a high back-extraction yield to the aqueous phase of these elements. This is also the case for Cm but for the extracted FP's and Np, the DF's are less than 100.

Table 4. **Decontamination factor of the organic phase (loaded solvent/stripped solvent)**

Isotope	DF	Isotope	DF
^{99}Tc	30	^{146}Nd	> 50 000
^{101}Ru	61	^{153}Eu	> 300 000
^{105}Pd	96	^{156}Gd	> 300 000
^{139}La	> 46 000	^{237}Np	29
^{140}Ce	> 22 500	^{243}Am	> 25 100
^{141}Pr	> 44 000	^{244}Cm	

Conclusions

A 16 stage extraction process using a centrifugal extractor battery allows to efficiently separate MA from genuine HLLW, obtained from PUREX reprocessing of commercial LWR fuel. The process represents an excellent compromise between reasonably good extraction and even better back-extraction properties. Thus, recovery better than 99.9% for Am and Cm was achieved, i.e. the losses of these elements in the process are very low. The experiments confirm the previous results obtained in a mixer settler experiment [6]. Oxalic scrubbing showed to be very efficient in preventing co-extraction of Mo and Zr. For Tc, Ru and also Pd which are slightly co-extracted, a process optimisation is needed. The actinide/lanthanide fraction is collected with an acidity of 0.5 M HNO_3 and can thus be introduced in a subsequent actinide-lanthanide separation process, without or little feed adjustment.

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