

## A Hot Test for Separating Americium from Fission Product Lanthanides by Purified Cyanex 301 Extraction in Centrifugal Contactors

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**ABSTRACT:** The purified Cyanex 301 has been proven to be able to separate Am from both tracer amount and macro amount of lanthanides in our previous work. In the present work, a countercurrent hot test of the separation of americium from fission product lanthanides (FPLns) by purified Cyanex 301 was carried out in miniature centrifugal contactors. The feed solution is an Am/Ln fraction originated from a HLW hot partitioning process. With 4 extraction stages and 3 scrubbing stages, 99.93% Am was extracted and the co-extracted FPLns was about 1%.

**Key Words:** americium, fission product lanthanides, Cyanex 301, separation

### I. Introduction

In the separation process of high level radioactive waste (HLW) treatment, fission product lanthanides (FPLns) always enter the Am fraction. For example, Am and FPLns are stripped together by 5.5M HNO<sub>3</sub> in the TRPO process<sup>1,2)</sup>. However, in the transmutation of Am, some lanthanides will become the neutron poison due to their high neutron-absorption cross-sections. The further separation of Am from FPLns becomes a key problem in the "partitioning-transmutation" nuclear fuel cycle.

In recent years, extractants containing soft donor S or N have been found to have a high selectivity for trivalent actinides<sup>3-8)</sup>. Among them, a commercial reagent named Cyanex 301, which contains ~80% bis(2,4,4-trimethylpentyl)dithiophosphinic acid (HBTMPDTP), has been proved able to separate Am from lanthanides effectively. While saponified to a proper extent, Cyanex 301 can separate Am from macro amount of lanthanides with a separation factor of ~500<sup>9)</sup>. The purified Cyanex 301, i.e. HBTMPDTP, can effectively separate Am from both tracer amount and macro amount of lanthanides<sup>7,9)</sup>. A satisfactory separation of Am from FPLns has been achieved in the cross-flow hot test<sup>10)</sup>. In the present work, a countercurrent hot test for separating Am from FPLns by HBTMPDTP extraction has been carried out in the centrifugal contactors.

### II. Experimental

#### 1. Reagents and analytical methods

Cyanex 301 containing ~80% bis(2,4,4-trimethylpentyl)dithiophosphinic acid (HBTMPDTP) was kindly supplied by Cytec Inc., Canada and was purified as described in reference [7]. 240<sup>#</sup> hydrogenated kerosene, obtained from Jinzhou petroleum refinery, China, was

redistilled and the fraction between 180°C and 220°C was used as the solvent. The feed was 5.5M HNO<sub>3</sub>-stripping fraction from TRPO process, which treated the Chinese high level waste. It contains ~4.7M HNO<sub>3</sub>, FPLns, micro amount of Cm and Tc, small amount of Am, Fe and Mo, Ru, Pd and so on. All the other reagents used were of analytical grade.

<sup>241</sup>Am was measured by Au-Si surface barrier  $\alpha$ -detector at 5.5MeV( $\alpha$ ). <sup>154</sup>Eu were measured by coaxial Ge(Li)  $\gamma$ -detector at 1276 keV( $\gamma$ ). Macro amount of lanthanides was determined by EDTA complexometric titration in aqueous phase. Lanthanides in organic phase were stripped into 0.5M HNO<sub>3</sub> before measurement. The pH value of aqueous phases was measured by PHS-B pH meter.

#### 2. Procedures

The feed solution was evaporated to remove nitric acid at 80°C. The residue was dissolved with 0.5M NaNO<sub>3</sub> solution (pH=1). Three times extraction of 0.5M HBTMPDTP-kerosene removed Fe(III), Mo(VI), Pd(II) and some Ru(II). Then, its pH was adjusted to 3.5 with 1M NaOH.

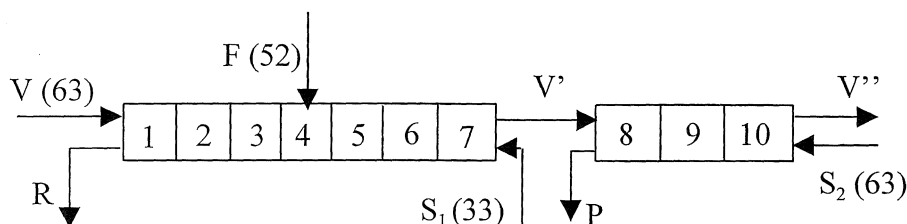
Figure 1 gives the schematic flowsheet. The flowsheet consists of 4-stage extraction, 3-stage scrubbing and 3-stage stripping. The miniature centrifugal contactors with 10mm rotor, which were used in the hot test for high level waste partitioning in 1996, were installed in the glove-box. The holdup in each stage was about 5ml. The feed, scrubbing solution, stripping solution were pumped into the centrifugal contactors by peristaltic pumps. The solvent was pumped by a gearwheel pump.

The outlet samples were collected after two-hour operation. The aqueous and organic phases of each stage were sampled after stopping the contactors. The experiment was carried out at ambient temperature.

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**Figure 1** Schematic flowsheet of Am separation from FPLNs by HBTMPDTP extraction

Where, the numbers in ( ) are the flow rates in ml/h.

F: hot feed,  $9.2 \times 10^4$  Bq/ml  $^{241}\text{Am} + 0.0116\text{M FPLNs} + 0.5\text{M NaNO}_3$ , pH=3.5

P: Am product

R: aqueous raffinate

S<sub>1</sub>: scrubbing solution, 0.5M NaNO<sub>3</sub>, pH=3.6

S<sub>2</sub>: stripping solution, 0.5M HNO<sub>3</sub>

V: 0.5M HBTMPDTP-kerosene with a saponification of 0.8mol%

V': loaded organic phase

V'': spent organic phase

### III. Results and Discussion

Table 1 lists the Am concentration in the loaded solvent (V') at different time. The results indicate that the extraction experiment reached the stationary state after 100 minutes.

**Table 1** The evolution of Am concentration in loaded solvent

*t (min)	**[Am] (Bq/ml)
60	$5.90 \times 10^4$
80	$6.19 \times 10^4$
100	$7.13 \times 10^4$
120	$7.13 \times 10^4$

\*t: experimental time;

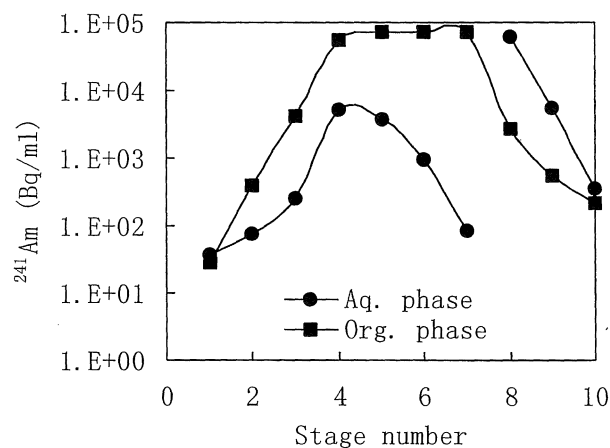
\*\*[Am]: Am concentration in loaded solvent)

Figure 2, Figure 3 give the concentration profiles of  $^{241}\text{Am}$  and  $^{154}\text{Eu}$ . The extraction of  $^{241}\text{Am}$  is 99.93%. The extraction behaviors of FPLNs is presumedly considered the same as  $^{154}\text{Eu}$ , so the estimated extraction of FPLNs is 1.01%. The separation of Am from FPLNs is more than 1000 and the separation of FPLNs from Am is about 100. In this work, the material balance (defined as  $100 \times \text{total outlet content} / \text{total inlet content}$ ) was found to be 93.8% for  $^{241}\text{Am}$  and 99.9% for  $^{154}\text{Eu}$ .

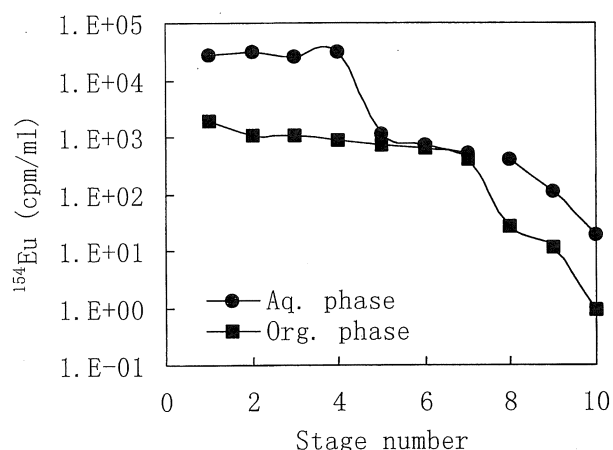
Boussier et al<sup>[11]</sup> indicates that the Am transmutation requires a minimum mass ratio of Am to FPLNs near to 1:1. Therefore, the co-extracted FPLNs is required <1.4% for the typical feed originated from the commercial reprocessing. However, the mass ratio of Am to FPLNs in the present feed

is fairly low. Although the extraction percentage of FPLNs is <1.4%, the mass ratio of Am to FPLNs in the product P is 1:27 which can not meet the above transmutation requirement. A higher separation of FPLNs from Am is needed.

The  $\alpha$  radioactivity in the aqueous raffinate R is <60 Bq/mL. It means that the  $\alpha$  radioactivity in FPLNs nitrate and NaNO<sub>3</sub> is  $<1.1 \times 10^6$  Bq/kg which is less than the non- $\alpha$  requirement of  $3.7 \times 10^6$  Bq/kg.



**Figure 2**  $^{241}\text{Am}$  concentration in each centrifugal contactor



**Figure 3**  $^{154}\text{Eu}$  concentration in each centrifugal contactor

Table 2 lists the pH values and the distribution ratios in the extraction section. The experimental distribution ratios of Am, especially in Stage 1 and Stage 2, are less than the calculated values according to reference [12]. However, the distribution ratios of Eu are consistent with the calculated values. This results in a lower separation factor of Am over Eu ( $\text{SF}_{\text{Am/Eu}}$ ) compared with the results in references [7,9]. The difference is probably attributed to two main reasons. The first is that a low mass-transfer efficiency occurred in the present system probably due to the short residence time. The second is that the empirical equations in reference [12] are probably not suitable for such low Am concentration in Stage 1.

**Table 2** Results of hot test

Stage No.	1	2	3	4
pH	3.95	3.86	3.74	3.68
$D_{\text{Am}}$	0.75	5.24	15.6	11.0
$D_{\text{Eu}}$	0.070	0.033	0.040	0.028
$\text{SF}_{\text{Am/Eu}}$	10.7	159	390	393

#### IV. Conclusions

The results of hot test show that Am and FPLns have been well separated from each other by HBTMPDTP extraction. Although the separation of FPLns from Am can not meet the transmutation requirement because Am concentration is too low, better results can be achieved by optimizing the process parameters including stage number and the pH of scrubbing solution. Anyway, the present work demonstrates further that HBTMPDTP is promising in the separation of Am/FPLns.

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