# DYNAMIC TEST OF EXTRACTION PROCESS FOR AMERICIUM PARTITIONING FROM THE PUREX RAFFINATE

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**Abstract.** The process for actinides (III) partitioning using solvent based on N,N,N',N'-tetraocthyl-diglycolamide (TODGA) in meta-nitrobenzotrifluoride (F-3) was proposed. The process involves actinides(III) and REE co-extraction, Zr and Pd removal, $HNO_3$ scrubbing, selective recovery of actinides with DTPA buffer solution and subsequent stripping of REE. The dynamic test using mixer-settlers was carried out. The feed solution contained about 4.5 g/L REE and trace amounts of $^{241}$Am. As found, the degree of americium recovery was no less than 99.97%. The decontamination factor of REE removal from Am product was about 100. Most of the zirconium, molybdenum and palladium were found in the raffinate.

**Key words:** partitioning of minor actinides, actinides (III) separation from REE, TODGA, PUREX raffinate

## 1. Introduction

The important challenge of the countries with developed nuclear industry is the environmentally safe management of radioactive waste. High-level waste (HLW) is most dangerous to the environment. For example, raffinate obtained during PUREX reprocessing of the spent nuclear fuel belongs to HLW. It contains most fission products and also minor actinides (MAs). Minor actinides are transuranium elements (except plutonium) generated in the reactor core; namely neptunium, americium and curium. Owing to their great half-decay, transuranium elements contained in such HLW provide radioactive hazard for long time (thousands and hundreds of thousands years). One of proposed ways of their management is transmutation of MAs (primarily Am and Np) in the fast reactors. At the same time, curium inclusion in the transmutation cycle is inadvisable. At present the fuel cycle technologies for fast reactors which consume MAs from the PUREX raffinate are extensively developed.

Therefore, the problem of minor actinides (Np, Am) recovery from the PUREX raffinates is rather actual for radiochemists. It should be noted that the separation of americium(III) from rare earth elements (REE) and curium(III) is the most difficult problem due to the chemical similarity of these elements.

The processes for americium(III) partition from PUREX raffinattes are extensively studied in Europe, USA, Russia, Japan, and some others countries. Among the methods of separation and pre-concentration of radionuclides the liquid-liquid extraction is one of the most developed. The lot of selective ligands and several extraction processes for americium (III) partition were proposed to date.

TALSPEAK (Trivalent Actinides Lanthanides Separation Process from Aqueous solution) is the first process for the actinides(III) (Am + Cm) separation from REE [1]. TALSPEAK is based on extraction of lanthanides using di-2(ethylhexyl)phosphoric acid (DEHPA or HDEHP) or similar liquid cation exchanger from a solution containing a polyaminopolyacetic acid (for example, N,N,N',N'-diethylenetriaminpentaacetic acid (DTPA)) as a selective complexing agent providing retention of actinides(III) in the aqueous phase, which is possible only in a weakly acid medium (pH ≈ 3). However, the concentration of nitric acid in the PUREX raffinates is often higher (3-4 M $HNO_3$). In reverse TALSPEAK, actinides(III) are selective removed from the loaded organic phase using the complexing agent solution after co-extraction of actinides(III) and lanthanides(III) from 0.1 M $HNO_3$ [2]. However, significant adjustment of the PUREX raffinate acidity is requires.

Several neutral ligands able to extract actinides(III) and REE from strongly acidic solutions were subsequently proposed. The most prominent of them are carbamoylphosphine oxides [3, 4, 5, 6], malonamides [7, 8] и diglycolamides [9, 10, 11, 12]. These ligands simultaneous extract actinides(III) and REE from the solutions, containing ≥2 M $HNO_3$. The actinides(III) can be separated from REE using the reverse TALSPEAK principle – coextraction of actinides(III) + REE and subsequent recovery of actinides(III). A solution containing a polyaminopolyacetic acid can be used for selective recovery of actinides(III). The Japanese SETFIX [13, 14, 15, 16], version of European i-SANEX [17] and American ALSEP [18] are the known processes of the actinide(III) removal with neutral ligands.

Some the ligands selective to actinides (III) were studied. These ligands extract the actinides(III) separately from REE in the first extraction step. The heterocyclic N-donor ligands such as bis-triazinylpyridines (BTP) [19, 20, 21], bis-triazinylbipyridines (BTBP) [22], bis-triazinylphenanthrolines (BTPhen) [23, 24] are the most promising ligands for separation of actinides(III) from REE. Using these ligands the r-SANEX [25] and 1c-SANEX [26] processes were developed. Diamides of N-heterocyclic carbonic acids such as diamides of pyridine-2,6-dicarboxylic (dipicolinic), 2,2-dipyridyl-6,6-dicarboxylic, and 1,10-phenanthroline-2,9-dicarboxylic acids are also of particular importance [27].

At the same time the new water-soluble complexing agents were proposed and studied as an alternative for DTPA and others polyaminopolycarbonic acids. These complexing agents are water-soluble derivatives of various selective to actinides(III) ligands – bis-triazinylpyridines [28], bis-triazinylbipyridines [29] ,bis-triazinylphenanthrolines [30], tetraalkyldiglycolamides [31,32, 33], dipicolinic acid [34, 35], crown-ethers [36,37]. Moreover, the possibility of americium(III) and curium(III) separation using these complexing agents was demonstrated. The processes of americium(III) removal from PUREX raffinates such as EXAm [31], TODGA-TPAEN [38] and AmSel [29] were recently developed in Europe.

Thus, the removal of americium(III) from the PUREX raffinates is a challenge for the researchers from different countries. Though a number of various approaches were proposed, none of them are used in industry. Of course, a series of hydrophobic and hydrophilic ligands developed in recent years is very promising, but their industrial application is the future.
In our opinion the most appropriate for industrial application is a process based on the neutral non-selective ligands for co-extraction of actinides(III) and REE from PUREX raffinates and on the solution containing polyaminopolyacetic acid for actinides(III) separation from REE.
We have developed the process using solvent based on well-known ligand N,N,N',N'-tetraoctyldiglycolamide (TODGA) in polar meta-nitrobenzotriflourite (F-3) diluent [39],

which significantly increases the capacity of solvent in comparison with traditional hydrocarbons and prevents the third phase formation [40].

The results of our dynamic test using a PUREX raffinate similar solution containing about 4.5 g/L REE and trace amount of $^{241}$Am are presented in this work.

## 2. Experimental

### 2.1. The dynamic test

The dynamic test using a mixer-settlers setup was carried out at the Production Association "Mayak", Ozersk, Russia. Total running time was 137 hours. The flow-sheet is shown in Fig.1.

The process includes the following steps:
  1. An(III) and Ln(III) co-extraction in the stages 1-10;
  2. Zr and Pd scrubbing in the stage 11-16;
  3. HNO$_3$ scrubbing in the stages 17 – 26;
  4. An (III) stripping in the stages 27 – 43;
  5. REE stripping in the stages 44 – 51.
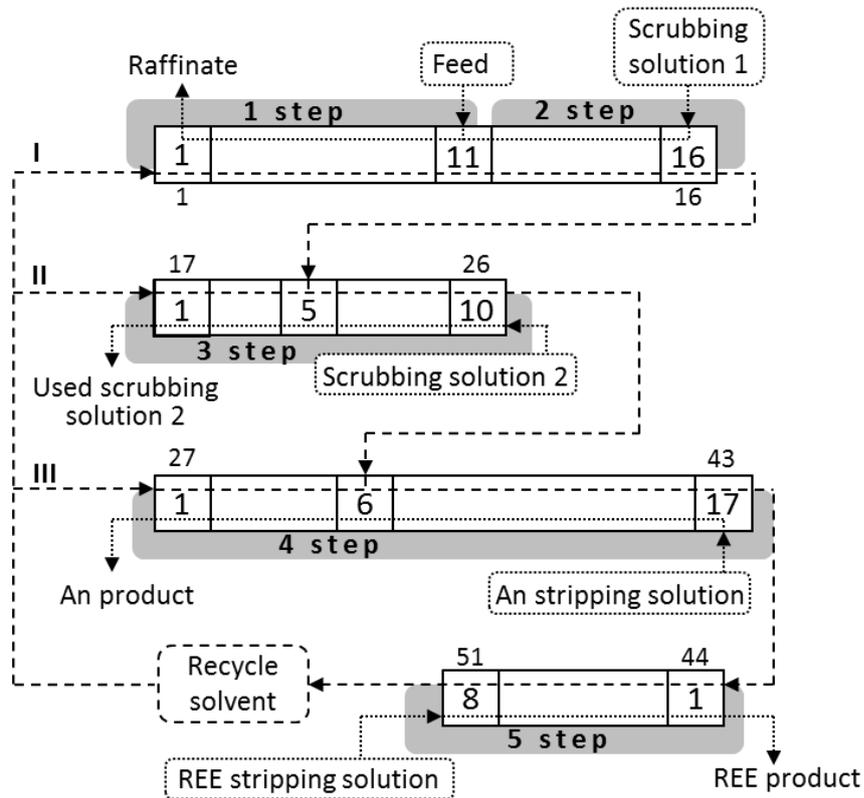


FIG. 1. THE FLOW-SHEET OF THE PROCESS FOR ACTINIDES(III) REMOVAL

The compositions and rates of the flows are shown in Tab. 1 and the composition of the similar solution are shown in Tab. 2.
The compositions and rates of some flows were adjusted during the test. Several operating modes can be identified (Tab. 3).

TAB. 1: COMPOSITIONS AND FLOW RATES OF THE PRODUCTS

| Product, product composition | Flow rate, mL/h |
|---|---|
| Feed (similar solution, Tab. 2) | 51 |
| Solvent: 0,1 M TODGA in F-3 | I – 63<br>II – 22<br>III – 62 |
| Raffinate | 64 |
| Scrubbing solution 1: 0,1 M $H_2C_2O_4$, 0,05 M HEDTA, 3 M $HNO_3$ | 13 |
| Scrubbing solution 2: 180 g/L $NH_4NO_3$ | 22 |
| Used scrubbing solution 2 | 22 |
| An stripping solution: 120 g/L $NH_4NO_3$; 10 g/L ДТПА; 5 g/L glycin; pH = 2,01 | 62 |
| An product | 62 |
| REE stripping solution: 20 g/L ДТПА, 20 g/L $(NH_4)_2CO_3$ | 55 |
| REE product | 55 |

TAB. 2: THE PUREX SIMILAR SOLUTION COMPOSITION

| Component | Concentration, g/L | Component | Concentration, g/L |
|---|---|---|---|
| Cs | 0,9 | U | 0,2 |
| Sr | 0,5 | La | 0,6 |
| Ba | 0,4 | Ce | 1,0 |
| Mn | 0,2 | Pr | 0,1 |
| Ni | 0,2 | Nd | 1,7 |
| Mo | 0,1 | Eu | 0,1 |
| Zr | 0,2 | Sm | 0,4 |
| Fe | 1,6 | Gd | 0,1 |
| Cr | 0,3 | Y | 0,2 |
| $^{99}Tc$ | 0,02 | $HNO_3$ | 189 |
| Pd | 0,03 | $^{241}Am$, MBq/L | 15 |

TABLE 3: THE OPERATING MODES OF THE MIXER-SETTLERS SETUP.

| Mode | Conditions | Key problem | Running time in the given mode, h |
|---|---|---|---|
| 1 | According to Tab. 1 | - | 37,5 |
| 2 | The solvent III flow rate was reduced to 34 mL/h, other products – according to Tab. 1 | Partial americium yield in step 4, its accumulation in stages 4-8 | 31,8 |
| 3 | The composition of scrubbing solution 1 was changed – 0,2 M $H_2C_2O_4$ + 0,05 M HEDTA + 1,5 M $HNO_3$ | Zr accumulation in stage 11 due to its high extraction in step 1 | 27 |
| 4 | The composition of scrubbing solution 1 was changed – 0,3 M $H_2C_2O_4$, 0,05 M HEDTA, 1,5 M | | 16 |

| Mode | Conditions | Key problem | Running time in the given mode, h |
|------|------------|-------------|-----------------------------------|
|      | $HNO_3$ |  |  |
| 5 | The An stripping solution flow rate was increased to 76 mL/h | Detection of 0,2 % Am in REE product | 24,6 |

## 2.2 Chemicals and reagents

N,N,N',N'-tetraoctyldiglycolamide (TODGA, purity not less than 98%) were purchased from Sorbent-Technology (Moscow, Russia) and used without further purification.

Meta-nitrobenzotrifluoride was procured from Rhodia (La Défense, France) and was conditioned. F-3 conditioning procedure includes the following steps: 1) alkaline scrubbing with 1 M NaOH (twice); 2) acid scrubbing with 3 M $HNO_3$ (twice); 3) stripping with $H_2O$ (until the acid is removed completely; usually required three contacts); 4) filtration; 5) drying over $Na_2CO_3$ for 24 hours; 5) filtration.

## 3. Results and discussion

The metals distribution between the products (material balance) is shown in Tab. 4 and 5. Fig. 2 and 3 demonstrate Am and REE profiles (for aqueous phase).

TAB. 4: MATERIAL BALANCE (AT END OF THE MODE 1), %

| Element/ isotope | Product | | | | | |
|------------------|---------|----------------------|------------|-------------|-----------------|-------|
|                  | Raffinate | Used scrubbing solution 2 | An product | REE product | Recycle solvent | Σ |
| $^{241}$Am | ≤0,03 | ≤0,01 | 49,4 | 1,8 | ≤0,05 | 51,2 |
| Tc | 23,9 | 2,9 | 4,1 | 1,5 | 44,4 | 76,8 |
| Pd | 87,8 | 1,4 | 6,1 | 7,3 | ≤80 | 103 |
| La | ≤0,001 | ≤0,001 | ≤0,001 | 46,3 | ≤1 | 46,3 |
| Ce | ≤0,001 | ≤0,001 | 0,1 | 90,2 | ≤0,2 | 90,3 |
| Pr | ≤0,001 | ≤0,01 | ≤0,01 | 102 | ≤2 | 102 |
| Nd | ≤0,001 | ≤0,001 | ≤0,01 | 124 | ≤0,1 | 124 |
| Eu | 0,1 | ≤0,001 | ≤0,01 | 133 | ≤2 | 133 |
| Sm | ≤0,001 | ≤0,001 | ≤0,001 | 130 | ≤1 | 130 |
| Gd | ≤0,001 | ≤0,001 | ≤0,01 | 134 | ≤2 | 134 |
| Y | ≤0,01 | ≤0,001 | ≤0,01 | 158 | ≤0,1 | 158 |
| U | 0,5 | 0,05 | 69,4 | 23,4 | ≤1 | 93,3 |
| Zr | 1,1 | 6,7 | 25,5 | 0,1 | ≤0,1 | 33,5 |
| Mo | 110 | 0,9 | 6,1 | 0,6 | ≤0,4 | 118 |

TAB. 5: MATERIAL BALANCE (AT END OF THE MODE 5), %

| Element/ isotope | Product | | | | | |
|---|---|---|---|---|---|---|
| | Raffinate | Used scrubbing solution 2 | An product | REE product | Recycle solvent | Σ |
| $^{241}$Am | ≤0,03 | ≤0,01 | 95,4 | 0,2 | 0,1 | 95,6 |
| Tc | 74,1 | 10,3 | 35 | 3,1 | 122 | 245 |
| La | 0,3 | 0,01 | 0,01 | 132,4 | ≤1 | 133 |
| Ce | ≤0,001 | 0,01 | 0,3 | 135 | ≤0,2 | 135 |
| Pr | ≤0,001 | 0,01 | 0,1 | 101 | ≤2 | 101 |
| Nd | ≤0,001 | ≤0,001 | 0,1 | 108 | ≤0,1 | 108 |
| Eu | 0,06 | ≤0,001 | 0,1 | 120 | ≤2 | 120 |
| Sm | ≤0,001 | ≤0,001 | 0,2 | 110 | ≤1 | 110 |
| Gd | ≤0,001 | ≤0,001 | 0,1 | 127 | ≤2 | 128 |
| Y | 0,01 | ≤0,001 | 0,03 | 157 | ≤0,1 | 157 |
| U | 0,06 | 1,9 | 33,6 | 90,2 | ≤1 | 126 |
| Zr | 248 | 0,9 | 0,1 | 0,03 | ≤0,1 | 249 |
| Mo | 86,6 | 4,7 | 3,1 | 0,6 | ≤0,4 | 95 |
| Pd | 88,3 | 0,3 | 0,8 | 3,1 | ≤80 | 92 |
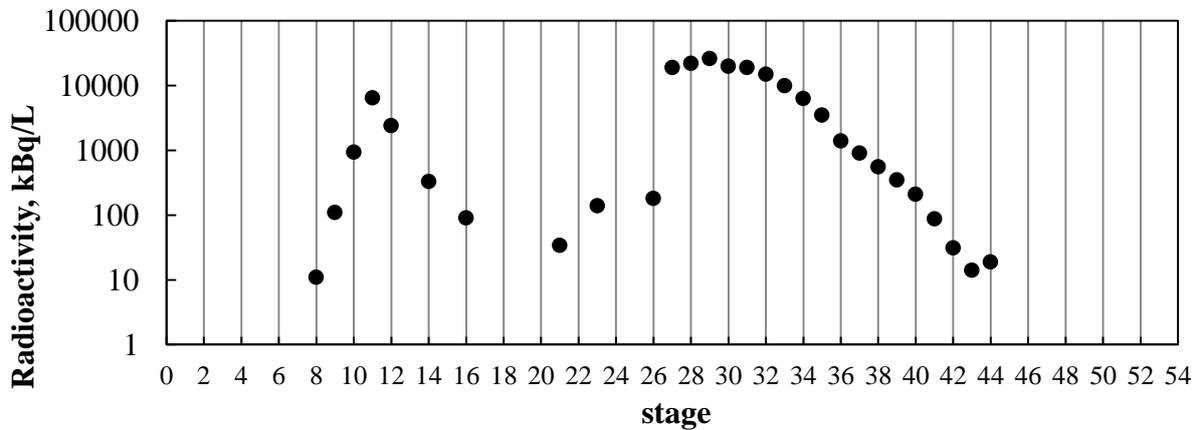


FIG. 2. AMERICIUM PROFILE (AQUEOUS PHASE)
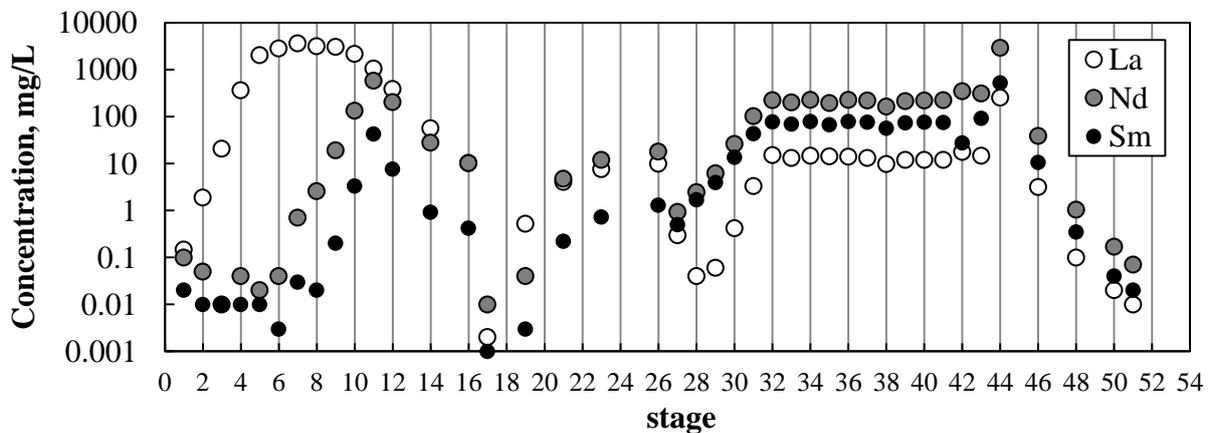


FIG. 3: REE PROFILE (AQUEOUS PHASE)

As stated above, some process parameters (the compositions and rates of some flows) were changed during the test (Tab. 1) due to unsatisfactory yields of some metals (Tab. 4).

At end of the test (mode 5, Tab. 5) the removal of Am and REE from the PUREX similar solution in step 1 was almost complete. The REE total concentration in the similar solution was 4.2 g/L, and the americium product contained not more 5 mg/L REE. REE were completely stripped from the organic phase in the final step, but Tc stripping was not efficient. More than 100% of Tc was found in the recycle solvent. We also had a problem with retaining Zr in the feed solution during the test. Zirconium was accumulated in extraction setup (stage 11). Change in the composition of the scrubbing solution 1 provided significant increase of Zr yield in the raffinate. At end of the test Zr content in the raffinate was still more than 100%.

## 4. Conclusion

The dynamic test of the process to remove actinides(III) from PUREX raffinates using solvent based on TODGA in F-3 was carried out. High recovery and purification of Am were attained. Not less than 99.97 % of americium was recovered from the PUREX similar solution containing 4.2 g/L REE. Decontamination factor of the REE removal from Am product was about 100. Most of the zirconium, molybdenum and palladium were retained in the raffinate. Unfortunately, technetium accumulation in the recycle solvent was observed. This problem is required closer consideration.

The improvement of the process is continuing.

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