

Hot test of technique separation of americium and curium

Milutin Vitaliy¹, Kharitonov Oleg¹, Firsova Lubov¹, Kozlitin Evgeniy¹, Yakovlev Nikolaiy², Fadeev Sergey², Logunov, Mikhail², Voroshilov Yuriy², Vidanov Vitaliy³, Shadrin Andrei³

¹Frumkin's Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences, Moscow, Russia

²Mayak Production Association, Ozersk, Russia

³INSTITUTION «ITC «PRORYV» PROJECT», Moscow, Russia

E-mail contact of main author: vvl@proryv2020.ru

Abstract. Two-stage technology of Cm and Am separation from REE-TPE concentrate was tested on Mayak Production Association. The used concentrate was produced from reprocessing SNF WWER-440.

Tokem-308 cation-exchange resin was used in the final separation stage. The resin grain size was 0.2 mm. About 14 g of Cm was separated. 9 g of pure Cm fraction contained 6 % by Am activity. The Cm-Am fraction contained about 4,6 g of ²⁴⁴Cm and about 40 g of ^{241,243}Am. Pure fraction of Am with 65 g of ^{241,243}Am was obtained. Content of Cm was lower than 0.8 % by mass and ^{154,155}Eu was lower than 0.1 % by activity in pure fraction of americium.

Key Words: separation Am-Cm, sorption, cation resin, SNF reprocessing.

1. Introduction

Nowadays long-term and sustainable development of nuclear power engineering is impossible without solving the problems of handling radioactive waste and spent nuclear fuel (SNF).

Modern technology of SNF reprocessing in concept of closing of the nuclear fuel cycle must involve partitioning and transmutation minor actinides. In general one of the parts of «PRORYV» project is separation of Am. The purified Am may be added into nuclear fuel composition for transmutation.

For the minor actinides separation several extraction processes have been developed such as TALSPEAK [1], DIAMEX [2], TRPO [3], TRUEX [4], SETFICS [5], ALSEP [6], SANEX [7], EXAm [8], GANEX [9]. Should be mentioned that only TALSPEAK process is used in industrial scale.

Available methods of the SNF reprocessing for production of pure americium intended for transmutation were considered and the method of displacement chelation chromatography involving the use of strong-acid cation-exchange resin with active sulphonic-acid groups as a sorbent was chosen [10].

2. Experimental

2.1. Reagents and materials

The oxalate precipitate of REE-TPE from concentrate from reprocessing SNF WWER-440 was used as start material. Am: REE and Am: Cm ratios in initial solution were 1:30 and 1:10 re-spectively. The radionuclides content and initial solution chemical analysis data are presented in table 1 and table 2.

KY-2-8 resin in Ni²⁺ form was used at the first stage for primary refining and concentration Am-Cm fraction. The DTPA 10g/l + HTA 10 g/l solution with pH 7-8 was used for elution.

«Tokem-308» resin with grain size 0.22 mm in Ni²⁺ and Ni²⁺-Zn²⁺ forms were used in Am-Cm separation stage. The DTPA 20g/l solution with pH 7,5 was used for elution.

TABLE 1: THE RADIONUCLIDES CONTENTS IN INITIAL SOLUTION FOR SEPARATION AM-CM

Radionuclide	Samples radioactivity, MBq/ml			
	Sample 1	Sample 2	Sample 3	Sample 4
Eu-155	64.9	73.9	70.2	69.6
Eu-154	119	145	144	136
Cs-137	79.5	91	98	89.5
Cs-134	35.8	41	44.3	38
Ce-144	665	682	705	684
Pr-144	528	-	-	528
Am-241	18.5	19.6	20.8	19.6

TABLE 2: THE CHEMICAL ELEMENTS IN INITIAL SOLUTION FOR AM-CM SEPARATION

Chemical element	Concentrations in the sample, mg/ml			
	Sample 1	Sample 2	Sample 3	Mean values
Am	146	154	164	154
Eu	130	150	101	127
Sm	1700	1500	1630	1610
Y	280	590	280	383
Nd	2800	3700	2400	2967
Pr	600	1100	800	833,3
Ce	1600	1700	2000	1767

La	1600	1400	630	1210
Al	≤130	≤100	31	≤100
Ca	≤130	≤260	144	≤260
Cr	≤132	≤100	12	≤100
Fe	380	800	300	490
Mn	≤50	-	≤5	≤50
Ni	≤130	≤260	18	≤260
Sr	≤50	90	60	70
Zn	≤320	-	≤13	≤320

2.2. The equipment and control methods

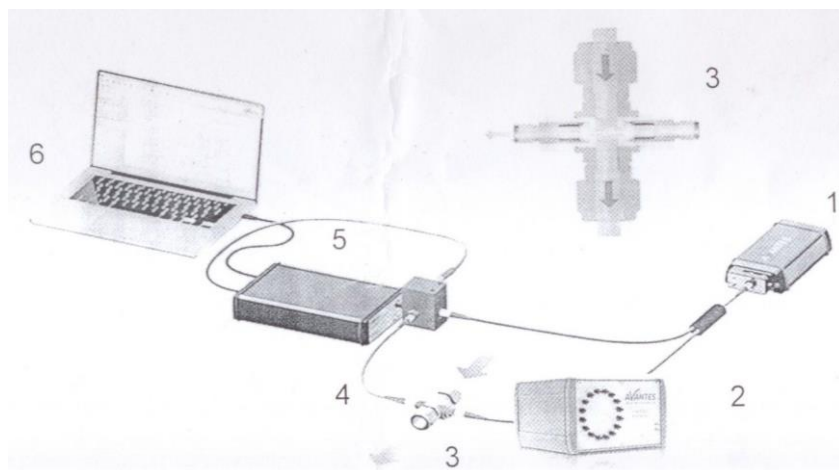
Chromatographic equipment of Mayak Production Association was used. The characteristics of chromatographic columns are shown in table 3.

TABLE 3: CHARACTERISTIC OF CHROMATOGRAPHIC COLUMNS

№	Inside diametr, mm	Height, cm	Cross-sectional area, cm ²	Volume, l
KB-1	253	250	502.9	125.7
KB-2	203	250	323.8	81.0
KB-3	147	250	169.8	42.4
KB-4	98	250.8	75.5	18.9
KB-5	66	250.8	34.2	8.6
KB-6	47	250.8	17.3	4.4
KB-7	25.4	204	5.1	1.0

The feed rates were controlled by measuring the rates of the solution in columns output. Elations of radioactive elements was controlled by the front boundary of current element. For front border control UIM-2-1 with two gamma detector were used. The first detector has Pb cover (attenuation of radiation 1:10) and the second has not protection. Mobile detector DG-2V with UIM-2-2 was used for express gamma analyses. UIO-01, PSO2-2EM with SNM-18 mobile detector was used for express neturon detection.

«Avantes» spectroscopy system (Fig.1) was used for direct element detection in technological solutions.



- 1 – Light source AvaLight-DH-S-BAL;
- 2 – Eight-channel multiplexer;
- 3 – In-line flowcell 1/2";
- 4 – fiber-optical cable;
- 5 – spectrometer AvaSpec 2048 XL5;
- 6 – PC with software «AvaSoft-ALL».

Fig. 1 – The Spectrometry equipment for In-process control

Metal concentration determination was carried out using an ICP-MS Agilent 7500CX with «ChemStation» software.

The SEG-01PPD gamma-spectrometer with DGDK-60V semiconductor detector was used for gamma analyses of technological products.

2.3. Technological process

Separation technology of REE - Cm and Am included two stages:

- first stage for primary refining and concentrating of Am-Cm fraction;
- second stage Am-Cm separation stage.

KY-2-8 resin with grain size 0.1-1.1 mm in column KB-1 was used at the first stage for cation sorption from start solution. The flow rate of the solution was about 2-4 ml/min · cm².

First stage - concentrating of Am-Cm fraction.

For concentrating of Cm and Am KB-1 – KB-6 columns with KY-2-8 resin in Ni²⁺ form were used. The DTPA 10g/l + HTA 10 g/l solution with pH 7-8 was used for elution. The elution temperature was 70-75°C. The flow rate of the elution was 4 ml/min · cm². Collection of Am-Cm was carried out from KB-6 column output.

At the end of the first stage two solutions were obtained. Volume of the first solution was 6300 l and element concentration [Am] – 5 mg/l, [Ni] – 1.6 g/l, [HNO₃] – 0.41 mol/l. Volume of the second solution was 377 l and element concentration [Am] – 141 mg/l, [Cm] – 26.4 mg/l, [REE] – 1228 mg/l, [Ni] – 351 mg/l, [HNO₃] – 0.38 mol/l.

Second stage - Am-Cm separation.

For Am-Cm separation KB-3 – KB-8 columns were used. KB-3 with KY-2-8 resin in Ni²⁺ form, KB-4 – KB-7 with «Tokem-308» resin with grain size 0.22 mm in Ni²⁺ form and KB-8 with «Tokem-308» resin with grain size 0.22 mm in Ni²⁺-Zn²⁺ form.

At this stage KB-3 column was used for sorption. The flow rate of the solution was about 60-100 l/hr. The first and then the second solutions were passed through a KB-6. After the sorption was completed, the column with the sorbent was washed with solution [Ni(NO₃)₂] - 0,05 mol/l.

The DTPA 20g/l solution with pH 7,5 was used for elution. The elution temperature was 70-75°C. For KB-3 – KB-7 column the flow rate of elution was 4 ml/min · cm². The flow rate of Cm elution from KB-8 column was 4 ml/min · cm² and Am elution – 8 ml/min · cm²

2.4. Result and discussion

Alfa-determination of the Am in the presence of a generous Cm amount is very difficult. For this reason the Am concentration was calculated by gamma-spectrometry data (line 59.6 keV). It is seen from gamma-analysis that ²⁴¹Am : ²⁴³Am ratio is about 1 : 1. Therefore for the next calculation ²⁴¹Am isotope gamma-spectrometry data was used with factor 2.

Output elution curves in the second stage of Am-Cm separation are presented in Fig. 2 and Fig. 3. According to the data in Fig. 2 and Fig. 3 Cm, Am and Eu are sequentially eluted forming small mixing zones. Explanation of that fact is the use of «Tokem-308» monodisperse cation-exchange resin.

As a result of these operations three fractions were obtained. The volume of pure Cm fraction is 2.5 l with 9 g of ²⁴⁴Cm. Pure Cm fraction contained 6 % of Am activity.

The volume of Cm-Am fraction is 5.5 l. Fraction contained about 4,6 g of ²⁴⁴Cm and about 40 g of ^{241,243}Am.

The volume of Am fraction is 8 l. The Am fraction contains 65 g of ^{241,243}Am. Content of Cm was less than 0.8 % mass and ^{154,155}Eu was lower than 0.1 % by activity in Am fraction.

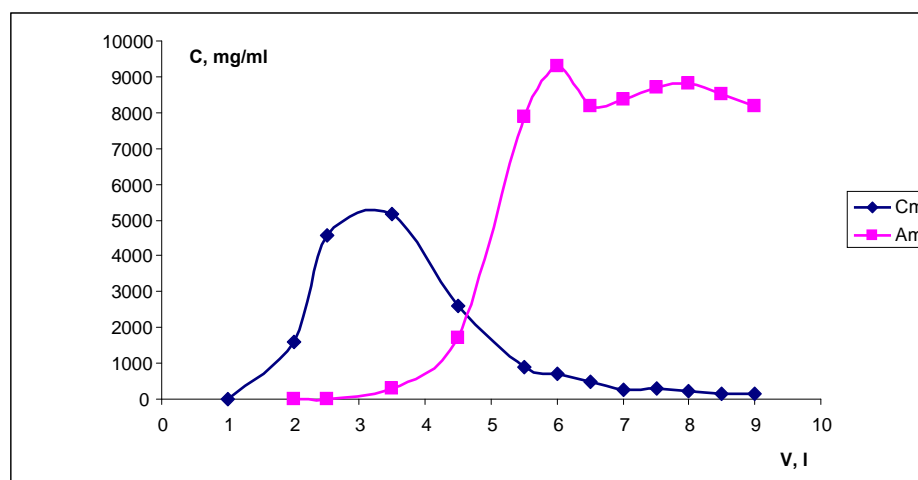


FIG. 2. OUTPUT AM-CM ELUTION CURVES AT THE SECOND STAGE - AM-CM SEPARATION

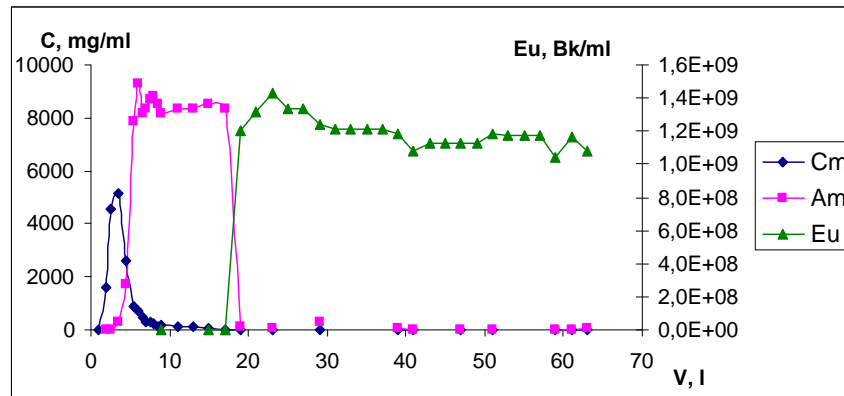


FIG. 1. OUTPUT AM-CM AND EU ELUTION CURVES AT THE SECOND STAGE - AM-CM SEPARATION

3. Conclusions

Two-stage technology of Cm and Am separation from REE-TPE concentrate was tested in Mayak Production Association. Used concentrate was produced from reprocessing of SNF WWER-440. «Tokem-308» cation-exchange resin was used in the final separation stage. The resin grain size was 0.22 mm.

About 14 g of Cm was separated. 9 g of pure Cm fraction contained 6 % of Am activity. The Cm-Am fraction contained about 4,6 g of ^{244}Cm and about 40 g of $^{241,243}\text{Am}$. Pure fraction of Am with 65 g of $^{241,243}\text{Am}$ was obtained. Content of Cm was lower than 0.8 % by mass and $^{154,155}\text{Eu}$ was lower than 0.1 % by activity in pure fraction of americium.

The use of «Tokem-308» monodisperse cation-exchange resin has allowed to get a insignificant by volume Am-Cm and Am Eu mixing zones.

4. References

- [1] F.A. Kappelmann, B. Weaver. Method for separating americium and curium from the lan-thanide rare earths and yttrium: US Patent. 3,230,036, Jan. 18, 1966
- [2] D. Serrano-Purroy, B. Christiansen, J.-P.Glatz, R. Malmbeck, G. Modolo, Towards a DIAMEX process using high active concentrate. Production of genuine solutions, Radi-ochim. Acta 93, 357–361 (2005)
- [3] Glatz J. P., Song C., Koch L. H. B., He X. M., Hot Tests of the TRPO Process for the Re-moval of TRU Elements from HLLW, Proc. Int. Conf. GLOBAL'95, Sep. 1995, Versailles, France
- [4] Koma Y., Watanabe M., Nemoto S., Tanaka Y. A counter current experiment for the separation of trivalent actinides and lanthanides by the SETFICS process. Solv. Extr. Ion Exch. (1998), 16(6), pp. 1357-1367
- [5] A. Shadrin, V. Kamachev, I. Kvasnitsky, V. Romanovsky, V. Bondin, Y. Krivitsky, S. Alekseenko. Extraction reprocessing of HLW by modified SETFICS-process. Proc. of Int. Conf. GLOBAL 2005, Oct 9-13, 2005, Tsukuba, Japan, Paper No. 129
- [6] U.S. Patent 8,354,085 B1, Jan. 15, 2013
- [7] A. Geist, G. Modolo, A. Wilden, P. Kaufholz. MINOR ACTINIDE SEPARATION: SIMPLIFICATION OF THE MEX-SANEX STRATEGY BY MEANS OF NOVEL

- SANEX PROCESSES, Global 2013, Salt Lake City, Utah, September 29-October 3, 2013, pp. 1054-1059
- [8] C. Rostainga, C. Poinssot, D. Warinb, P. Barona, B. Lorraina. Development and validation of the EXAm separation process for single Am recycling, *Procedia Chemistry* 7 (2012) 367 – 373
- [9] E. Aneheim, C. Ekberg, A. Fermvik, Mark R. St. J. Foreman, T. Retegan, G. Skarnemark, TBP/BTBP-based GANEX Separation Process. *Solvent Extraction and Ion Exchange*, 28: 437–458, 2010
- [10] Vladimir Gelis, Oleg Kharitonov, Lubov Firsova, Vitaliy Milutin, [etc], «SELECTION OF THE SORBENT FOR SEPARATION OF CURIUM AND AMERICIUM BY SORPTION TECHNIQUE», Actinide and Fission Products Partitioning and Transmutation, 13 Information Exchange Meeting, Seoul, Republic of Korea, 23-26 September 2014, p. 335-343