

# Separation Features of TPE and REE by Complex Displacement Chromatography from Highly Active Solutions Formed after SNF Processing

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**Abstract**—Radiation loads and compositions of solid phases are calculated during the separation of TPE and REE from solutions generated in the course of SNF reprocessing. Sorption from weakly concentrated solutions under the action of high radiation loads in the upper part of the sorption column leads to the sorbent decomposition, up to 30% of its original capacity. The hydroxide forms of iron, chromium, aluminum and nickel pass from the solid to the liquid phase and generate gel-like precipitates under the action of high radiation loads, which block the sorption column. During elution, aluminum is washed out in the TPE region and forms a protonated complex with diethylenetriaminepentaacetic acid (DTPA), which precipitates at room temperature. This precipitate in the unheated connecting lines of the plant can bring about blocking of the separation columns.

**Keywords:** complex displacement chromatography, cation exchange resin, rare earth elements, iron, chromium, aluminum, purification, separation, absorbed dose, destruction

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## INTRODUCTION

Chromatographic methods, in particular, complex displacement chromatography (CVC), are widely used to separate substances with similar properties. For the first time, this method was successfully applied for recovering individual natural rare earth elements (REE) [1, 2]. The CVC method has gained particular importance in solving the problem of separating pure radioactive REE and transplutonium elements (TPE) from solutions resulting from the reprocessing of spent nuclear fuel (SNF).

The CVC method has been used in the USSR for the separation of <sup>147</sup>Pm since the 1970s [3, 4]. In 1975, Mayak Production Association manufactured a pilot chromatographic setup (OPKhU-1) with a total volume of 229 L (Table 1) for separating TPE and fragmented REE from solutions resulting in SNF reprocessing. In 1989, the chromatographic setup was upgraded (Table 1).

Both chromatographic setups were successfully used to recover both <sup>147</sup>Pm and also Cm and Am radionuclides, as well as <sup>151</sup>Sm [5–9].

However, in 2017, during the the OPKhU operation for the implementation of an international project to create an artificial source of antineutrinos based on high-purity <sup>144</sup>Ce dioxide, first column 1 was blocked in the course of elution of the separated mixture with an 0.0509 M diethylenetriaminepentaacetate (DTPA) solution. The permeability of the column was restored by washing the column from bottom to top and unloading therefrom a gel-like mass of black-brown color. After that, successive locking of the separation columns occurred. As a result, it was not possible to get a pure <sup>144</sup>Ce preparation. Thus, the project was not implemented. The reasons for the blocking of both the sorption and separation columns were not clear.

This work is aimed at clarifying the causes leading to the locking of columns. In this regard, it is necessary to evaluate the dose loads and the destruction of the sorbent that occurs in this case, to study the processes taking place on chromatographic columns during the separation of TPE and REE from highly active solutions formed during the SNF reprocessing.

**Table 1.** Pilot plant for the separation of TPE and fragment REE from solutions formed as a result of spent nuclear fuel reprocessing

Column no.	1975–1984, pilot plant OPKhU-1, 229 L			1989, modernized OPKhU plant, 282 L		
	<i>H</i> , cm	diameter, cm	<i>V</i> , L	<i>H</i> , cm	diameter, cm	<i>V</i> , L
1	200	22.4	80.8	250	25.3	126
2	200	20.0	62.8	250	20.3	81.0
3	200	20.0	62.8	250	14.7	42.4
4	200	10.0	15.7	250	9.8	18.9
5	200	5.0	3.9	250	6.6	8.6
6	200	2.54	1.0	250	4.7	4.4
7	200	2.54	1.0	204	2.54	1.0
8	200	2.54	1.0	203	1.6	0.4

## EXPERIMENTAL

Table 1 shows the setup parameters for the separation of TPE and fragmented REE from solutions resulting in SNF reprocessing at the Mayak PA. The setups were made of stainless steel and equipped with heating jackets.

**Table 2.** Chemical composition of sorption solutions

Component	Solution 1, 2017	Solution 2, 1989
Al, mg/L	42.9	24.2
Fe, mg/L	368.6	223
Cr, mg/L	40.0	19.4
La, mg/L	143.9	1306
Ce, mg/L	319.0	2468
Pr, mg/L	131.9	1210
Nd, mg/L	460.6	6774
Pm, mg/L	25.9	33.9
Sm, mg/L	68.3	1452
Eu, mg/L	9.6	155
Gd, mg/L	2.5	145
Y, mg/L	71.0	968
Am, mg/L	105.7	465
Cm, mg/L	10.6	46
HNO <sub>3</sub> , M	0.715	0.82
Na, M	0.0298	0.097
K, M	0.0252	–

Preparation of initial solutions intended for REE and TPE sorption includes hydroxide and oxalate precipitation of REE and TPE from solutions after SNF reprocessing followed by dissolution, destruction of oxalates with nitric acid, and evaporation. The as-prepared concentrate is diluted with water so that the sum of singly charged cations (H<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>) does not exceed an 1 M concentration.

Tables 2 and 3 demonstrate compositions of sorption solutions. Solution 1 was obtained by a single oxalate precipitation and was used in the implementation of the international project in 2017. For comparison, the composition of solution 2 during the <sup>147</sup>Pm and TPE separation in 1989, which was produced by a double oxalate precipitation, is shown. Solutions of approximately the same composition were utilized at the OPKhU-1 and OPKhU setups from 1975 to

**Table 3.** Radiochemical composition of sorption solution 1 (2017)

Element	Concentration, Ki/L
<sup>144</sup> Ce	64.3
<sup>144</sup> Pr	64.3
<sup>147</sup> Pm	22.2
<sup>241</sup> Am	0.363
<sup>154</sup> Eu	0.718
<sup>155</sup> Eu	0.324
<sup>137</sup> Cs	0.027
<sup>125</sup> Sb	0.079

1992. The difference between solutions 1 and 2 is that the concentration of TPE and REE in solution 2 is approximately 15 times higher than in solution 1.

The radiochemical composition was determined by  $\gamma$ -spectrometry; the chemical composition, by optical emission and mass spectrometry according to the Mayak AP software methods.

The first column of the OPKhU setup was filled with Tokem 308 monodisperse sulfonic cation exchange resin with a grain size of 545  $\mu\text{m}$  in hydrogen form, and a similar cation exchange resin with a grain size of 220  $\mu\text{m}$  in nickel form was utilized in the separation columns. After sorption, to remove singly charged cations and transfer the resin to the nickel form, washing was carried out with an 0.05 M  $\text{Ni}(\text{NO}_3)_2$  solution. A solution of 0.0509 M DTPA, pH 7.5, was used as an eluent. Sorption and elution were carried out at a temperature of 70°C. The rate of sorption and elution was 4 mL/(min  $\text{cm}^2$  of column cross-section).

Separation of elements under laboratory conditions was carried out on glass columns 80 cm high and with a cross section of 2.1 (sorption column) and 0.53  $\text{cm}^2$  (separating column). We also used monodisperse sulfonic cation exchange resin Tokem 308 with granulation size of 545 and 220  $\mu\text{m}$  in the sorption and separation columns, respectively. Sorption and separation conditions were similar to production conditions. The composition of the separated mixture approximately corresponded to solution 1, in which Cm and Am were replaced by Ho, and Sm was used instead of Pm.

## CALCULATION TECHNIQUE

**Calculation of the solid phase composition.** With complete saturation of the ion exchange resin in the column for the simple ion exchange option, the distribution of concentrations of REE, TPE, and hydrogen ions in the solid phase is determined by Eqs. (1) and (2):

$$1 = \sum \bar{x}_{\text{Mi}} + \bar{x}_{\text{H}} + \bar{x}_{\text{Na}}, \quad (1)$$

$$\sum K_{\text{Mi-H}} Q^2 \frac{M_i}{[\text{H}]^3} \bar{x}_{\text{H}}^3 + \left( 1 + K_{\text{Na-H}} \frac{[\text{Na}]}{\text{H}} \right) \bar{x}_{\text{H}} - 1 = 0, \quad (2)$$

where  $[M_i]$ ,  $[\text{Na}]$ ,  $[\text{H}]$  are concentrations of trivalent elements (An, Ln, Al, Cr, Fe), Na and H in solution, g-equiv./L, respectively;  $\bar{x}_{\text{Mi}}$ ,  $\bar{x}_{\text{H}}$ ,  $\bar{x}_{\text{Na}}$  are the contents of components in the sorbent (fractions of the capacity);

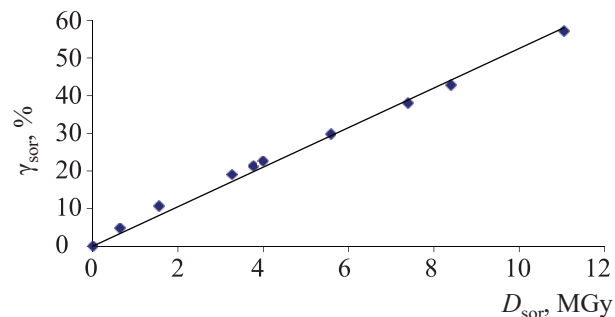


Fig. 1. Destruction of the KU-2 sorbent vs. the absorbed dose [15].

$K_{\text{Mi-H}}$ ,  $K_{\text{Na-H}}$  are concentration constants of ion exchange [10, 11];  $Q$  is the volumetric capacity of the cation exchange resin, g-equiv./L.

The doses absorbed by the sorbent during chromatographic processes were calculated by Eq. (3) [12–14]:

$$D_{\text{sor}} = k \frac{\left( \sum A_i p_i \right) \tau}{m_{\text{sor}}} \times \left( \frac{m_{\text{sor}} N_{\text{sor}}}{m_{\text{sor}} N_{\text{sor}} + m_{\text{sol}} N_{\text{sol}}} \right), \quad (3)$$

where  $D_{\text{sor}}$  is dose absorbed by the sorbent, Gy;  $k$  is the conversion factor equal to  $3.584 \times 10^6$ , g Gy/(W h);  $\tau$  is the contact time, h;  $N_{\text{sor}}$ ,  $N_{\text{sol}}$  are the electron densities of the sorbent and solution, respectively, electron/g;  $m_{\text{sor}}$ ,  $m_{\text{sol}}$  are the weights of the sorbent and solution, respectively, g;  $\sum A_i p_i$  is the total energy release of the mixture of radionuclides, W;  $p_i$  is the specific energy release of the  $i$ th radionuclide, W/Ci;  $A_i$  is the activity of the  $i$ th radionuclide, Ki.

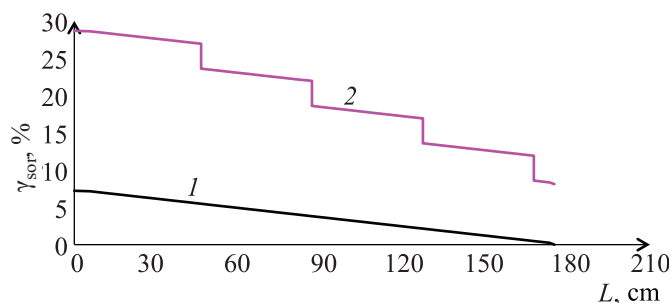
The destruction of the sorbent ( $\gamma_{\text{sor}}$ , %) was calculated by Eq. (4) from the experimental data we obtained earlier [15] by the change in the capacity of the KU-2 cation exchange resin depending on the absorbed dose (Fig. 1).

$$\gamma_{\text{sor}} = \left( \frac{Q_0 - Q_D}{Q_0} \right) \times 100, \quad (4)$$

where  $Q_0$  the initial capacity of the cation exchange resin, g-equiv./L;  $Q_D$  is the capacity of the cation exchange resin at the dose  $D_{\text{sor}}$  absorbed by the sorbent, g-equiv./L.

## RESULTS AND DISCUSSIONS

When carrying out work at the OPKhU setup for the



**Fig. 2.** Destruction of the sorbent along the column length from top to bottom (2017, Mayak PA); (1) Destruction of the sorbent upon sorption, (2) total destruction of the sorbent.

implementation of the international project to create an antineutrino source based on  $^{144}\text{Ce}$  in 2017, during the sorption operation, it was necessary to dilute the initial solution to an 0.7 M acidity (2.3 times). The sorption apparatus volume was only 700 L. The time of each solution preparation (dilution) was about 7 h. Then, the sorption operation lasted another 7 h. Four such dilution operations should be performed. The total volume of the sorption solution was 3030 L; it contained 4.1 kg of REE and TPE, which amounted to 30–40% of the total capacity of the cation exchange resin in the sorption column. At the end of sorption, nickel washing was carried out to transfer the cation exchange resin into the form of a retaining ion. Due to the incomplete loading of the column,  $1.5 \text{ m}^3$  of  $\text{Ni}(\text{NO}_3)_2$  decinormal solution was required. The operation time was 15 h, and water washing proceeded during another 2 h. Thus, the total time of sorption operations was more than 3 days, after which the elution was started.

The solid phase composition at the end of the sorption, calculated by Eqs. (1) and (2), is given in Table 4. The composition of the phases during sorption from a more

concentrated solution 2 (1989) is also presented for comparison.

Analysis of Eq. (2) evidences that the content of hydrogen ions in the resin will be the lower, and the content of REE will be the greater, the higher the ion exchange constant and the higher the ratio of triply charged and singly charged cations  $[\sum M_i]/[\text{H}]^3$ . As follows from Table 4, for solution 2  $[\sum M_i]/[\text{H}]^3$  is 0.606, and for solution 1 it is 0.151. Therefore, the sum of the concentrations of singly charged cations in the resin during sorption from solution 1 is 11% higher than during sorption from solution 2.

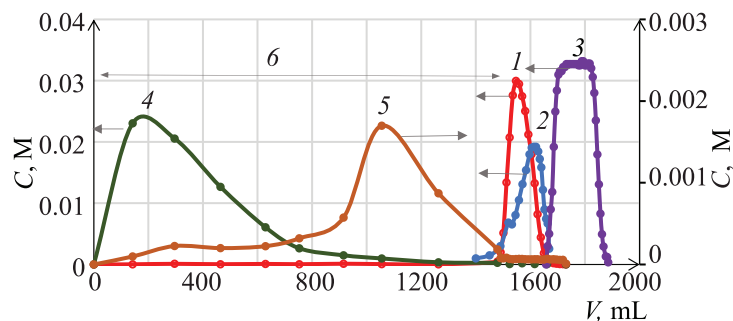
The ratio of the REE and TPE sum to the sum of impurity elements  $\sum(\text{Ln}+\text{An}):\sum(\text{Al}+\text{Fe}+\text{Cr})$  in solution 1 is about 1, and in solution 2 it is about 20. Despite the fact that the  $K_{\text{Mi-H}}$  exchange constant for REE and TPE are 2–3 times higher than those for iron, chromium, and aluminum [10, 11], at the sorption from solution 1 on a sorbent the impurity elements (Al, Cr, and Fe) occupy about 20% of the resin capacity. Therefore, in this case, REE and TPE in total occupy less than 50% of the total capacity of the cation exchange resin.

At the same time, during sorption from a more concentrated solution (sorption solution 2), the impurity elements occupy less than 2% of the resin capacity, and the total REE on the sorbent occupies almost 80% of its total capacity. Sorption from more concentrated solutions enhances the plant performance and improves the separation efficiency due to the implementation of more trays.

During a long sorption, the sorbent in the column was subjected to significant radiation exposure. When calculating the dose absorbed by the sorbent, the activities of  $^{144}\text{Ce}$ ,  $^{144}\text{Pr}$ , and  $^{147}\text{Pm}$  were taken into

**Table 4.** Distribution of concentrations in phases upon sorption from sorption solutions of various concentrations

Component	Liquid phase composition, M		Solid phase composition, % of capacity	
	solution 1, 2017	solution 2, 1989	solution 1, 2017	solution 2, 1989
Al	$1.59 \times 10^{-3}$	$8.99 \times 10^{-4}$	3.6	0.30
Fe	$6.58 \times 10^{-3}$	$3.97 \times 10^{-3}$	15.0	1.32
Cr	$7.69 \times 10^{-4}$	$3.72 \times 10^{-4}$	1.9	0.14
$\sum(\text{Ln}+\text{An})$	$9.41 \times 10^{-3}$	$1.07 \times 10^{-1}$	48.8	79.00
$\text{HNO}_3$	$7.15 \times 10^{-1}$	$8.23 \times 10^{-1}$	27.2	16.52
Na	$2.98 \times 10^{-2}$	$9.68 \times 10^{-2}$	1.6	2.72
K	$2.52 \times 10^{-2}$	–	1.8	–



**Fig. 3.** Washout of (1) aluminum, (4) iron, and (5) chromium during the separation of REE and TPE on the Ni(6) form of the KU-2 cation exchange resin using an eluent of 0.0509 M DTPA; (2) Ho(Am, Cm), (3) Nd.

account; the contribution of other radionuclides was less than 1%. In case of diluting the initial solution and washing the sorbent, Eq. (3) the dose was calculated for static conditions. For calculation of the absorbed dose in the dynamic sorption, we took into account, on average, half the load on the sorbent.

Figure 2 plots the calculated data on the sorbent destruction along the length of the column (2017, Mayak PA); Table 5 shows doses obtained by the sorbent depending on the filling of the column, and Table 6, doses and sorbent destruction during various operations.

The total dose taken by the sorbent is distributed along the height of the column (Table 5, Fig. 2) and it is 5.49 MGy. The sorbent at the top of the column sorbs the maximum dose. The destruction of the sorbent during the actual sorption process (Fig. 2, curve 1) is 7.3%. The total sorbent destruction (curve 2) is 28.8%. The steps on the curve of capacity loss vs. the column length are due to process stops for loading the next portion of the initial solution (the first 4 steps) and the washing the sorbent upon sorption completion (the fifth step). The high absorbed dose taken by the sorbent is due to auxiliary operations when there is no movement of the sorption front along the column. During preparing the solution and washing, the sorbent takes 75% of the total absorbed dose (Table 6).

During elution at the interface between the eluent zone with pH 7–8 and the components to be separated, the impurity elements Fe, Cr, Al, and Ni, in addition to the cationic form, generate hydroxide and metahydroxide forms, which are sorbed by the physical adsorption mechanism, which depends on the size of the sorption surface. Due to the significant sorbent destruction in the upper part of the column, these forms pass into the liquid phase. Under conditions of ionizing

radiation at absorbed doses above  $10^4$  Gy, the system becomes unstable, which leads to the formation of gel-like precipitate blocking the sorption column [16]. In addition, under the action of radiation, the radiation-

**Table 5.** Estimated dose absorbed by the sorbent on the first column vs. the filling

Column filling, %	Absorbed dose $D_{\text{sor}}$ , MGy
0.0	1.55
4.6	2.33
9.3	2.42
13.9	2.51
18.5	2.60
23.2	3.33
27.8	3.42
32.4	3.51
37.1	4.24
41.7	4.33
46.3	4.42
51.0	4.51
55.6	5.24
60.2	5.33
64.9	5.43
70.2	5.49

**Table 6.** Destruction ( $\gamma_{\text{sor}}$ ) and absorbed doses ( $D_{\text{sor}}$ ) generated by the sorbent during various operations (2017)

Operation	Absorbed dose $D_{\text{sor}}$ , MGy	Sorbent destruction $\gamma_{\text{sor}}$ , %
Preparing solution	2.55	13.4
Sorption	1.38	7.3
Washout	1.55	8.1
Total absorbed dose	5.49	28.8

chemical reduction of many metal ions to metallic forms can occur, which brings about the formation of colloidal solutions [17–19], which are unstable under radiation conditions, coagulate, and can also precipitate.

Thus, the locking of the first column is caused by the effect of radiation and the formation of gel-like precipitates due to the sorbent destruction during the sorption.

At elution with a solution of 0.0509 M DTPA, as shown in the experiment carried out in the laboratory (Fig. 3), the cationic forms of iron are mainly washed out before the retaining ion, and the cationic forms of chromium, together with the retaining ion. Aluminum (curve 1, Fig. 3) is washed out in the zone of holmium (curve 2) and TPE. The maximum concentration of aluminum is quite high and amounts to 0.03 M.

Aluminum with DTPA forms two types of monocomplexes: medium of MeA compositions ( $\log K = 18.7$ ) and protonated of MeHA compositions ( $\log K = 4.3$ ) [20–22]. When DTPA is used as eluents, the eluate pH is 2.0–2.2. At this pH value, aluminum is mainly in the form of a protonated complex. At 70°C this complex is highly soluble, and at room temperature it precipitates (amorphous, white precipitate).

In OPKhU-1 setup, the columns were connected with the help of bayonet connections on vacuum hoses. The volume of such connecting lines between the columns was only about 50 mL. When eluates pass through such compounds, they do not have time to cool. In the upgraded OPKhU, the length of each connecting metal line between the columns is over 10 m and the volume is over 2 L. Therefore, in the unheated connecting lines of this OPKhU columns, precipitates of aluminum complexonate is formed, which block the separation columns.

## CONCLUSIONS

The reasons leading to the blocking of columns during the TPE and REE separation from solutions formed after SNF reprocessing are high radiation loads on the sorbent, which are caused by the time of the sorption operation from weakly concentrated solutions (more than 3 days). The sorbent undergoes the main load during auxiliary operations associated with the solution preparation and washings.

To diminish the sorption time and radiation load on the sorbent, it is necessary to prepare sorption solutions

with a REE and TPE concentration of at least 15 g/L and reduce the time of additional operations. If the sorption column is not fully loaded, the nickel form of the cation exchange resin should be used for sorption.

To avoid precipitation of aluminum complexonates, the volume of the connecting lines of the separation columns in the chromatographic installation should be minimized and the lines should be designed with heating.

## CONFLICT OF INTEREST

The authors declare no conflict of interest.

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