



Radiochemical characterization and decontamination of rare-earth-element concentrate recovered from uranium leach liquors

Vladimir N. Rychkov¹ · Vladimir S. Semenishchev² · Evgeny V. Kirillov¹ · Sergey V. Kirillov¹ · Viktoria G. Ryabukhina² · Denis V. Smyshlyaev¹ · Grigory M. Bunkov¹ · Maxim S. Botalov¹

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Abstract

The paper deals with two rare earth elements (REE) concentrates recovered from uranium leach liquors after sorption separation of uranium. Activity of the REE concentrates was found to be 10^6 Bq kg⁻¹; Ac-227 and its short-lived daughter products were the main radioactive impurities contributing more than 99% of total activity. Activity of both U-238 + Th-232 in the REE concentrates did not exceed 0.2% of total activity. Extraction by 2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester (P-507 extractant) in Shelsol D90 diluent was suggested for REE deactivation. It was shown that thorium may be eliminated by extraction in strong acidic media (pH – 0.5 to – 1), whereas radium extraction was suppressed over the whole studied pH range. Further REE separation to heavy and light groups at pH 1 resulted in selective concentration of actinium in light REE group. The suggested separation flowsheet was tested on the real REE concentrate. It was shown that obtaining non-radioactive fraction of heavy REE is possible.

Keywords Rare earth elements · Actinium · Uranium leach liquors · Extraction · 2-Ethylhexylphosphonic acid mono-(2-ethylhexyl) ester

Introduction

It is well known that rare earth elements (REE) and scandium are strategic raw materials in modern industry. Almost all REE are used in production of monocrystals for solid-state lasers, the main of them are neodymium, yttrium, cerium, gadolinium and erbium [1]. Due to their high values of neutron-capture cross-section, gadolinium, erbium, dysprosium, samarium and europium are added to control rods and fuel rods in nuclear reactors [2]. Addition of REE to steel provides cold-, heat- and corrosion-resistance, higher malleability and toughness [3]. REE are used as alloy addition to titanium [4], aluminum [5] and some other nonferrous metals. Samarium-cobalt and

neodymium-iron-boron alloys are widely used for production of permanent magnets for electronics [6]. REE are also used in luminescent materials, sound systems and in medicine as markers [7].

China became the main worldwide manufacturer of REE and scandium since the end of 1980s. Today China is the monopolist of mining, pre-concentration, primary processing, separation of rare earth elements with the production of individual elements and marketable compounds. During last decades, China significantly increased REE using in its own high-tech production resulting in a decrease of export of REE as raw compounds. Therefore, today all developed countries are trying to reconstitute or modernize their own REE production based on new technologies. This resulted in an intensive study on new sources of REE and technologies of their treatment [8]. Many countries draw a special attention to recovery of REE from some industrial waste containing reasonably high amounts of REE [9, 10]. Household waste and electronic scrap are considered to be an alternative potential source of REE [11–13].

✉ Vladimir S. Semenishchev
vovius82@mail.ru

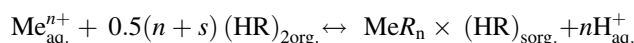
¹ Department of Rare Metals and Nanomaterials, Ural Federal University, 19, Mira Street, Ekaterinburg, Russia 620002

² Department of Radiochemistry and Applied Ecology, Ural Federal University, 19, Mira Street, Ekaterinburg, Russia 620002

Monazite concentrate [14] and industrial products after uranium ores treatment [15, 16] are anthropogenic sources rich in REE. Low REE content and a complex chemical composition are the main problems of REE recovery from poor uranium ores. Therefore, many standard technologies of REE separation and recovery become unsuitable and low productive in these cases [17]. The presence of natural radionuclides of uranium and thorium radioactive chains provides additional problems in technologies of REE recovery from these sources [18, 19]. As a rule, actinium, thorium or uranium may be concentrated together with REE from uranium ores. Decontamination of REE from actinium is a very complex technological problem due to their very similar chemical properties [20].

Liquid–liquid extraction (LLE) is well known as a prospective method for various elements separation [21]. Significant development of LLE was in the middle of twentieth century because of nuclear technologies development. Further intensive studies resulted in ascertainment of the main mechanisms of extraction processes. At present, extraction is one of the most popular hydrometallurgical technologies for commercial separation of elements with similar chemical properties including separation of individual REE [22]. Acidic and neutral monodentate extractants are widely used in industrial processes of REE and scandium recovery due to their commercial availability. Among other, organic phosphorous containing acids (see Fig. 1) are the most effective extractants for REE.

Gupta et al. [23] reported that di(2-ethyl-hexyl) phosphoric acid extracts REE from weak acidic solutions as Ln^{3+} cations due to cation exchange mechanism. Overall, the mechanism can be described as the following reaction:



where n is charge of the cation, s is the quantity of the acid molecules being additionally solvated, $(\text{HR})_2$ is the dimer acid molecule.

A number of examples of organic phosphorous containing acids effective use for REE extraction from multicomponent solutions is described in literature. 2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester (EHEHPA, HEHEHP, P507, PC-88A, Inquest 801) is the most popular extractant used for REE sequential separation; it also was used for Th(IV) elimination and further separation of REE with a high chemical yield from sulfate acidic solutions obtained as a result of recovery of some minerals [24] and permanent magnets [25].

The main goals of this work were to determine the cause of radioactive contamination of the REE concentrates being recovered from uranium leach liquors and to find a method for decontamination of the REE concentrate.

Materials and methods

Obtaining and chemical characteristics of REEs concentrates

A series of experiments on REE sorption from uranium leach liquors after uranium separation is described in our previous work [26]. This paper deals with a REE carbonate immediately after separation from uranium leach liquors (REE concentrate I) and a REE carbonate after primary decontamination from aluminum and iron (REE concentrate II). Chemical composition of the concentrates is given in Table 1.

Radiochemical characterization of REEs concentrates

Radiometric and spectrometric measurement of the REE concentrates were performed 3 weeks after their separation from uranium leach liquors. The following equipment was used for radiochemical measurements:

- NaI(Tl) scintillation gamma spectrometer MKS-AT 1315 (Atomtech, Belarus). 63×63 mm NaI(Tl) detector, 60 keV energy resolution, relative error = 30%, minimal detectable activity (MDA) = 3 Bq.
- Low background alpha beta radiometer UMF-2000 (Dosa, Russia). 450 mm² semiconductor detector, relative error = 15%; beta particles energy range 50–3500 keV, alpha particles energy range 3500–8000 keV; MDA = 0.01 Bq for alpha- and 0.1 Bq for beta-emitters.
- Alpha spectrometer Multirad-AC (Amplituda, Russia). 450 mm² semiconductor surface barrier detector, 40 keV energy resolution, relative error 15%, MDA = 0.01 Bq.

All radionuclides were determined via their alpha and gamma energies using the data given in Karlsruhe Chart of Nuclides [27].

Alpha spectrometric measurements of the REE concentrates were performed in order to prove the presence of Ac-227. We have tried to prepare an alpha source of untreated REE concentrates, but failed because all sources with acceptable activity were too thick due to relatively low activity of the concentrates. So, obtaining of a good quality alpha spectrum with acceptable resolution using raw REE concentrates was impossible. Therefore, we have performed analysis of radium isotopes in the REE concentrate II (as more active product). The concentrate was dissolved in 0.5 M HCl, then pH value was adjusted to 6–7. The solution contacted with a disk of triacetate cellulose with a thin layer of MnO₂ (developed and produced by Department of Radiochemistry and Applied Ecology, Ural

Fig. 1 Structure of phosphorous containing extractants used for REE extraction: di(2-ethyl-hexyl) phosphoric acid (**a**), 2-ethyl-hexyl phosphonic acid mono-2-ethyl-hexyl ester (**b**); di-(2,4,4'-trimethylpentyl)-phosphinic acid (**c**)

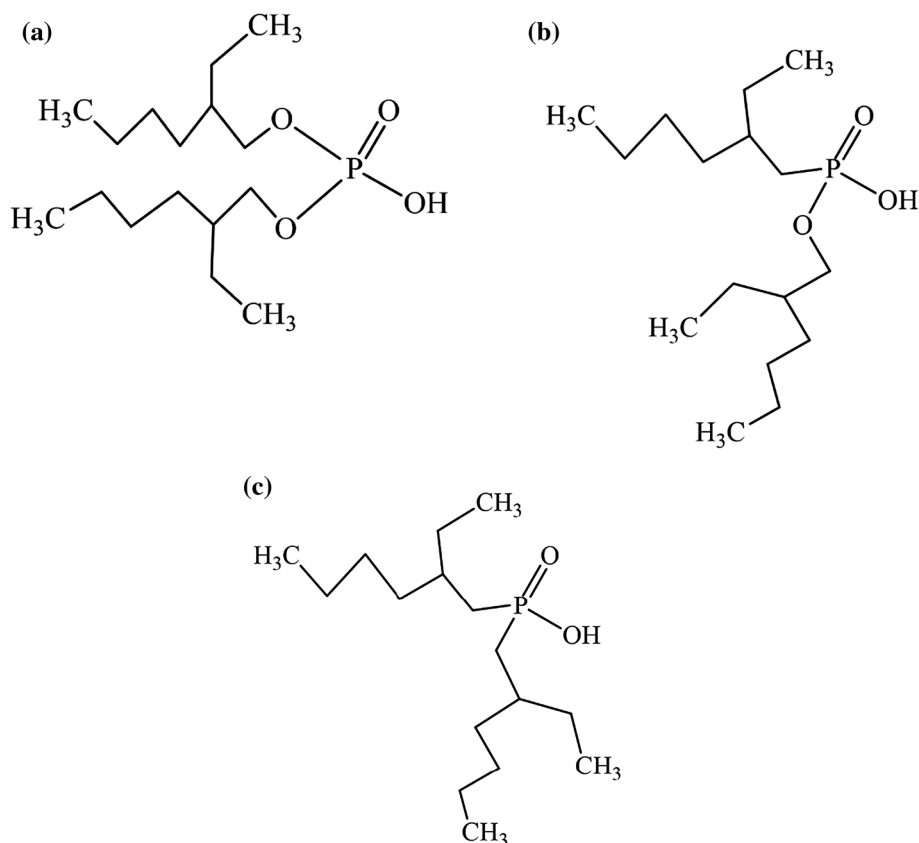


Table 1 Chemical composition of the REE concentrates

	Al ₂ O ₃	CaO	Fe ₂ O ₃	Y ₂ O ₃	ΣLn ₂ O ₃	ThO ₂	UO ₂
Content (%)							
REE concentrate I	17.05	0.16	0.20	2.06	38.57	0.02	0.02
REE concentrate II	0.12	0.65	0.033	2.98	56.81	0.001	0.003

Federal University) for 8 h at a shaker. Manganese dioxide is a well-known selective sorbent for radium, and the thin layer of this compound allows for obtaining good energy resolution of measured alpha spectrum.

The study of REE, Ac, Ra and Th extraction

Behavior of REE and the main radioactive impurities in liquid–liquid extraction was studied using simulated solutions in HCl medium. An extraction system containing 30% of P507 (2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester, see Fig. 1b) in Shelsol D90 diluent was used in all extraction experiments. The influence of pH on distribution of elements was studied at the organic/aqueous phases ratio of 1:1. pH value of the simulated solution before extraction was adjusted by addition of HCl or NaOH. Liquid phases were mixed at room temperature for 30 min; after that, phases were separated using a separating funnel. The aqueous phase was filtered through a paper

filter in order to separate traces of the organic phase and then pH value and chemical composition of the aqueous phase was determined. pH values of solutions were determined using pH-meter Satorius PB-11 (Germany), sensitivity is 0.01 of pH unit. Chemical composition of the aqueous phase was determined by ICP-MS using the spectrometer NexION 350 (Perkin Elmer, USA). Sensitivity of ICP-MS measurements was within 3500–39,000 cps per ppb, detection limit was 6 ng L⁻¹, relative error was within 1–3%.

Extraction behavior of thorium and actinium was studied using Th-234 and Ac-228 short-lived radioactive tracers in order to avoid formation of long-lived radioactive waste as well as to perform easier measurements via gamma spectrometry. Methods of separation of these short-lived tracers are described below. The study of Ra-223 extraction was performed immediately on the REE concentrate II after elimination of Th-227. The organic/aqueous phases ratio in experiments was also 1:1. Activities of

Th-234, Ac-228 and Ra-223 were determined by gamma spectrometric measurements of aqueous solutions before and after extraction in the same measurement geometry using gamma peaks of 91 keV (Th-234), 338 keV (Ac-228) and 269 keV (Ra-223). Elimination of Th-227 from samples containing Ra-223 was necessary because these radionuclides have interfering gamma peaks with similar energies (269 keV for Ra-223 vs. 236 + 256 keV for Th-227).

Dimensionless values of distribution coefficients D and separation factors K_s were calculated in accordance with the Eqs. (1, 2):

$$D = \frac{C_{\text{org}}}{C_{\text{aq}}} \quad (1)$$

$$K_s = \frac{D_{\text{REE}}}{D_i} \quad (2)$$

where C_{org} and C_{aq} are concentrations of a metal ions in organic and aqueous phases respectively; D_{REE} and D_i are distribution coefficients of a REE and a metal respectively.

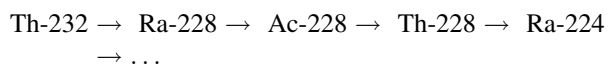
The method of Th-234 separation

Th-234 is a gamma- and beta-emitting daughter of U-238 with the half-life of 24 days. Th-234 was separated from an old uranyl sulfate salt containing pure depleted U-238. Five gram of the dry UO_2SO_4 was dissolved in 50 mL of 3.5 M HCl and passed through a column with KU-2 resin (a strong acid sulfate cation exchange resin based on polystyrene and divinylbenzene copolymer) at the flowrate of 1 mL min^{-1} . After loading, the column was rinsed by 100 mL of 3.5 M HCl at the flowrate of 3 mL min^{-1} in order to eliminate the traces of uranium.

Desorption of Th-234 was performed using a strong oxalic acid solution, controlling the residual activity of Th-234 in the column by gamma spectrometry. Then 10 mL of a mixture of concentrated nitric acid and hydrogen peroxide (1:1) was added to the eluate and evaporated to dryness. This procedure was repeated several times until the complete destruction of oxalates. The final residue was dissolved in 0.5 M HCl under heating.

The method of Ac-228 separation

Ac-228 is a gamma- and beta-emitting daughter of Th-232 with the half-life of 6.13 h. Th-232 decays to Ac-228 in accordance with the following scheme:



Fraction of radium (Ra-228 + Ra-224) was previously separated from an old thorium nitrate salt. Thorium nitrate

was dissolved in water with addition of EDTA; then the solution loaded through a column with T-5 sorbent (granulated hydrated titanium dioxide obtained via sol-gel technology, Termoxid, Russia [28]). In these conditions thorium isotopes (Th-232 + Th-228) were retained on the column, whereas radium isotopes (Ra-228 + Ra-224) remained in the loading solution. Then the solution was evaporated to dryness; the residue was dissolved in 0.05 M HCl, pH was adjusted to 1.7. The solution was stored for a month allowing for complete decay of Ra-224 and its daughters.

The final solution containing only Ra-228 to Ac-228 was used as an actinium generator. After Ac-228 ingrowth, the solution with pH 1.7 loaded through the LN Resin (produced by TrisKem Int., France [29]); in these conditions, actinium is retained on the column, whereas radium remained in the loading solution. Actinium was stripped from the LN resin by a small volume of 0.5 HCl.

Results and discussion

Radiochemical characterization of REEs concentrates

Alpha and beta activities of REE concentrates were measured in a thin layer using the alpha-beta radiometer UMF-2000 3 weeks after the separation of the concentrates. The results are given in Table 2.

This can be seen that REE concentrates have too high activity; they do not meet technical requirements for primary REE concentrates (activity should not exceed 10^3 Bq kg^{-1}), therefore deactivation of the concentrates with a decontamination factor of at least 6×10^3 is necessary. A higher activity of the REE concentrate II as compared with the REE concentrate I was condition by the fact that the primary decontamination resulted in elimination of aluminum and iron (and weight reduction) without any deactivation.

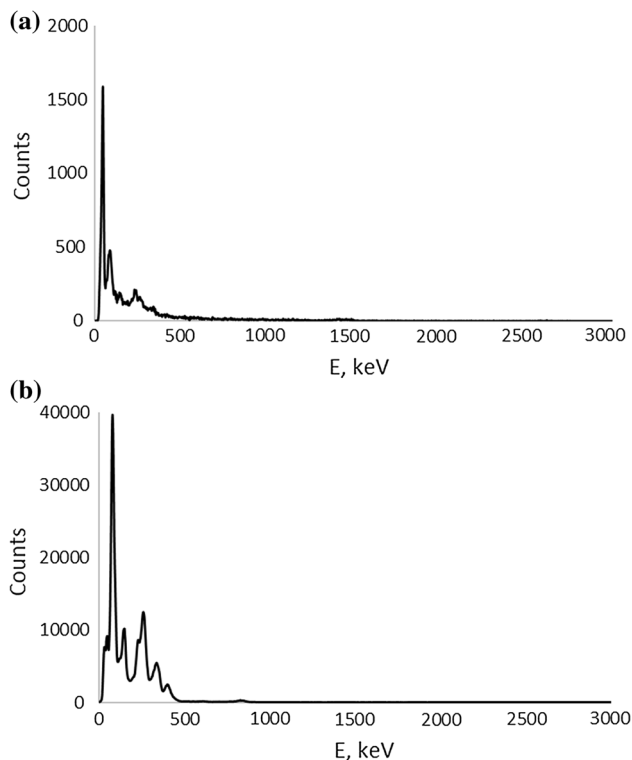
Determination of isotopic composition of the REE concentrates was necessary for development of a deactivation technology. The methods of gamma spectrometry and alpha spectrometry were used for determination of radionuclides. Untreated samples of the REE concentrate I (0.3 g) and REE concentrate II (4 g) were measured on the NaI(Tl) scintillation gamma spectrometer. The obtained gamma spectra of the REE concentrates are presented at Fig. 2.

The results of gamma spectrometry have shown that:

- Peaks at 236 and 269 keV corresponding to Th-227 and Ra-223 (daughters of Ac-227, a long-lived daughter of U-235) respectively were found. A high activity of

Table 2 Alpha and beta activities of REE concentrates

No.	Sample	Activity (Bq kg^{-1})		Total activity (Bq kg^{-1})
		Alpha	Beta	
1	REE concentrate I	$(1.0 \pm 0.2) \times 10^6$	$(1.0 \pm 0.2) \times 10^6$	$(2.0 \pm 0.2) \times 10^6$
2	REE concentrate II	$(4.0 \pm 0.6) \times 10^6$	$(1.8 \pm 0.3) \times 10^6$	$(5.8 \pm 0.7) \times 10^6$

**Fig. 2** Gamma spectra of the REE concentrate I (a) and REE concentrate II (b)

short-lived daughters in a relatively old product indicates to the presence of their mother radionuclide Ac-227, that can be easily explained by very similar chemical properties of REE and actinium. In addition, according to the literature data [30], the gamma peak at 81 keV corresponds to Ac-227; however, using this gamma peak for analysis is not reliable, because it is very similar to characteristic X-ray radiation of heavy elements such as uranium and thorium.

- No significant gamma peaks of Pb-214 (295 keV), Bi-214 (609 keV), Pb-212 (239 keV) and Tl-208 (585 and 2614 keV) were found in gamma spectra of the REE concentrates. This indicates the very low activity of radium isotopes (Ra-226, Ra-224, daughters of U-238 and Th-232 respectively) in the concentrates. Therefore, the sorption technology of REE recovery from uranium leach liquors allows for eliminating radium isotopes.

The obtained alpha spectrum of radium fraction from the REE concentrate II is presented at Fig. 3.

The following alpha peaks corresponding to Ra-223 and its short-lived daughters were found in the radium fraction separated from the REE concentrate II: 5.60–5.71 MeV (Ra-223), 6.63 MeV (Bi-211), 6.82 MeV (Rn-219), 7.4 MeV (Po-215). Other alpha-emitting daughters of Ra-223 (At-215 and Po-211) were not found due to their very low yield in the U-235 radioactive chain (2.5×10^{-4} and 0.32% respectively).

According to the content of uranium and thorium (as chemical impurities) given in Table 1, activities of U-238 and Th-232 were calculated. These values are given in Table 3.

The most publication concerning REE recovery from radioactive industrial sources usually consider that radioactive contamination of REE is conditioned by the presence of uranium and thorium [22, 31–34]. However, the results of alpha and gamma spectrometry as well as the data from Tables 2 and 3 show that activity of U-238 and Th-232 did not exceed 0.2 and 0.01% of the total activities of the REE concentrates I and II respectively. All results indicate that Ac-227 and its daughter products have given the main contribution to activity of the REE concentrates. Recovery of actinium together with REE can be easily explained by their similar chemical properties.

Thus, decontamination of the REE concentrates from Ac-227 is the necessary procedure, since Ac-227 is a quite long-lived radionuclide (half-life is 21.77 years [27]) and it comes to radioactive equilibrium with its daughter products only for 2–3 months. Besides Ac-227, elimination of radium isotopes seems to be very desirable, because the long-lived Ra-226 was found in the radium fraction (Fig. 3). Finally, Th-227 separation is desirable too; otherwise, storage of the REE concentrate during 2–3 months will be required for Th-227 total decay.

The study of REE, Ac, Ra and Th extraction

As it was shown above, actinium, radium and thorium were the main radioactive elements contributing to radioactivity of the REE concentrates. Extraction by the 2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester (P-507) was chosen for separation of these elements from the REE concentrates.

Fig. 3 Alpha spectrum of radium separated from the REE concentrate II (counting time was 16,000 s)

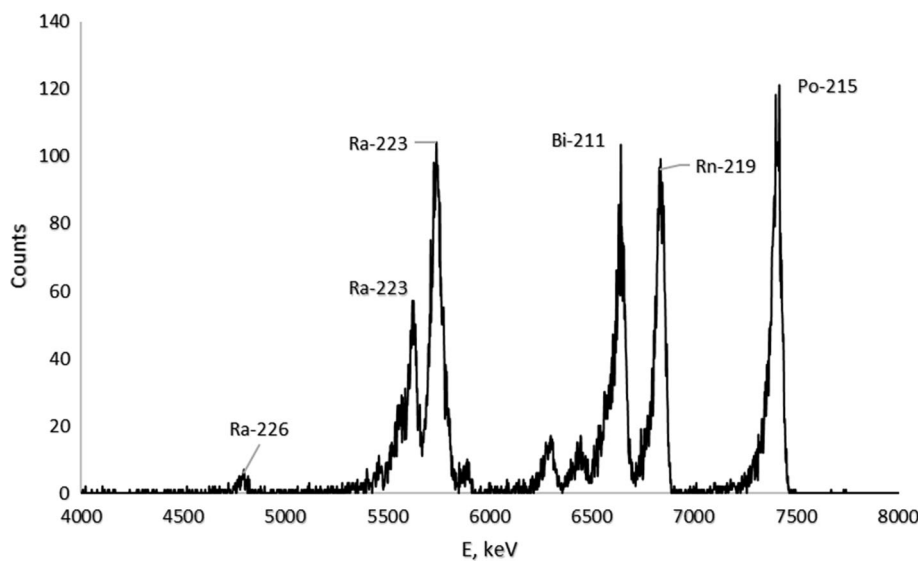
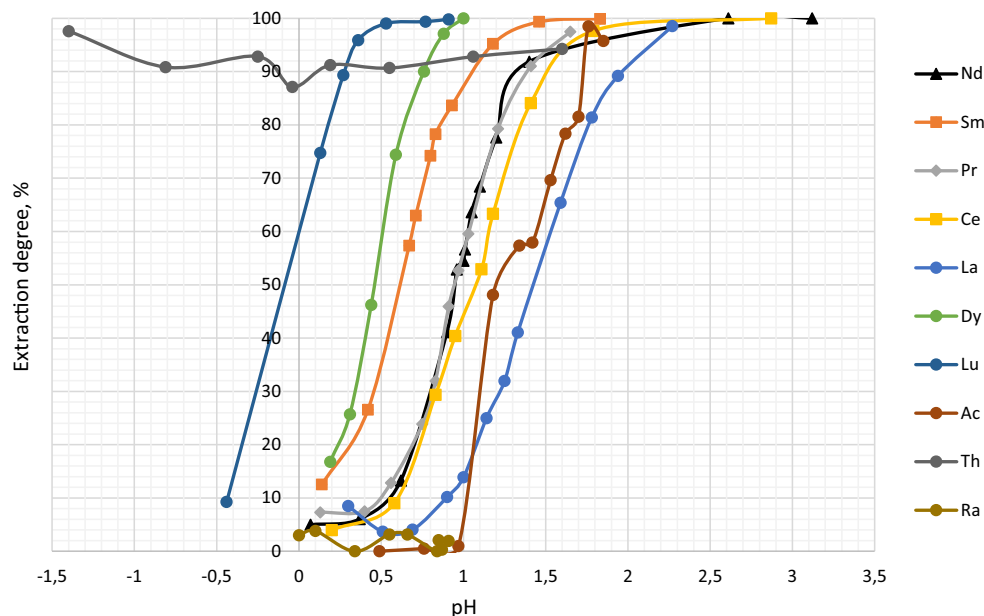


Table 3 Calculated activities of U-238 and Th-232 in the REE concentrates

Sample	A (U-238) (Bq kg ⁻¹)	A (Th-232) (Bq kg ⁻¹)	A _Σ (Bq kg ⁻¹)
REE concentrate I	2500	1700	4200
REE concentrate II	370	80	450

Fig. 4 pH dependences of extraction of selected elements by the P-507 extractant in HCl media



The dependences of extraction of selected REE as well as for radium, actinium and thorium by the P-507 extractant on pH value from HCl media are given at Fig. 4. Among REE, representatives of light (La, Ce, Pr, Nd) and heavy (Sm, Dy, Lu) REE were tested.

The results have shown that S-curves were typical for all REE and actinium; the dependences drifted to more acidic pH ranges for heavier REE. pH dependence of actinium

extraction was very similar to that obtained for lanthanum. Thus, it could be expected that REE separation to light and heavy fraction in Nd/Sm line will result in actinium concentration in the light group. For example, at pH 1 extraction degree for actinium was near to 0, whereas it was $\approx 90\%$ for samarium and almost 100% for dysprosium and lutetium.

At the same time, extraction behavior of thorium and radium significantly differed from behavior of REE and actinium. Radium extraction was very low over the whole studied pH range (0–1), whereas thorium extraction was very high (87–97%) at the pH range of – 1.4 to 1.6. This can be explained by different charges of extracting ions Ra^{2+} , Ln^{3+} and Th^{4+} . Thus, it is obvious that extraction of various cations by the P-507 extractant from HCl media increases in the series: $M^{2+} < M^{3+} < M^{4+}$.

Table 4 gives distribution coefficients for studied elements as well as separation factors for Ac/REE calculated for pH 1.

The data given in Table 4 and Fig. 4 have shown that strong acidic medium (at pH – 0.5 to – 1.0) should be suitable for thorium elimination. In these conditions thorium was extracted well, whereas extraction of all other elements was strongly suppressed by hydrogen ions. There is a very limited number of works concerning extraction behavior of actinium in presence of REE. Szełowski and Kubica [35] studied the effect of concentration of lanthanum, neodymium and samarium on actinium extraction by di-(2-ethylhexyl)phosphoric acid in n-hexane as a diluent. The results of this work show that all REE suppress actinium extraction in equal degree; however, Ac/REE separation is not studied in this work. Mikhailychenko et al. [36] suggested an extraction scheme for Ac/La separation mixture of trialkylmethylammonium nitrate and tributyl phosphate. It is shown that pure tributyl phosphate

does not provide Ac/La separation at all; use of pure trialkylmethylammonium nitrate results in separation factors of 2.30–2.38; whereas, use of mixture of these extractants allows increasing Ac/La separation factor up to 3.55. Considering the possibility of organizing extraction cascade, this value is enough for commercial separation of actinium and lanthanum. However, there are two reasons why the results of this study are not applicable in our case. The first one is that the study is performed on micro-amounts of radioisotopes La-140 and Ac-227; whereas, our REE concentrate contains elevated amounts of REE. The second reason is that extraction of La-140 and Ac-227 is studied from 3 M NH_4NO_3 solutions. Use of chloride media in Ac/REE separation looks preferable than nitrate media because nitric acid is more expensive than hydrochloric acid. Furthermore, data from Table 4 showed that P-507 in chloride media provide higher Ac/REE separation factors.

Since actinium shows extraction behavior very near to light REE, especially to lanthanum and cerium, we decided that the easiest way of REE decontamination is to separate REE to heavy and light groups. We expected that actinium will be concentrated in LREE, whereas HREE will not be radioactive. This is reasonable from the economical point of view because HREE cost significantly more than LREE (see Table 5).

The following flow sheet for REE deactivation (Fig. 5) was suggested using all considerations described above.

Table 4 Values of D for Ac, Ra and selected REE and Ac/REE separation factors calculated for pH 1

Element	Ac	Ra	La	Ce	Pr	Nd	Sm	Dy	Lu
D	0.011	0.20	0.16	0.68	1.11	1.20	5.1	33.2	505.3
Ks (REE/Ac)	–	–	15	61	100	108	461	2992	45,547
Ks (REE/Ra)	–	–	0.8	3.4	5.7	6.1	26	169	2569

Table 5 Prices for rare earth metals (31.12.2017). Reproduced with Permission from [37]

Element	Price for metal ($\geq 99.9\%$), USD/kg	Price for oxide ($\geq 99.5\%$), USD/kg
Mischmetal	6.00	–
Light rare earth metals		
Lanthanum	7.00	2.00
Cerium	7.00	2.00
Praseodymium	85.00	52.00
Neodymium	62.00	42.00
Samarium	7.00	No data
Heavy rare earth metals		
Europium	No data	150.00
Gadolinium	55.00	32.00
Terbium	550.00	400.00
Dysprosium	350.00	230.00
Erbium	95.00	34.00

Extraction tests on the real REE concentrate sample

The conceptual flowsheet was tested on the REE concentrate (II) in order to check workability of the method. A sample of the REE concentrate (II) was dissolved in concentrated HCl and then diluted by water in order to achieve pH = 0.5. Chemical composition of the solution is given in Table 6.

Extraction of Th-227 was performed at pH -0.5, volume of aqueous phase was 50 mL, volume of the P-507 extractant was 10 mL. Time of phases contact was 30 min. After Th-227 separation, the raffinate was adjusted to pH 1

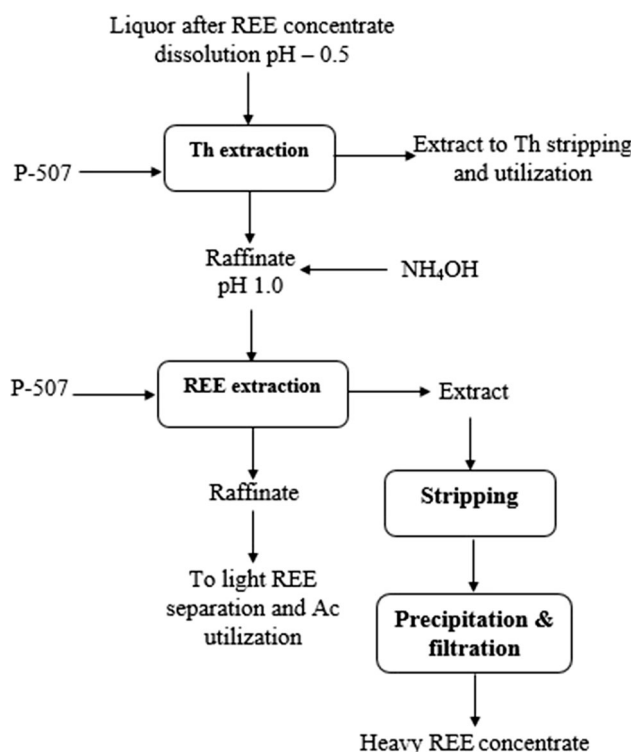


Fig. 5 The conceptual flow sheet for REE deactivation

Table 6 Chemical composition of the solution obtained from the REE concentrate (II)

Light REE		Heavy REE		Other	
Element	Concentration (ppm)	Element	Concentration (ppm)	Element	Concentration, (ppm)
La	5510	Eu	329	Y	2971
Ce	15,968	Gd	1265	Sc	104
Pr	1984	Tb	128	Th	0.5
Nd	8507	Dy	668	U	18
Sm	1527	Ho	97		
		Er	275		
		Tm	25		
		Yb	155		
		Lu	20		

by concentrated ammonium hydroxide solution. Extraction of heavy REE was performed at the same conditions, but volume of aqueous phase was 60 mL because of ammonium hydroxide addition. pH of the aqueous phase was controlled and adjusted during extraction; at the end of extraction, pH value was 1.08. After each stage of extraction, 10 mL of organic and aqueous phases were sampled for gamma spectrometric measurements and 1 mL of aqueous phase was sampled for elemental analysis by ICP-MS. Figure 6 shows gamma spectra of the initial solution, extractant after Th-227 extraction, raffinate after heavy REE extraction and extractant with heavy REE. All samples were measured at equal conditions. Figure 7 shows extraction degrees of REE at two extraction stages.

The results have shown that the suggested flowsheet is quite workable. Almost all Th-227 (> 98%) was extracted at pH = 0.5, whereas Ra-223 and the main part of Ac-227 remained in the raffinate after two stages of extraction at pH = 0.5 and pH 1. The extract with heavy REE contained only traces of Th-227 and probably Ac-227. As it can be seen at Fig. 7, extraction degrees for all REE were lower than in experiments with simulated solutions containing pure REE (Fig. 4). This can be explained by mutual competitive interference of all REE at the conditions of limited extraction capacity. This phenomenon agrees well with data from the article of Szegełowski and Kubica [35] in which they reported that presence of La, Nd and Sm suppresses extraction of actinium.

Based on the results of the experiment with the real REE concentrate, distribution coefficients for REE as well as separation factors for REE/Th at pH = 0.5 were calculated (see Table 7). Distribution coefficient for Th-227 was found to be 5.1.

Two problems of this flowsheet were found. The first one is that a significant percent of heavy REE (Er–Lu) will be lost after Th-227 extraction at pH = 0.5. The second problem is that only partial LREE/HREE separation was achieved as a result of single extraction. Nevertheless, it

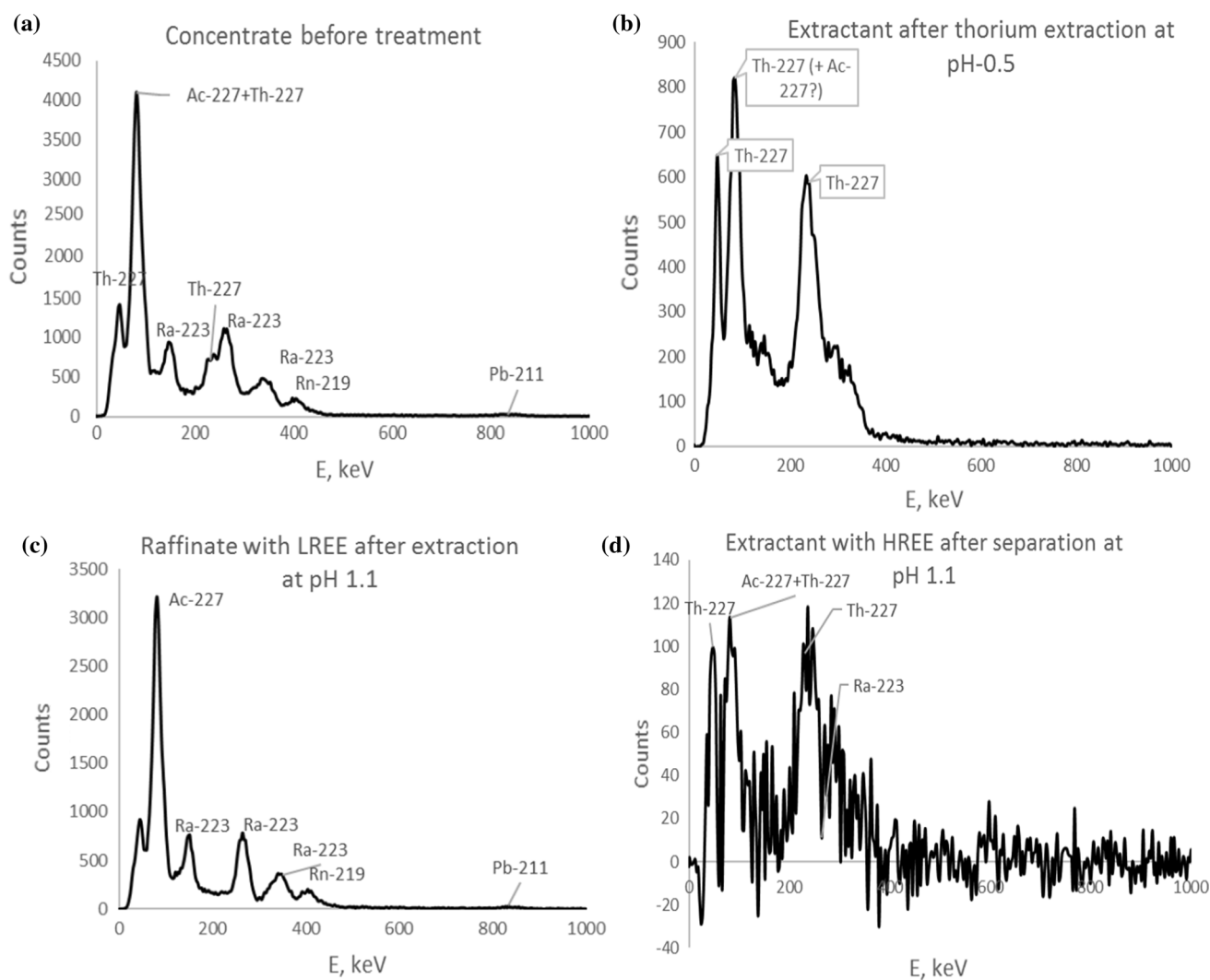


Fig. 6 Gamma spectra of the initial solution (a), extractant after Th-227 extraction (b), raffinate after heavy REE extraction (c) and extractant with heavy REE (d). Counting time was 300 s for (a), (b), (c) and 3000 s for (d). Background was deducted from the spectrum (d)

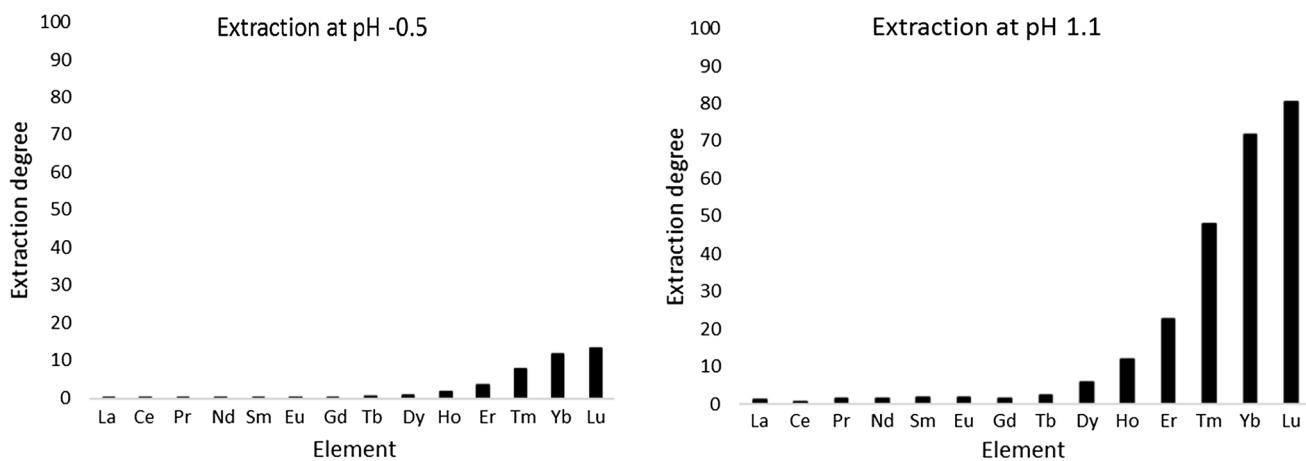


Fig. 7 Extraction degrees (%) of lanthanides by P-507 at pH – 0.5 and pH 1.1 in HCl media

Table 7 Distribution coefficients for REE and separation factors for REE/Th at pH = 0.5

Element	La	Ce	Pr	Nd	Sm	Eu	Gd
D	0.015	0.004	0.008	0.016	0.01	0.015	0.018
K _s (REE/Th)	329	1193	665	308	527	347	283
Element	Tb	Dy	Ho	Er	Tm	Yb	Lu
D	0.023	0.05	0.096	0.19	0.43	0.67	0.77
K _s (REE/Th)	222	100	52	27	12	7.5	6.6

should be noted that a multistage extraction should result in good separation even if separation factors are low. Thus, it could be expected that both problems will be dissolved by organizing multistage extraction in cascade. As for the first problem, alternatively it is possible to exclude the stage of Th-227 separation in order to prevent the loss of heavy REE. In this case storage of the heavy REE fraction for 2–3 months will be required.

Conclusions

Radiochemical characterization of the REE concentrates obtained from uranium leach liquors was performed in the work. It was shown that total activity of the REE concentrates was 10^6 Bq kg⁻¹ due to the presence of Ac-227 and its short-lived daughter products.

Extraction of REE, radium, actinium and thorium by the P-507 extractant from hydrochloric acid was studied using simulated solutions. It was shown that REE separation to heavy and light groups at pH 1 resulted in selective concentration of actinium in light REE group. The conceptual flow sheet for REE deactivation was suggested.

The suggested separation scheme was tested as single extraction scheme on the REE concentrate. It was shown that actinium is concentrated in fraction of light REE, whereas fraction of heavy REE contained only traces of Th-227. It could be expected that pure separation is possible by organizing multistage extraction in cascade.

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