

Separation of Rare Earth Elements in the Tributyl Phosphate– Ln(NO₃)₃–Ca(NO₃)₂ System in the Counter Current Process

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Abstract—The 40-step extraction process to separate rare earth elements (REEs) according to the praseodymium–cerium line with the use of mixer–settler extractors in a 100% TBP–Ln(NO₃)₃–Ca(NO₃)₂ system is implemented. A lanthanum–cerium concentrate containing less than 0.03 wt % of the remaining REEs is obtained. The flow diagram of the separation process of a rare earth (RE) concentrate isolated from phosphogypsum is considered.

Keywords: extraction, phosphogypsum, rare earth elements, tributyl phosphate, calcium nitrate, extraction cascade, separation coefficient

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The waste product from processing apatite by the sulfuric acid technology, phosphogypsum, may become a source of rare earth (RE) concentrates. Phosphogypsum contains 0.3–0.6% rare earth elements (REEs) (as oxides), admixtures of fluoride and phosphate ions, as well as iron, aluminum, titanium, and thorium cations. To isolate REEs from phosphogypsum, various technical solutions were suggested [1–4], which were mainly based on leaching REEs by a mineral acid and keeping the main mass of phosphogypsum in the solid phase. Quite a high degree of recovery was achieved when leaching REEs by a solution containing 300 g/dm³ calcium nitrate and 1 mol/dm³ nitric acid [5]. After isolating REEs from phosphogypsum, the separation of all of the REEs into concentrates is assumed. It seems reasonable to further separate REEs using calcium nitrate or a melt of calcium nitrate, the waste product of processing apatite by the nitric acid technology, as the leaching agent. In this article, the results of studies on separating an RE concentrate on a 40-step counter current reactor in the counter current mode via extraction with 100% tributyl phosphate (TBP) are presented.

EXPERIMENTAL

The extraction process was carried out according to a standard procedure by shaking the aqueous and organic phases in a separatory funnel at 22 ± 2°C. The counter current process was fulfilled on a 40-step mixer–settler extractor with the volume of one step of

0.6 dm³. Technical TBP (TU 2435-305-05763458-2001) was used as the extracting agent. The reagents were nitric acid, calcium nitrate, sodium carbonate, ammonium hydroxide, barium nitrate, sulfuric acid, and oxalic acid (all chemically-pure grade). The total concentration of the REEs was determined via the sedimentation of REE oxalates followed by annealing at 800–850°C to oxides, and the concentration of individual elements was determined on an iCAP 6300 Duo optical emission spectrometer with inductively coupled plasma. Carbonates of the RE concentrate isolated from phosphogypsum (AO Voskresenskie mineral'nye udobreniya) were used for the study (Table 1).

When processing apatite by the sulfuric acid technology, up to 20% thorium and the main mass of radium remain in the phosphogypsum [6]. Phosphogypsum is more radioactive than the wet-process phosphoric acid. During recrystallization, radioactive admixtures are distributed between the purified phosphogypsum and the solution of calcium nitrate. The RE concentrate isolated from the solution by leaching contains admixtures of iron, aluminum, titanium, and partially radioactive products of the decay of the thorium series. The total activity of the isolated REE carbonates was 700–1500 Bq/kg.

The concentrate was dissolved in nitric acid to obtain solutions containing 150–200 g/dm³ REEs (oxides) and 0.05–0.1 mol/dm³ nitric acid. Thorium, together with the decay products, was isolated accord-

Table 1. Composition of RE concentrate isolated from phosphogypsum (wt %)

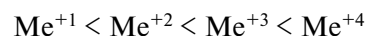
Compound	Concentration, wt %	Compound	Concentration, wt %
CeO ₂	46.4	Ho ₂ O ₃	0.17
La ₂ O ₃	22.7	Tb ₂ O ₃	0.24
Nd ₂ O ₃	15.4	Yb ₂ O ₃	0.13
Pr ₆ O ₁₁	4.4	Er ₂ O ₃	0.32
Sm ₂ O ₃	2.37	Tm ₂ O ₃	0.03
Gd ₂ O ₃	1.79	Lu ₂ O ₃	0.012
Dy ₂ O ₃	1.04	Y ₂ O ₃	4.40
Eu ₂ O ₃	0.67	—	—

Table 2. Redistribution of REEs during purification from radioactive admixtures

Element	Concentration, wt %		Ln _s /Ln _p ratio
	precipitate	solution	
La	14.55	28.77	1.97
Ce	53.34	50.80	0.93
Pr	5.89	5.56	0.94
Nd	19.31	19.09	0.98
Sm	3.39	2.84	0.83
Eu	0.97	0.83	0.85
Tb	0.33	0.26	0.78
Dy	1.79	1.26	0.70
Ho	0.27	0.20	0.74
Er	0.60	0.40	0.66
Tm	0.07	0.036	0.51
Yb	0.39	0.15	0.38
Th	3.47	3 × 10 ⁻⁴	—

ing to the known procedure [7]. Ammonium sulfate (up to 2.1–2.5 g/dm³) was added to the solution, and barium nitrate (up to the concentration of 2 g/dm³) and ammonium hydroxide were introduced until the pH reached 3.3–3.6. The precipitate of thorium hydroxosulfates and coprecipitated REEs was separated by filtration. The concentration of REEs in the purified solution and precipitate is presented in Table 2. As is seen from the obtained results, the concentration of thorium in deactivated solutions decreases to 3 × 10⁻⁴ wt %. According to the requirements of radiation safety standards (RSSs) [8], such solutions can be handled without special protection measures. It should be noted that REEs are redistributed between the precipitate and the solution in accordance with the value of the pH of the precipitation of the corresponding elements; i.e., the precipitate is expectedly

enriched with the elements of the yttrium group. The ratio of the concentration of individual REEs in the precipitate to the concentration in the purified solution ($K = [Ln]_s/[Ln]_p$) decreases from lanthanum to lutetium, which corresponds to an increase of the basicity and decrease in the pH of precipitation in the lanthanide series. Since calcium nitrate is used for leaching REEs from phosphogypsum, it is reasonable to further separate REEs using calcium nitrate as the leaching agent. Note that when the leaching agent is changed, the efficiency of separating the neighboring REEs increases in series



with a decrease in the size of the cation [9]. In this series, calcium nitrate is more efficient than ammonium nitrate but is inferior to aluminum nitrate with respect to the leaching capacity. The number of steps at the extraction stage was calculated according to the formula [9]:

$$n = \frac{\log[q(\beta(1 - X_0\Gamma) - 1)/\beta(1 - X_0\Gamma)]}{\log[\beta(1 - X_0\Gamma)]}, \quad (1)$$

where X_0 is the relative total concentration of cerium and lanthanum in the initial mixture, q is the enrichment factor ($q = X_n(1 - X_0)/X_0(1 - X_n)$), where X_n is the relative concentration of cerium and lanthanum in the aqueous phase of the raffinate, Γ is the extraction, i.e., the fraction of the pure component of the initial amount introduced into the system which remains in the raffinate or extract, and β is the separation coefficient of praseodymium and cerium.

Figure 1 shows the number of steps required to be installed in the raffinate section of the cascade depending on the required purity of the raffinate and the separation coefficient of praseodymium and cerium. The material balance of the distribution of REEs by the currents of the separation cascade at the separation coefficient $\beta_{Pr/Ce} = 1.7$ and extraction $\Gamma = 0.33$ is presented in Fig. 2.

REEs were separated on a 40-step mixer-settler extraction cascade with the mechanical stirring of the phases. The volume of the mixing and settling chambers was 100 and 500 cm³, respectively. As the extracting agent, 100% TBP was used. The initial solution contained 300 g/dm³ RREs (calculated as oxides), 280–300 g/dm³ calcium nitrate, and 0.05–0.1 mol/dm³ nitric acid. The separation was carried out according to the praseodymium–cerium line in order to obtain lanthanum and cerium with the concentration of the rest of the RE impurities being less than 0.05 wt %. The latter requirement is explained by the need to further isolate pure cerium oxide with the concentration of the main substance of not less than 99.9%. Table 3 presents the distribution of REEs in the aqueous phase by the compartments of the cascade. The ratio of the organic and aqueous phases ($V_o : V_a$) was maintained

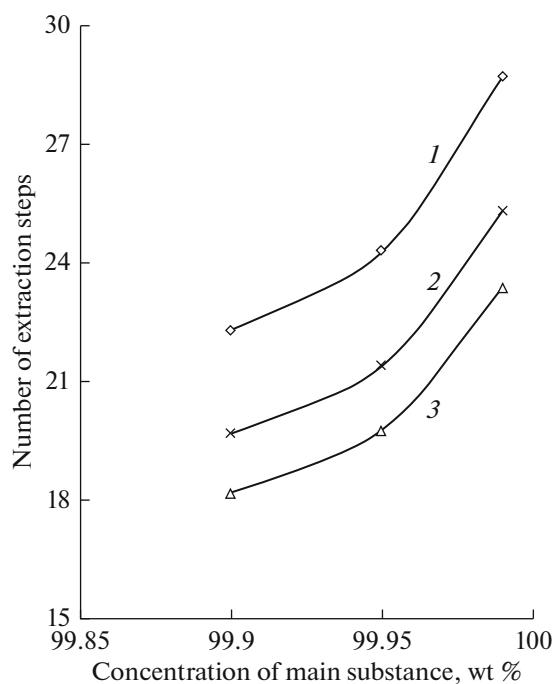


Fig. 1. Number of steps required for preparation of product with specified quality (X_n) depending on separation coefficient of praseodymium and cerium: (1) $\beta = 1.7$, (2) $\beta = 1.8$, and (3) $\beta = 1.9$.

at 1.64 : 1. The calculated concentration of the REEs in the raffinate was 56–60 g/dm³. In the organic phase, the sum of the REEs, including the praseodymium, neodymium, and yttrium elements was concentrated. Calcium and strontium were recovered insignificantly with the distribution coefficient of 0.005–0.008. In the raffinate, a lanthanum–cerium concentrate containing less than 0.03% other REEs was obtained. As a result of the experiments carried out under static conditions, it was found that the separation coefficient of praseodymium and cerium varies within the range of 1.7–1.9.

Table 4 presents the results of the calculation of the distribution of REEs by the compartments of the cascade in the mode of complete internal irrigation with extraction $\Gamma = 0$ and at various values of the separation coefficient $\beta_{Pr/Ce}$. The total concentration of cerium

and lanthanum in the initial solution was 45.17% (A), while the total concentration of the praseodymium, neodymium, and yttrium REEs was 54.83% (B).

It is seen that 14–15 steps are sufficient for the formation of the zone of separation of praseodymium and cerium at $\beta_{Pr/Ce} = 1.9$, while the number of steps increases to 20–24 with the decrease in the separation coefficient to 1.5. In the mode of the complete counter current with the real value of extraction, the number of steps increases in accordance with formula (1) but the character of the formation of the separation zone persists. When Tables 3 and 4 are compared, it is seen that the calculated distribution of the REEs agrees with the experimental distribution to the best extent at $\beta_{Pr/Ce} = 1.7$, which confirms the earlier assumptions. It was found that the selectivity of separating praseodymium and cerium increases with a decrease in the concentration of praseodymium from macroconcentrations to microconcentrations (Table 5), which is explained by the leaching effect of the lanthanum and cerium nitrates.

The raffinate solution contains 50–60 g/dm³ lanthanum and cerium and 300 g/dm³ calcium nitrate. REE nitrates can be recovered on five steps via extraction with 100% TBP and then reextracted on five steps with acidified water (0.1–0.3 mol/dm³ HNO₃). In the presence of a leaching agent, distribution coefficients increase sharply with the decrease in the concentration of REEs (Fig. 3), which promotes complete recovery in five steps. In the raffinate, the solution of calcium nitrate contains less than 0.1 g/dm³ REEs and can be returned to the step of preparing the initial solution for the preparation of new portions of a RE concentrate.

During the separation, a concentrate of lanthanum and cerium containing less than 0.03 wt % of the remaining REEs was obtained. In the following stage, it is planned to prepare cerium oxide with the concentration of the main substance of 99.9% from the prepared product via extraction. The flow diagram of the process of separating the cascade is presented in Fig. 4. The complete counter current cascade includes the extraction and washing sections. It is planned to wash the extract saturated up to 150–160 g/dm³ with respect to the REE oxides in the counter current mode using

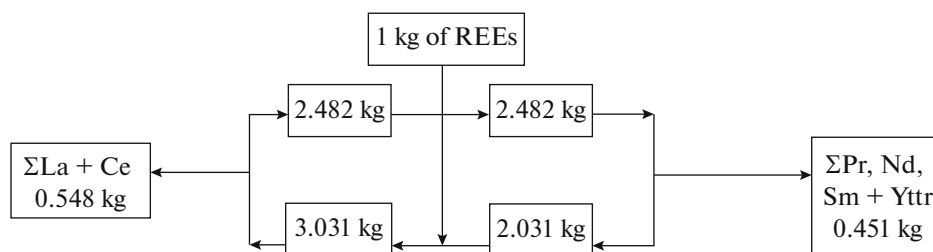


Fig. 2. Distribution of REEs by currents of separation cascade.

Table 3. Distribution of elements by steps of counter current cascade (organic phase was introduced in 1st step; and aqueous phase, in 40th step)

Element	Number of chamber							
	1	7	10	14	21	25	30	40
	Concentration of REEs in aqueous phase, g/dm ³							
Lanthanum	24.78	53.01	51.28	53.28	50.3	52.14	49.76	50.22
Cerium	18.05	134.8	137.9	143.3	132.7	139.2	130.1	112.8
Praseodymium	<0.1	<0.1	<0.1	0.2	0.242	0.957	2.836	11.88
Neodymium	1 × 10 ⁻⁴	1 × 10 ⁻⁴	1 × 10 ⁻⁴	1 × 10 ⁻⁴	1 × 10 ⁻⁴	0.02	0.047	17.14
Samarium	1 × 10 ⁻⁴	1 × 10 ⁻⁴	1 × 10 ⁻⁴	1 × 10 ⁻⁴	1 × 10 ⁻⁴	0.01	0.56	1.291
Europium	1 × 10 ⁻⁴	1 × 10 ⁻⁴	1 × 10 ⁻⁴	1 × 10 ⁻⁴	1 × 10 ⁻⁴	1 × 10 ⁻⁴	0.14	0.351
Gadolinium	2 × 10 ⁻⁴	2 × 10 ⁻⁴	2 × 10 ⁻⁴	2 × 10 ⁻⁴	2 × 10 ⁻⁴	0.02	0.49	1.189
Yttrium	2 × 10 ⁻⁴	2 × 10 ⁻⁴	2 × 10 ⁻⁴	2 × 10 ⁻⁴	2 × 10 ⁻⁴	0.09	0.75	1.969
Calcium	92.1	68.180	68.27	70.41	67.69	69.92	66.89	71.8
Strontium	1.519	1.195	1.206	1.237	1.206	1.237	1.183	1.258

Table 4. Distribution of elements, wt %, by steps of counter current cascade calculated for mode of complete internal irrigation

Number of steps (n)	$\beta_{Pr/Ce}$							
	1.9		1.8		1.7		1.5	
	A	B	A	B	A	B	A	B
2	60.9	39.1	59.72	40.28	58.3	41.7	11.0	89.0
4	84.9	15.1	82.73	17.27	80.1	19.9	75.0	26.5
6	—	—	93.94	6.06	92.0	8.0	86.2	13.8
8	98.6	1.4	98.05	1.95	97.1	2.9	93.36	6.64
10	99.62	0.38	99.39	0.61	98.97	1.03	96.93	3.07
12	99.894	0.106	99.81	0.19	99.64	0.36	98.61	1.39
14	99.992	0.008	99.94	0.06	99.87	0.13	99.30	0.70
16	99.998	0.002	99.98	0.02	99.978	0.03	99.72	0.28
18	99.999	0.001	99.994	0.006	99.985	0.015	99.87	0.13
20	—	—	99.998	0.002	99.995	0.005	99.94	0.06

A is concentration of cerium and lanthanum and B is concentration of praseodymium, neodymium, and yttrium REEs, wt %.

Table 5. Change in selectivity of separation by steps of cascade

Separation coefficient	Steps of cascade						
	1	7	10	14	21	25	30
$\beta_{Ce/La}$	2.15	2.65	2.77	2.71	2.7	2.62	2.59
$\beta_{Pr/Ce}$	1.82	1.80	1.92	1.70	1.65	1.63	1.63
Concentration of Pr, wt %, in aqueous phase	8 × 10 ⁻³	0.039	0.081	0.23	1.31	3.17	7.08

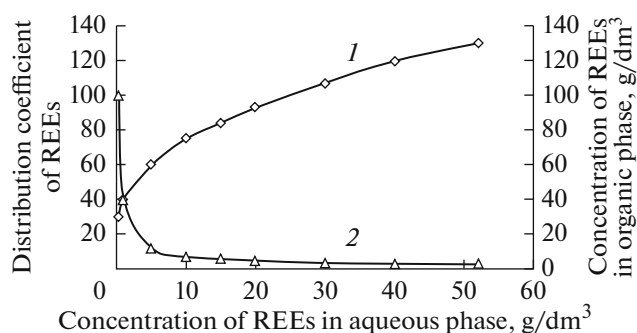


Fig. 3. (1) Isotherm of extraction and (2) change in distribution coefficient during extraction of REE nitrates with 100% TBP from solution of calcium nitrate (300 g/dm³).

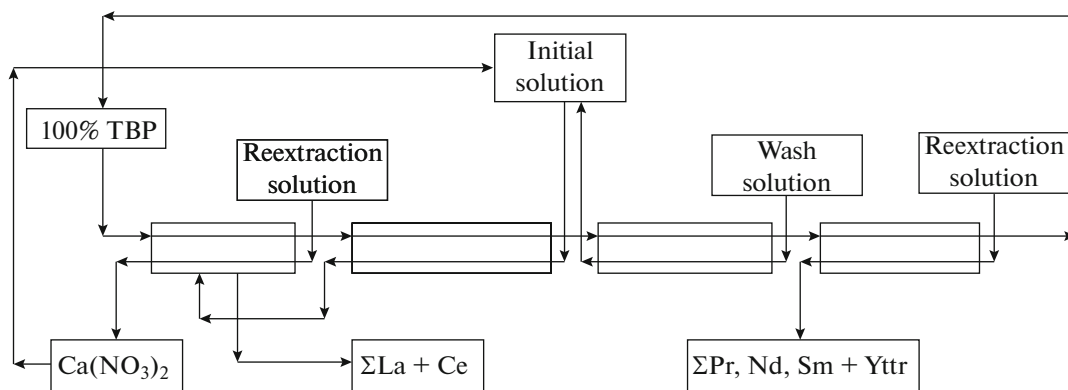


Fig. 4. Flow diagram of separation process of RE concentrate isolated from phosphogypsum.

some concentrated reextract to prepare praseodymium + neodymium + yttrium REE fractions containing less than 0.01 wt % lanthanum and cerium, followed by the isolation of didymium with a purity of 99.95%.

CONCLUSIONS

(1) A 40-step extraction process of separating REEs isolated from phosphogypsum has been fulfilled in a 100% TBP–Ln(NO₃)₃–Ca(NO₃)₂ system in the counter current mode with the use of mixer–settler extractors.

(2) It has been found that the selectivity of separating praseodymium and cerium increases (the separation coefficient increases from 1.6 to 1.8) with the decreases in the concentration of praseodymium from macroconcentrations to microconcentrations, which can be explained by the leaching effect of the lanthanum and cerium nitrates.

(3) It has been found that, during the selective precipitation of thorium, the precipitate of hydroxides is enriched with the elements of the yttrium group.

(4) A lanthanum–cerium concentrate containing less than 0.03% of the remaining admixtures of REEs which is suitable for isolating cerium oxide with the concentration of the main substance of 99.9% on the following cascade has been obtained.

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