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Extraction of rare earth elements from hydrate-phosphate precipitates of apatite processing

M O Andropov^{1,2}, A V Anufrieva¹, A S Buynovskiy¹, Y N Makaseev¹, I N Mazov^{1,2}, R A Nefedov^{1,2}, V I Sachkov^{1,2}, O B Stepanova², and AV Valkov¹

¹Seversk Technological Institute of National Research Nuclear University "MEPhI",
Tomsk 634050, Russian Federation

²Siberian Physical-Technical Institute of Tomsk State University, Tomsk 634050,
Russian Federation

Email: oyuna12@yandex.ru

Abstract. The features of extraction of rare earth elements (REE) were considered from hydrate-phosphate precipitates of REE of apatite processing by nitric acid technology. The preliminary purification of nitrate solution of REE from impurities of titanium, aluminum, iron, uranium and thorium was suggested to obtain stable solutions not forming precipitates. Washing the extract was recommended with the evaporated reextract that allows to obtain directly on the cascade of REE extraction the concentrated solutions suitable for the separation into groups by the extraction method. Technical decisions were suggested for the separation of REE in groups without the use of salting-out agent.

1. Introduction

The apatite raw materials contain up to 1 % (wt.) of rare earth elements (REE) and present a very important potential source of cheap rare earth concentrates [1]. Depending on the accepted technology of processing the REE present in apatite are concentrated in a nitrogen-phosphate solution (NPS) or in phosphogypsum. The most promising variant is the extraction of REE at the opening of apatite by nitric acid. REE content in the resulting nitrogen-phosphate solution is 6 – 7 g / l. Standard extraction technology of REE from NPS provides (after freezing calcium nitrate and separation of fluorine) the selective extraction of hydrate-phosphate precipitates of REE at pH 1.1 - 2.0, filtration and washing the precipitate. Previously the technology has been tested in variant of the integrated tests on Dneprodzerzhisk "Azot" and Kirov-Chepetz factory [1-3].

The various methods of extraction of REE from the concentrate were suggested. The results of studies were published on the extraction of REE in the form of oxalate by precipitation followed by conversion of oxalates into hydroxides [4], by treatment of the precipitate by sulfuric acid with formation sulfates of REE [5] or by extraction with neutral organophosphorus compounds [6]. According to [6] the hydrate-phosphate precipitate containing 20 – 30 % of REE is dissolved in nitric acid to the residual content of nitric acid 4 - 6 mol/l, then the excess of nitric acid is neutralized with ammonium hydroxide to obtain a solution containing 60-70 g/l of REE (per oxides), 1.5 - 2 mol/l of nitric acid, 500 g/l of ammonium nitrate and a significant amount of phosphate and fluoride ions. In the process of countercurrent extraction the authors [6] noted the intense sedimentation, which



increases with advancing aqueous solution by extraction steps. The resulting solutions are extremely unstable, affected to form precipitates which are formed during standing solutions or during the extraction process. Since phosphates of REE, iron, aluminum and titanium are not soluble, and then the increase of stability of the system is reached by introducing nitric acid or salting-out agent. However, this does not always lead to stop sedimentation.

In this paper the results of studies on the extraction purification of hydrate-phosphate precipitate of REE and the subsequent division into groups in the mode, decreasing significantly the possibility of sedimentation, are given.

2. Experimental procedure

2.1 Processing of the initial apatite by nitric acid technology with separation of the sum of REE as a precipitate

The nitrogen-phosphate solution was prepared by treatment of apatite with nitric acid at temperature of 50 - 70 °C for 3 hours, the precipitate of the unopened apatite on the filter was separated and calcium nitrate (strontium) was separated by freezing. After purification from the fluorine the solution contained 400 – 500 g/l of phosphoric acid, 80 - 120 g/l of nitric acid, 50 - 80 g/l of calcium (as the oxide) and 6 – 7 g/l of REE (as oxide). To isolate REE the solution was treated with gaseous ammonia to pH = 1.8 - 2.0. The resulting precipitate was badly filtered. The increase of the filtration rate was provided by delay or by the step neutralization. The total content of REE reached 24 – 26 % in good filter precipitate. The impurities of iron, aluminum, partially calcium, as well as uranium and thorium, contained in the apatite in minor amounts, transferred in the precipitate from the solution. The resulting precipitate contains (depending on the humidity) (wt.%): 20 - 25 % of REE oxides, titanium 0.16 %, thorium 0.05 %, uranium 0.01 %, impurities of iron (III) and aluminum.

2.2 Dissolution of the hydrate-phosphate precipitates of REE and precipitation affinage of the resulting solution

The hydrate-phosphate precipitate of REE was dissolved in nitric acid to neutralize the excess of nitric acid with the source precipitate and the salting-out agent was added – NH_4NO_3 (500 - 600 g/l) or $\text{Ca}(\text{NO}_3)_2$ (400 - 500 g/l). The pulp was filtered. To the filtrate the ammonium hydroxide was added to pH = 0.2 - 0.7, and the precipitate was separated by filtration. In the precipitate the impurities were concentrated: iron, aluminum, thorium, titanium, uranium and partially REE. The precipitate is removed from the process, and the filtrate was acidified up to 1 - 1.5 mol/l of nitric acid. When performing recommended parameters the thorium and the titanium are removed almost completely, and uranium by 70 – 80 %. Experimentally it is found that if you do not remove the thorium by chemical precipitation, it is extracted into the organic phase during the extraction with 100 % tributyl phosphate (TBP). In the absence of salting-out agent the distribution coefficient of uranium varied within values of 30 - 40, of thorium - 0.3 - 0.5, the distribution coefficient of REE - 0.2 - 0.3.

2.3 Investigation of extraction processes of separation of the sum of REE into groups

Experiments were carried out according to the method by shaking the organic and aqueous phases in separating funnels with subsequent slicing. The content of individual REE was determined by atomic emission spectrometry with the inductively coupled plasma on spectrometer "VISTA-PRO" of company "VARIAN".

REE were extracted in the presence of salting-out agents (the distribution coefficient of REE reached values of 1 - 3) by extraction with 100 % tributyl phosphate. As the wash solution the 15 - 20 % evaporated reextract of the purified sum of REM was used, concentration of 250 - 300 g/l. The remainder of the evaporated reextract was deduced as finished products to be separated into groups. Composition of total REE isolated from the apatite concentrate (wt. %): La_2O_3 - 25.5; CeO_2 - 46.4; Pr_6O_{11} - 4.0; Nd_2O_3 - 11.6; Sm_2O_3 - 1.7; Eu_2O_3 - 0.5; Gd_2O_3 - 1.4; Tb_4O_7 - 0.2; Dy_2O_3 - 0.7; Ho_2O_3 - 0.2; Er_2O_3 - 0.3; Yb_2O_3 - 0.4; Y_2O_3 - 7.0.

The division into groups was carried out by extraction in system 100 % TBP- nitrates of REE (300 - 350 g/l). As the wash solution the evaporated reextract was used, concentration of 250 - 300 g/l, the reextracted solution is 0.1 - 0.2 mol/l of nitric acid. From the rare earth nitrate solution the cerium was recovered by electrolytic oxidation. Extraction of cerium is 95 %. Composition of REE of solution without cerium (wt. %): La_2O_3 - 45.0; CeO_2 - 5.3; Pr_6O_{11} - 7.7; Nd_2O_3 - 20.5; Sm_2O_3 - 3.0; Eu_2O_3 - 0.9; Gd_2O_3 - 2.5; Tb_4O_7 - 0.4; Dy_2O_3 - 1.2; Ho_2O_3 - 0.3; Er_2O_3 - 0.5; Yb_2O_3 - 0.7; Y_2O_3 - 12.0. To separate into groups the scheme of successive separation was adopted on the first cascade through line of neodymium - samarium, and on the second cascade - through line of praseodymium-cerium.

The calculated parameters of the first separation cascade: the capacity of the organic phase - 150 g / l, the separation coefficient samarium-neodymium $\beta = 2.0$, the number of stages in the extraction 35, in the washing 30, in the reextraction 10, the ratio phases Vorg : Vinit : Vprod: Vreextr = 4 - 6 : 1.0 : 1.8 : 3.0. The reextract was evaporated to concentration of 250 - 300 g/l and the calculated amount was used as the wash solution. The remaining amount was output from the process in the form of solution containing elements of the average and the yttrium groups. Composition of REE of the reextract (wt. %): La_2O_3 - < 0.05; CeO_2 - < 0.05; Pr_6O_{11} - < 0.05; Nd_2O_3 - 6.4; Sm_2O_3 - 12.7; Eu_2O_3 - 3.7; Gd_2O_3 - 10.5; Tb_4O_7 - 1.5; Dy_2O_3 - 5.2; Ho_2O_3 - 1.5; Er_2O_3 - 2.3; Yb_2O_3 - 3.0; Y_2O_3 - 52.

In the raffinate phase the less extractable elements are concentrated, composition (wt. %): La_2O_3 - 58.9; CeO_2 - 7.0; Pr_6O_{11} - 9.2; Nd_2O_3 - 24.5; Sm_2O_3 - <0.02; Eu_2O_3 - <0.02; Gd_2O_3 - <0.02; Tb_4O_7 - <0.02; Dy_2O_3 - <0.02; Ho_2O_3 - <0.02; Er_2O_3 - <0.02; Yb_2O_3 - <0.02; Y_2O_3 - <0.02. At the second separation cascade the division was carried out through line of cerium-praseodymium to yield pure didymium in the extract. The calculated parameters of the second separation cascade: the capacity of the organic phase - 150 g l, the separation coefficient praseodymium - cerium $\beta = 1.6$, the ratio of phases: Vorg : Vinit : Vprod: Vreextr = 5-6 : 1.0 : 2.3 : 3.0. The extractant was entered into the first stage, the starting solution in step 35, the wash solution in step 65, the reextracted solution was injected into step 75. Composition of REE in the reextract (wt. %): La_2O_3 - <0,01; CeO_2 - <0,01; Pr_6O_{11} - 25; Nd_2O_3 - 75; Sm_2O_3 - <0,02; Eu_2O_3 - <0,02; Gd_2O_3 - <0,02; Tb_4O_7 - <0,02; Dy_2O_3 - <0,02; Ho_2O_3 - <0,02; Er_2O_3 - <0,02; Yb_2O_3 - <0,02; Y_2O_3 - <0,02.

In the raffinate the lanthanum with residues of cerium and part of praseodymium was concentrated (wt. %): La_2O_3 - 88; CeO_2 - 10.3; Pr_6O_{11} - 1.5; Nd_2O_3 - 24.5; Sm_2O_3 - <0.02; Eu_2O_3 - <0.02; Gd_2O_3 - <0.02; Tb_4O_7 - <0.02; Dy_2O_3 - <0.02; Ho_2O_3 - <0.02; Er_2O_3 - <0.02; Yb_2O_3 - <0.02; Y_2O_3 - <0.02. Both in the first and second cascades of the extraction process was carried out in a transient mode, with accumulation distinguishable component in the first cameras of the extraction part of the cascade.

3. Research results and discussion

As a result of these experiments the nitrogen-phosphate solution has been obtained by nitric acid technology used in industry. To solve the problem of complex processing of apatite from the resulting solution the strontium nitrate and nitrate solution of the sum of REE were isolated for further processing.

Mode of extraction of REE is shown from this solution by precipitation with ammonia and subsequent dissolution of the resulting precipitate with nitric acid, to remove the impurities, preventing the extraction, wherein, titanium and thorium are removed almost completely, and uranium by 70 - 80 %.

The suggested scheme of the extraction separation of the sum of REE allows you to extract of cerium with the degree of extraction of 95 % and groups of REE on lines samarium-neodymium and cerium-praseodymium in the form of products. The obtaining didymium in the extract is suitable for production of alloys or the manufacture of magnets. The raffinate, containing 80 - 90 % of lanthanum, is suitable for producing lanthanum with content of 99.99 % of the main substance.

4. Conclusions

1. The features of REE extraction are found from the hydrate-phosphate precipitates of apatite processing by nitric acid technology.

2. It is proposed to output impurities by selective precipitation and to carry out the process of extraction purification with saturation of the organic phase by the evaporated reextract.
3. Possible technical decisions for the separation into groups of the evaporated reextract of the purification cascade were discussed.

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