A research on the extraction of ree from a flotation concentrate

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ABSTRACT. Industrially significant reserves represented by granular phosphorite varieties are concentrated in Kyzylkum in two adjacent Middle Eocene depressions - Jeroy and Sardara. In the granular phosphorites of the Kyzylkum basin, REE impurities of the cerium group are established in an amount of 0.024-0.055 %. The degree of extraction of rare-earth elements during decomposition of phosphorites is on the average 75-80% and practically does not depend on the concentration of nitric acid in the range of 35-55% and the acid norm from 110 to 120%.

I.INTRODUCTION

Industrially significant reserves represented by granular phosphorite varieties are concentrated in Kyzylkum in two adjacent Middle Eocene depressions - Jeroy and Sardara. In them, Middle Eocene deposits, represented by limestones with a different proportion of clay, phosphatized marls and phosphorites. Productive mineralization medium Eocene represented by two flat-lying layers of phosphate rock (3^0-5^0) which are opened by ells of the depth of 280-300 m from the surface, on an area of about 2500 km^2 [1].

The main ore mineral of these two layers is Francolite, which is apatite-like calcium phosphate fluoride, containing about 33% P_2O_5.

Among other rock-forming minerals calcite (26-43 %), gypsum (1.0-3.5 %), silica (1.0-5.0 %) and mineral clay (3.0-8.0 %) are determined.

Phosphate layers marked by gamma-ray logging with natural radioactivity (uranium, thorium), in phosphorites, there were detected high-Clarke content of rare earth elements (lanthanum, cerium, neodymium, samarium, europium, terbium, dysprosium, ytterbium, cesium) and quite substantial range of rare elements (beryllium, lithium , Zirconium, hafnium, tin, molybdenum, bismuth, antimony, arsenic, strontium, fluorine, niobium, vanadium).

However, some chemical elements (F, V, Vb, Dy, Tb, Nd, Ce) give a concentration of 5-10 times the Clarke content that introduces practical interest to the associated extraction, in the manufacture of fertilizers. Deposits of phosphorites exploited in the United States, where uranium, fluorine, vanadium and selenium are produced in small quantities as associated by-products can be quite a good example [2].

II. SIGNIFICANCE OF THE SYSTEM

In the granular phosphorites of the Kyzylkum basin, REE impurities of the cerium group are established in an amount of 0.024-0.055 % (0.04 %avg). The content of REE of Khibiny apatites, of Karatau and Kizilkum phosphorite pools obtained from the various sections of deposits has been provided in the table for comparison (Table. 1).

The total content of rare earths in the Khibina apatites is 2.6 times higher than in the phosphatites of Karatau and 22 times more in comparison to the phosphorites of the Kyzylkum. The difference in the content of rare earths of the cerium group ("light" REE) is higher than the elements of yttrium ("heavy" REE). In all three types of phosphate ores, the maximum amounts fall on Ce, La, and Nd, with a difference in content by an order of magnitude or more.

III. LITERATURE SURVEY

Determination of the correlation of REE contents in flotation concentrates depending on the content of P_2O_5. For this purpose, various types of flotation concentrates with P_2O_5 content – 9 %, 18 %, 24 % and 27 % are used [3].

The flotation concentrate at a temperature of 40-45 ^{0}C is decomposed with nitric acid at 110% of the stoichiometric norm relative to CaO for 60 min. The nitrogen-acid extract obtained after the decomposition of the flotation concentrates is a suspension with the ratio S: L 1: $45 \div 50$. The solid phase of the nitric acid is released by thickening (settling) $t^0 = 30 \div 40$ ^{0}C within 2-3 h, followed by filtration underflow in vacuum filter.

Table 1. The content of lanthanides in phosphates, %

REE	Khibiny apatites	Phosphorites of Karatau	Phosphorites of Kyzylkum
La	$1.9 \cdot 10^{-1}$	$2.3 \cdot 10^{-2}$	$(1.8-10.1) \cdot 10^{-3}$
Ce	$3.6 \cdot 10^{-1}$	$2.9 \cdot 10^{-2}$	$(3.1-21.0) \cdot 10^{-3}$
Nd	$1.1 \cdot 10^{-1}$	$1.9 \cdot 10^{-2}$	$(1.8-13.6) \cdot 10^{-3}$
Sm	$2.4 \cdot 10^{-2}$	$4.1 \cdot 10^{-3}$	$(0.51-3.6) \cdot 10^{-3}$
Eu	$4.5 \cdot 10^{-3}$	$3.9 \cdot 10^{-4}$	$(0.06-0.33) \cdot 10^{-3}$
Tb	$1.0 \cdot 10^{-3}$	$5.3 \cdot 10^{-4}$	$(0.63-5.4) \cdot 10^{-3}$
Dy	$6.7 \cdot 10^{-3}$	$3.9 \cdot 10^{-3}$	$(0.11-0.77) \cdot 10^{-3}$
Yb	$8.5 \cdot 10^{-4}$	$2.9 \cdot 10^{-3}$	$(0.29-2.3) \cdot 10^{-3}$
Total	0.697	0.083	$(8.3-55.2) \cdot 10^{-3}$

Further, the clarified solution enters the reactor to precipitate silicon-sodium fluoride by treatment with a solution of sodium sulfate in a ratio of 1: 1. This ratio is matched by the fact that the content of silicon oxide in the flotation concentrate is less than that of other phosphorites. With the acidic decomposition of flotation concentrates, most of the fluorine is released in the form of HF, which when converted to alkali metal salts is converted to a well solubile soluble fluoride salt. Therefore, when sodium carbonate sulfates are desaturated, slightly soluble sodium hexafluorosilicates are formed. The precipitate of sodium silicofluoride is separated in the settler, followed by centrifugation of the condensed part. After that, the defluorinated solution is sent to the precipitation unit of the rare-earth concentrate. The method of isolating rare earths is based on the relatively low solubility of their phosphates in weakly acidic solutions at pH = 0.9-2.5, as well as their solubility with increasing t^0.

IV. METHODOLOGY

Therefore, we are undertaking a study of the effect of pH in the interval $0.9 \div 2.5$ and t^0 - $40 \div 80$ ^{0}C on the degree of precipitation of REE at an elevated CaO content in the liquid phase of nitric acid leaching (NAL).

We conducted our research according to the following scheme (Fig. 1). The flotation concentrate contains about 0.9 % of the rare earths of the cerium group (lanthanum, cerium, niobium, yttrium, etc.). The share of lanthanum in the total amount of rare earths is approximately 30 %. Experiments on the solubility at 80 °C of phosphate, lanthanum in phosphoric acid gave the following results (Table 2.).

As can be seen, the solubility of lanthanum phosphate in phosphoric acid is very low. The basis of the method for the isolation of rare earths is the comparatively low solubility of their phosphates in weakly acid solutions at pH = 2-2.5. With complete neutralization of HNO_3 and neutralization of the first hydrogen ion H_3PO_4 by approximately 20-15 %, rare earths begin to precipitate, with averaging of solutions possible by limestone, lime, ammonia, soda or other alkali.

Investigating the solubility and degree of precipitation of rare earth phosphates from solutions, depending on the degree of neutralization and temperature, it is established that the solubility of phosphates of rare earths decreases with increasing temperature at the same degree of neutralization. Thus, at a temperature of 35-40 °C and a degree of neutralization of phosphoric acid of 40 %, the content of rare earth oxides in solution equals to 0.12-0.13 %, with the same degree of neutralization, but at a temperature of 60 and 80 °C not higher than 0, 07-0.09 %. Thus, as the temperature rises to 60-80 °C, the precipitation of rare earth phosphates into the precipitate starts from more acidic solutions.

Fig. 1. Scheme of the nitric acid processing of the flotation concentrates of the CK with the associated recovery of the REE concentrate

According to M.N. Nabiev, with the nitric acid decomposition of phosphorites, regardless of acid concentration,
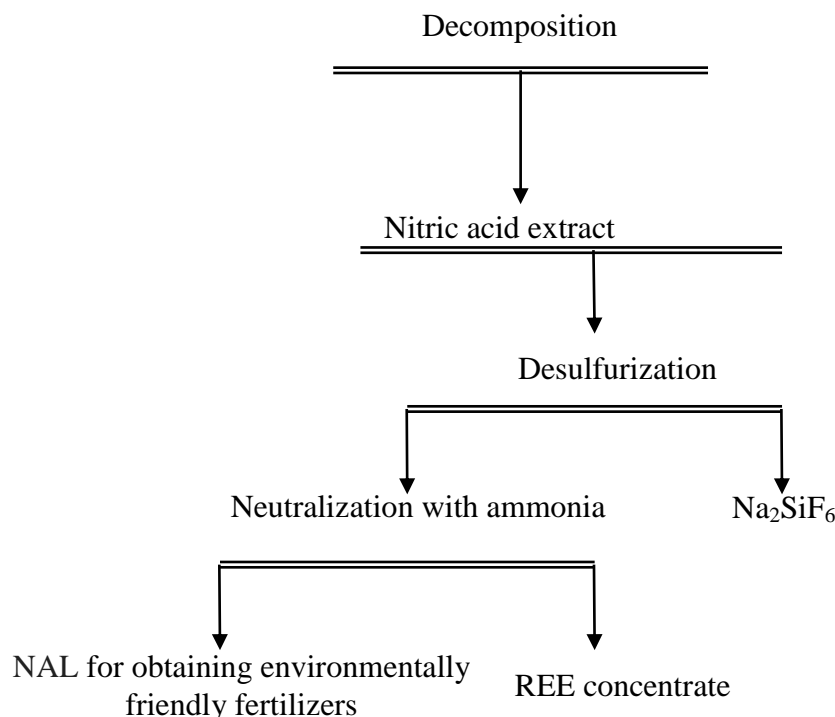
the extraction of rare earths from the solution is about 88-99%). He established the following optimal conditions for the extraction of rare earth phosphates: a) the concentration of the liquid phase is 35 %, Ca $(NO_3)_2$ and 9.5 % P_2O_5, respectively; b) the temperature of the separation process is 60-80 °C; c) neutralization with ammonia of free nitric acid and about 50% of the first hydrogen ion of phosphoric acid; d) the isolation of rare earth phosphates from the solution is expediently carried out by decantation. Under these conditions, the degree of precipitation of rare earths is about 70-80 % of the total amount in apatite.

The percentage of precipitation of rare earths can be increased with a higher degree of neutralization of the acid, followed by precipitation washing with phosphoric acid solution.

Table 2. Solubility of Lanthanum phosphate at 80 °C in phosphoric acid

Liquid phase, %		$La_2O_3/P_2O_5*100\%$
P_2O_5	La_2O_3	
10.39	0.0102	0.090
2102	0.0207	0.098
31.72	0.0349	0.110
42.05	0.0525	0.125

Studying the possible optimal conditions for the separation of rare-earth elements in the nitric acid processing of the phosphorites of the CK, it was established that the total content of the rare-earth elements in the phosphorite sample accounts for average percentage of 0.04 %. In addition, the effect of the concentration and rate of nitric acid, the process temperature on the degree of extraction of rare earths in solution, was determined. With an acid norm of 110 % of stoichiometry on CaO phosphate and a temperature of 30 °C, the change in acid concentration practically does not affect the degree of transition of rare earths to the solution, as can be seen from the data given below (Table 3).

V. EXPERIMENTAL RESULTS

The effect of the norm of 55 % nitric acid at 30 °C on the extraction of rare earths into the solution was studied with the following amounts of acids: 90, 120 and 200 % of stoichiometry. The degree of transition to the liquid phase of rare earths at an acid rate of 5 % below the stoichiometric is 45 %. An increase in the excess of the acid to 10% over stoichiometry sharply increases the extraction of rare elements in the solution (up to 78.33 %). A further increase in the acid norm almost does not affect the process (81.60 %). A change in temperature from 10 to 30 °C (55 % HNO_3, the rate of 110 %) increases the transition of rare earths in the solution from 61.66 to 78.83 %.

Table 3. Effect of nitric acid concentration on the degree of extraction of REE in solution

Acid concentration, %	TR content in Liquid phase, %	Extraction rate in solution, %
35	0.018	76.00
45	0.028	76.66
55	0.032	78.83

VI.CONCLUSION AND FUTURE WORK

Thus, the degree of extraction of rare-earth elements during decomposition of phosphorites is on the average 75-80 % and practically does not depend on the concentration of nitric acid in the range of 35-55 % and the acid norm from 110 to 120 %.

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