

## Rare earth elements materials production from apatite ores

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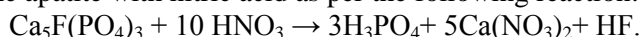
**Abstract.** The paper deals with the study of processing apatite ores with nitric acid and extraction of the rare earth elements. The rare earth elements can be successfully separated and recovered by extraction from the nitrate- phosphate solution, being an tributyl phosphate as extraction agent. The developed scheme of the processing apatite concentrate provides obtaining rare earth concentrates with high qualitative characteristics.

### 1. Introduction

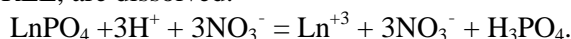
Rare earth elements (REEs) are a group of 15 chemical elements in the periodic table, specifically the lanthanides. Although relatively abundant in the earth’s crust, they rarely occur in concentrated forms, making them economically challenging to obtain. These elements comprise critical components of many of our modern-day technological devices and everyday electronics. The increased use of REEs in magnets, modern electronics and in a variety of commercial products has led to a shortage of REEs for production purposes. Currently, REEs are being disposed in large quantities rather than being recovered and reused. The two major mineral sources of REEs are bastnasite and monazite and will be the focus of this section. However, it is important to note that production can come from a variety of minerals, such as xenotime, apatite, yttrifluorite, cerite, and gadolinite[1].

The general formula for apatite is  $\text{Ca}_5\text{F}(\text{PO}_4)_3$ , where the part of the calcium can be substituted mainly by Na, Sr, Mn, and the REEs. Apatite contains an average of 0.1–0.8 % of rare earth oxides [2, 3].

The two primary methods for extracting REEs from apatite are selective acid extraction and physical separation techniques. The use nitric acid for processing of apatite is the most perspective. The total dissolution of the apatite with nitric acid as per the following reaction:



All impurities, including REE, are dissolved:



The formed calcium nitrate is separated by filtration. The rare earths are ended up in the nitrate-phosphate solution.



For the extraction from nitrate solutions, organic extractants based on neutral organophosphorous compounds (preferably tributylphosphate - TBP) are typically used. By choosing suitable process conditions (nature of the extraction system, the ratio of the organic extractant/aqueous solution, amount of extraction and re-extraction stages, REEs precipitation mode), up to 98% REEs contained in the solution can be extracted into concentrate [4, 5].

The purpose of this work is to study the complex processing apatite ores with nitric acid and to extract the rare earth metals and radionuclides.

## 2. Experimental procedure

### 2.1 The process of opening apatite concentrate

The decomposition of samples of apatite raw was carried out using excess of nitric acid with concentration of 56 wt % at 50 °C for 1.5 hours. Scheme of the processing apatite concentrate is shown in the Figure 1.

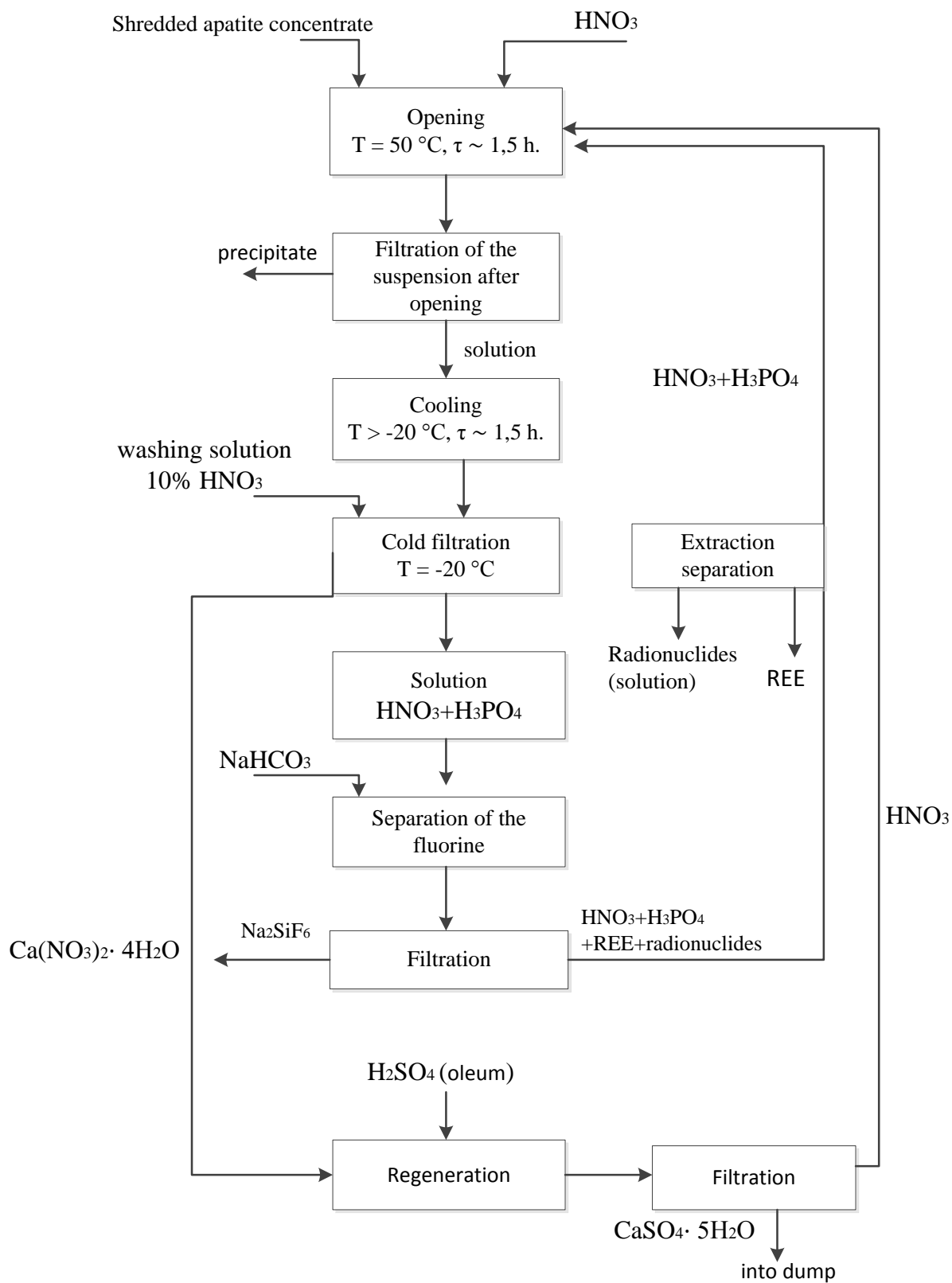
The following measuring instruments, auxiliary equipment, materials and reagents were used:

- glass reactor with the main technical specifications: volume 5 L, rotational speed of the stirring device: 0-700 / min, working pressure: 0.2-1.2 kg / cm<sup>2</sup>, working temperature range (– 20) - 180 °C;
- cryostat to the reactor, providing a temperature of from – 30 to 100 ± 2 °C;
- vacuum pump;
- Thermo Scientific iCAP 6200 inductively coupled optical emission spectrometer (ICP-OES);
- electronic scales GR 120 «A&D Company Ltd.»;
- laboratory shaker LOIP LS-110;
- nitric acid CAS № 7697-37-2;
- sodium bicarbonate CAS № 144-55-8;
- sulfuric acid CAS № 7664-93-9;
- ammonia CAS № 7664-41-7;
- tributyl phosphate CAS № 126-73-8.

Composition of apatite sample was studied with the help of Thermo Scientific iCAP 6200 inductively coupled optical emission spectrometer (ICP-OES). Results of this study are shown in Table 1.

**Table 1.** Composition of apatite sample

Oxide	Content, wt %	Oxide	Content, wt %	Oxide	Content, wt %
SiO <sub>2</sub>	1.73	ΣREE <sub>2</sub> O <sub>3</sub>	0.90	TiO <sub>2</sub>	0.45
CaO	51.64	La <sub>2</sub> O <sub>3</sub>	0.25	Eu <sub>2</sub> O <sub>3</sub>	0.01
P <sub>2</sub> O <sub>5</sub>	39.93	CeO <sub>2</sub>	0.38	Gd <sub>2</sub> O <sub>3</sub>	0,022
MgO	0.10	Pr <sub>2</sub> O <sub>3</sub>	0.04	SrO	0.64
Fe <sub>all</sub>	0.46	Nd <sub>2</sub> O <sub>3</sub>	0.14	Tb <sub>2</sub> O <sub>3</sub>	0.002
Na <sub>2</sub> O	0.42	Sm <sub>2</sub> O <sub>3</sub>	0.02	Dy <sub>2</sub> O <sub>3</sub>	0.01
F	3.14	Y <sub>2</sub> O <sub>3</sub>	0.04	Yb <sub>2</sub> O <sub>3</sub>	0.00



**Figure 1.** Scheme of the processing apatite concentrate.

The sample of apatite concentrate was placed in a reactor, the concentrated nitric acid with excess 10-15% by weight was added and at temperature of 50 °C it was stirred for 1.5 hours at frequency of rotation 120 rev / min.

The suspension was filtered after opening. The solid precipitate was separated and was dried in the oven at temperature of 60 °C to constant weight. The resulting solution after filtration of the suspension was placed in a glass reactor, it was cooled to – 20 °C and was stirred for 1.5 hours. Then it was washed by nitric acid with concentration of 10 % wt. Thus about 90 % of  $\text{Ca}(\text{NO}_3)_2$  was allocated to a solid phase.

The formed crystals of calcium nitrate were separated from the mother liquor by filtration and were washed by nitric acid at temperature of – 10 °C. The concentrated sulfuric acid (oleum) was added to the filtered precipitate of calcium nitrate under stirring. The obtained precipitate of calcium sulfate was filtered at temperature of 20 °C, additionally was washed with distilled water at a ratio of  $S : L = 1 : 5$  on the filter, the precipitate of calcium sulfate was dried. The washing solution ( $\text{REE}$ ,  $\text{HNO}_3 + \text{H}_3\text{PO}_4$ , radionuclides) was directed to the stage of decomposition of apatite.

The mother liquor ( $\text{HNO}_3 + \text{H}_3\text{PO}_4$ ) after the cold filtration was directed to obtain fluorine. The mother liquor at room temperature was mixed with twice excess of  $\text{NaHCO}_3$ , F – ion was precipitated as a poorly soluble silicic sodium fluoride, to increase degree of extraction of REE. After precipitation of  $\text{Na}_2\text{SiF}_6$  the solution was neutralized by ammonia to pH 2.5 to obtain REE phosphates. After repeated water washing (decantation) the separated phosphates are the technical product containing 25-30 % of  $\text{Ln}_2\text{O}_3$ , 30 % of  $\text{P}_2\text{O}_5$ , 10 % of  $\text{SiO}_2$ , 5-8 % of  $\text{Ca}(\text{NO}_3)_2$ , 3 % of  $\text{Fe}_2\text{O}_3$ , 1.5 % or less of F, 5-10 % of  $\text{H}_2\text{O}$ .

The solution containing the composition of  $\text{HNO}_3 + \text{H}_3\text{PO}_4$ , rare earth metals and radionuclides was directed to the extraction of REM and radionuclides.

## 2.2 Extraction from the obtained solution of rare earth elements and radionuclides

The extraction was carried out in separating funnels of 100 ml. The undiluted tributyl phosphate (TBP) was used as an extractant. The extractant was previously saturated by nitric acid with a concentration corresponding to the working solution. After saturation the extraction process was carried out.

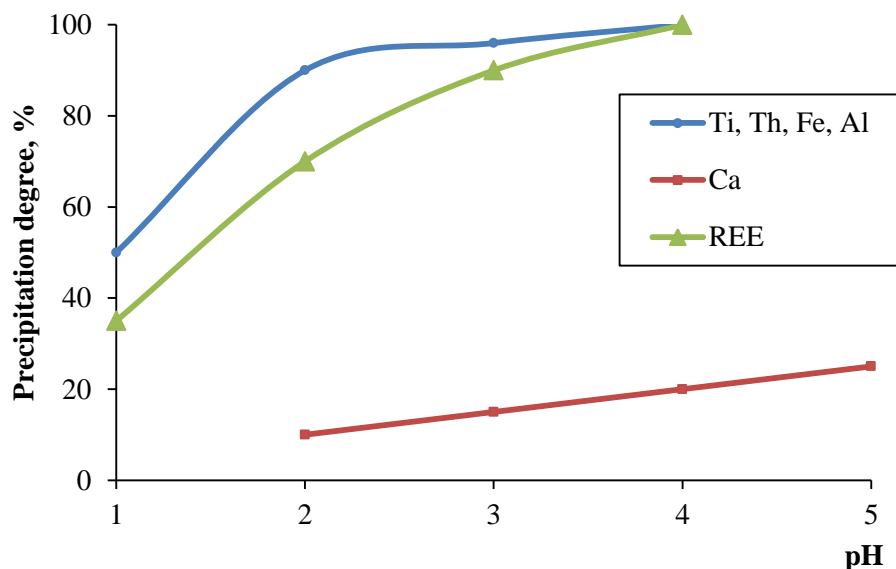
The shaking of funnels was carried out using a laboratory shaker LOIP LS 110. The composition of the initial solution was determined by the evaporation of the starting solution. For this purpose the single-stage extraction was carried out with a ratio of organic phase and water phase ( $O : W$ ) = 1 : 1 (15 ml : 15 ml) by 100 % TBP in a volumetric flask of 50 ml. Re-extraction was carried out with 0.1 M solution of  $\text{HNO}_3$ ,  $O : W = 1 : 1$ .

Investigation of the process of re-extraction was carried out at temperature of 60 °C. After the purification steps of impurities from the solution REM were extracted with 100% TBP in ratio of  $O : W = 1 : 1$ . Separation on a subgroup was performed in step of the washing of extract: for selective washout of light REE the concentrated solution of medium and heavy REE was used as wash solution. Next on stage re-extraction REE were washout by 0.1 M  $\text{HNO}_3$ . Solutions of the various steps were combined, thereby obtaining two solutions - solution after washing containing light REE and reextract, containing medium and heavy REE.

## 3. Research results and discussion

Nitric acid was selected to allow most complete dissolution of components contained in apatite. Use of  $\text{HNO}_3$  at concentration of 56 wt % was especially preferred. The concentration of acid in the solution should prevent REM precipitation in form of phosphates, fluorides, double sulphates. The resulting nitrate - phosphate solution was suitable to isolate the rare earth elements.

As a result of researches it is established that the degree of precipitation and the content of the rare earth elements in the precipitate depend on the pH value. A series of experiments was carried out in the pH range 1 - 5 to study the effect of pH on precipitation degree of a number of elements (figure 1).



**Figure 1.** The precipitation degree of a number of elements depending on the pH

It was observed that about 90-95 % of the rare earth elements from nitrate - phosphate solution were precipitated at  $\text{pH} = 2.3-2.7$ , but the content of rare earth elements in this precipitate was decreased because the significant amount of calcium was co-precipitated. The degree of precipitation of the rare earth elements was about 50 % at  $\text{pH} 1.4-1.6$ , but the content of the rare earth elements in this precipitate was increased. In addition the filtration rate of the precipitate was decreased at higher pH. Thus, the precipitation of REE from solution was carried out under  $\text{pH} = 2.5$ .

In order to avoid any contamination problems due to the fluorinated acids (in particular,  $\text{H}_2\text{SiF}_6$ ), it was necessary to eliminate such acids before extraction. On this purpose, the precipitation in the form of  $\text{Na}_2\text{SiF}_6$  after addition of a sodium salt  $\text{NaHCO}_3$  was chosen. The precipitation of  $\text{Na}_2\text{SiF}_6$  was more effective at room temperature. Analysis of the obtained precipitate showed that more than 80 % of the fluorides initially present in the apatite can be recovered as  $\text{Na}_2\text{SiF}_6$ .

The use of the crystallization of calcium nitrate makes it possible to regenerate a significant part of nitric acid. The resulting calcium sulphate is a product suitable for additional industry.

The use of 100% of tributyl phosphate as an extractant significantly reduced the volumes of solutions and provided recovery of rare earth elements.

To determine the optimum ratio of the organic /water phase we conducted a single-stage extraction. We investigated the following ratios of O: W = 0.5:1; 1:1; 1.5:1; 2:1; 4:1; 6:1; 10:1. It was found that extraction of rare earth elements should be carried out under the following conditions: temperature - 22-25 °C, the ratio of organic/water phase = 1:1.

#### 4. Conclusion

The method of opening of apatite ores involves the decomposition of the apatite concentrate by nitric acid, the separation of the insoluble residue, freezing and subsequent separation of crystals of calcium nitrate tetrahydrate, the precipitation of fluorine from the nitrate-phosphate solution, the neutralization of the purified solution to a final pH 2,5, the separation of the precipitate of phosphates of rare earth elements and radionuclides, the extraction of rare earth metals and radionuclides from the solution. The choice of the above conditions, the sequence of operations, modes and parameters of the process was based on the analysis of the results of studies and the data obtained from the tests. This scheme of the processing apatite concentrate provides obtaining rare earth concentrates with high qualitative characteristics.

### Acknowledgment

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### References

- [1] R J Weber, D J Reisman 2012 *Rare Earth Elements; A Review of Production, Processing, Recycling and Associated Environmental Issues* US EPA Region 7: Kansas, KS, USA.
- [2] K A Bolshakov 1976 *Chemistry and Technology of Rare and Scattered Elements* (Moscow: Vysshaya Shkola)
- [3] L Alders 1957 *Solvent Extraction* (Moscow: Foreign Literature Publishing House)
- [4] D I Rjabchikov and V A Riabukhin 1966 *Analytical Chemistry of Rare Earth Elements and Yttrium* (Moscow: Nauka)
- [5] S D Moses, V A Semenov and G L Shelekhova 1981 *Chem. Industry* **8** 24