

## Conference Paper

# Rare-Earth Concentrate Production from Technogenic Mineral Formations

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## Abstract

Based on the analysis technology of processing of uranium-containing raw materials, identified potential sources of rare earth elements from among the industrial products and waste: uranium sorption tails, sulfuric acid solutions of heap leaching of uranium, man-made mineral formations from phosphate processing of uranium ores. Based on the analysis technology of processing of uranium-containing raw materials, identified potential sources of rare earth elements from among the industrial products and waste: uranium sorption tails, sulfuric acid solutions of heap leaching of uranium, man-made mineral formations from phosphate processing of uranium ores.

**Keywords:** rare-earth elements, technogenic mineral formations, leaching, extraction, concentrate

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Received: 6 June 2017

Accepted: 9 July 2017

Published: 24 August 2017

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Selection and Selection and Peer-review under the responsibility of the Technogen Conference Committee.

## 1. Introduction

Scientific and technological progress in modern conditions is largely due to the widespread use of rare-earth elements. There are many areas for their effective utilization. For instance, rare earth elements are needed to manufacture the consumer electronics for which the world has an exponentially expanding appetite. To fulfill this increasing demand the search for new sources of raw materials of REEs is constantly performed. Technogenic mineral formations (TMF), obtained during processing of phosphate uranium ores, where the content of REE reaches 5.0 % can be considered as a viable source of REEs. The utilization of technogenic mineral formations besides solving the primary task, i.e. extraction of REEs, also touches upon issues of environmental safety.

## 2. Results and Discussion

The composition of the averaged TMF sample is given in Table 1. This work was done in three stages. During the first stage the conditions for TMF winning were studied: acidic

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Name	Content, %												
	heavy REE												
	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Y	$\Sigma TR_Y$	$\Sigma TR$	
TMF	0.182	0.037	0.162	0.027	0.175	0.041	0.196	-	0.670	1.030	1.917	4.952	
	Content, %												
	light REE						Impurities						
	La	Ce	Pr	Nd	$\Sigma TR_{Ce}$	Fe	Mg	Al	Th	Ca	P		
	0.940	1.430	0.091	0.574	3.035	11.10	1.20	3.06	0.05	2.65	15.50		

TABLE 1: Chemical composition of the averaged TMF sample.

Name	Content, %												
	Heavy REE												
	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Y	$\Sigma TR_Y$	$\Sigma TR$	
Cake	0.297	0.063	0.295	0.051	0.339	0.082	0.715	0.002	0.153	2.180	4.177	8.873	
	Content, %												
	Light REE						Impurities						
	La	Ce	Pr	Nd	$\Sigma TR_{Ce}$	Fe	Mg	Al	Th	Ca	P		
	1.520	2.150	0.146	0.880	4.696	16.50	1.38	6.33	0.08	4.69	28.71		

TABLE 2: Chemical composition of the averaged TMF sample after calcination and sulfatisation.

and alkaline methods were tested. The averaged raw material sample contains more than 20% of moisture and about 5% of organic compounds, therefore it was calcined at 450°C in a muffle furnace for 2 hours. Further, the calcined sample was mixed with concentrated sulfuric acid and sintered in a muffle furnace at a temperature of 230°C for 2 hours with the ratio of TMF:H<sub>2</sub>SO<sub>4</sub> = 1: 1.5. The chemical composition of the cake is presented in Table 2. As can be seen from Table 2 the removal of moisture and volatile organic substances resulted in almost doubling of the content of rare-earth elements in the sinter.

We found that above the sulfatisation temperature of 240°C a hardly soluble thorium pyrophosphate is formed, which partially captures REEs. Thus, the increase in the sulfatisation temperature leads to the excretion of thorium at this stage, but as a consequence it results in losses of REE.

The cake obtained after sulfatisation was then leached with water. During aqueous leaching the recovery of REE was 87.5% and the extraction of impurities, respectively, %: 57.6 Fe; 37.7 Mg; 60.5 Al; 50.0 Th; 56.1 Ca; 90.1 P.

Alkaline opening was investigated in two ways: direct leaching of the TMF in the alkali solution and with preliminary sintering with alkali. The concentration of alkali during leaching was varied from 80 to 300 g/dm<sup>3</sup>. It was established that the increase in alkali concentration leads to a higher degree of conversion of phosphorus compounds into solution, but the cost of the final product increases. The optimal concentration of alkali was found to be around 180-200 g/dm<sup>3</sup>.

The cake after filtering the pulp was washed with water and leached with sulfuric acid in the pH range 1.2-4.0, and sodium orthophosphate was precipitated from the alkaline solution by evaporation and subsequent cooling. We found that the maximum recovery of REEs from cake 79.98% is observed at pH = 1.2; at pH = 2.3 it drops to 48.2 %; and at pH = 4 it is less than 1 %.

Alkali melting was done with the ratio of TMF to alkali 1: 0.6-1.2. Then the cake was washed with water at 90°C to reach pH of 5.0-6.0. In the course of the experiment more than 70 % of the phosphorus passed into the solution. REEs almost completely remained in the cake. The washed cake was leached with sulfuric acid at pH = 1.2. The obtained results demonstrate that the degree of extraction of REEs decreases from 92.2 to 56.7 % as the ratio of TMF : alkali during melting increases. Analyzing the results of acid leaching of the cake after alkaline opening of TMFs, we conclude that the degree of transition of REE to the solution does not depend on the pre-opening method (direct alkaline leaching or sintering with alkali). The second method, however, is more energy-intensive, and, therefore, less preferable.

The analysis of two methods of opening of TMFs, acidic and alkaline methods, shows that the first one is less advantageous compared to another. The reason for this is that in acidic method phosphorus passes into the solution together with REE, thus complicating the salt composition of the productive solution, directed to the subsequent concentration. The alkali method makes possible isolation of phosphates into a separate product.

Next, the raw material was opened with alkali at a concentration of 180 g/dm<sup>3</sup>, and the cake obtained after filtration was divided into 2 parts and leached with sulfuric and nitric acids in order to select the optimum acid concentration and temperature regime of the process. As a result, nitric acid was chosen as more preferable.

In the course of work we also found that by increasing temperature to 50-60°C, the degree of extraction of rare-earth elements increases, and then decreases. This fact is related to the isomorphous crystallization of REE with calcium sulphate and calcium phosphate, the solubility of which determines the degree of leaching of rare-earth elements.

Thus, our studies show that it is beneficial to perform TMF opening in two stages: first, alkali leaching with alkali concentration of 180-200 g/dm<sup>3</sup> at 80°C and solid:liquid

ratio 1: 3 for 4 hours; second, leaching with 2.5M nitric acid. Remarkably, more than 75% of the phosphorus passes into the solution in the first stage.

Another issue of this work is that thorium and iron pass into the solution during leaching of TMFs together with REEs. To obtain a higher REE content concentrate they must be removed from the solution. The second part of the work was devoted to purification of productive solutions from impurities, in particular, from iron and thorium.

Iron was removed by previously developed method consisting of a partial precipitation of ferric iron with alkali at pH 2.7-7.8 and the reduction of the remaining iron by sodium sulfite. Stepwise neutralization with the following filtration through dust was utilized to get rid of thorium. After purification from iron and thorium the solutions had the following composition, g/dm<sup>3</sup>: 0.123 Fe; 0.055 Al; 0.001 Th; 3.93 Ca; 4.82 P; 9.56 ΣTRY; 9.46 ΣTRCe.

The third part of this work is devoted to the concentration of REE. The method of concentrating by precipitation was tested. The rare earth elements were precipitated with sodium hydroxide, the precipitate was separated by filtration, washed, dried and calcined in a muffle furnace at a temperature of 600°C. The resulting calcined sediment is a concentrate of rare earth elements with a total REE content of 36.5 %. A stoichiometric amount of oxalic acid was also used as a precipitant yielding a concentrate with REE content of 47.8 %.

The rare-earth elements are more fully concentrated by the extraction method. For the extraction of REEs from nitrate solutions, a commonly available tributyl phosphate was used. As a result of extraction with tributyl phosphate and subsequent reextraction with ammonium carbonate, a concentrate with REE content of 66.4% was obtained. However, in order to create a rational technology, and also from the economic point of view is more advantageous to direct the productive solution, after purification from iron and thorium, to chromatographic separation of REEs by known methods [1, 2].

### 3. Summary

Thus, the our results demonstrate that rare-earth elements can be extracted from TMFs of phosphate uranium ores in the form of a concentrate with a high degree of recovery.

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