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Influence of adding ammonium bifluoride when leaching monazite using sulphur acid

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Abstract

The following shows the results of the leaching of monazite concentrate with sulfuric acid in the presence of ammonium bifluoride. It was established that the addition of ammonium bifluoride increases the degree of the leaching monazite concentrate and allows the separation of phosphorous from a mixture of rare earth and radioactive elements.

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Keywords: monazite, sulfuric acid leaching, ammonium bifluoride, rare earth elements, thorium, uranium

1. Introduction

Monazite concentrate is an industrial raw material for the production of rare earth elements (REE) of the cerium group and thorium[1,2]. Leaching monazite concentrate basically involves two methods of decomposition: heating with sulfuric acid or sodium hydroxide[3,4]. Both methods have industrial applications; however, when the purpose is to obtain the production of rare commodity products, the preferred leaching method is using alkali. The main advantage of the alkaline method is the separation of phosphorus in the first step of the process in the form of sodium phosphate[5].

It is known that the interaction P_2O_5 with NH_4HF_2 or NH_4F occurs at 135 °C with the release of large amounts of heat and the formation of $NH_4PO_2F_2$ or $(NH_4)_2PO_3F$[6]. With an excess of ammonium fluoride, NH_4PF_6 can be

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formed, which undergoes thermolysis in the range of 150 to 400 °C to form gaseous PF_5[7]. PF_5 is readily hydrolyzed with the formation of phosphoric acid[8]. Phosphoric acid and phosphates are used in many areas, so they are subject to strict requirements on the content of radioactive elements. Adding NH_4HF_2 or NH_4F to sulfuric acid allows the phosphorous to separate from the mixture of REE and radioactive elements, thereby reducing the cost of the final products and the reduction of the amount of radioactive waste. Besides this, ammonium fluorides are able to effectively interact with the silicate component of monazite concentrate with the formation of $(NH_4)_2SiF_6$, which will increase the degree of its leaching[9,10]. The fluorinating agent of greatest interest is NH_4HF_2, therefore in this study it was used as an additive for sulfuric acid.

The purpose of this research was to develop a method of leaching monazite concentrate with sulfuric acid in the presence of ammonium bifluoride, allowing the separation of phosphorus from a mixture of rare and radioactive elements.

2. Experimental

In the study H_2SO_4 (analytical grade), NH_4HF_2 (analytical grade), NH_4OH (analytical grade) and monazite concentrate of Tugansk deposit were used. H_2SO_4 was used diluted in a volume ratio of 1:1. Monazite concentrate was milled using the Planetary Mono Mill PULVERISETTE 6. The range of particle sizes after grinding of the monazite concentrate ranged from 1 to 10 microns. The powder of monazite concentrate thus obtained was used without further classification. Particle size was determined by the particle size analyzer DelsaMax PRO.

The laboratory unit for leaching monazite concentrate is shown in Fig. 1. Added to the monazite concentrate, with mass 0.5 g, were 2 to 6 ml of H_2SO_4 (1:1) and 0.5 to 4 g of NH_4HF_2 in the desired ratio. The resulting mixture was placed in a glass made of glassy carbon and heated for 1 hour at a temperature of 160 °C. To remove NH_4HF_2, and the decomposition products of the reaction, the temperature was raised to 300 °C and calcined for 1 hour. Gaseous products were caught with NH_4OH. After heating the powdered material it was leached with 15 ml of H_2SO_4 (1:1), adjusted to 50 ml with water, and the contents of its components were analyzed on an atomic emission spectrometer with inductively coupled plasma (iCAP 6300 Duo). For calibration the multielement solutions MES-1, MES-2, MES-3 were used.

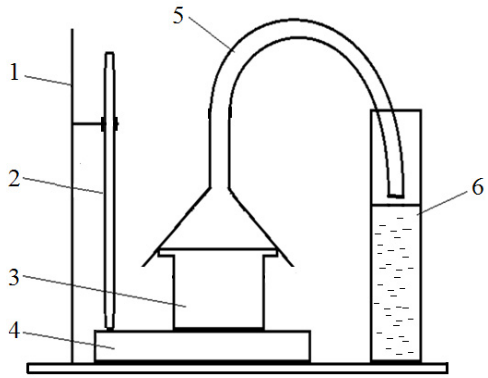

Fig. 1. The features of the laboratory unit for leaching monazite concentrate: 1 – stand; 2 – thermometer; 3 – glass made of glassy carbon; 4 – rangette; 5 – fluoroplastic funnel and fluoroplastic tube; 6 – cyilinder with solution of NH_4OH

After leaching the monazite concentrate with H_2SO_4 (1:1) without additives of NH_4HF_2 the degree of extraction of total REE increased to 12.3% with a solid–liquid ratio equal to 1:6. Further increase of the amount of H_2SO_4 have little influences an increase in the degree of extraction of total REE. Fig. 2 shows the total REE content in relation to the mass of NH_4HF_2 and volume of H_2SO_4 (1:1). In the case of leaching solution containing 6 ml of H_2SO_4 (1:1) and 4 g of NH_4HF_2 the maximum degree of extraction of total REE was 42.3%.

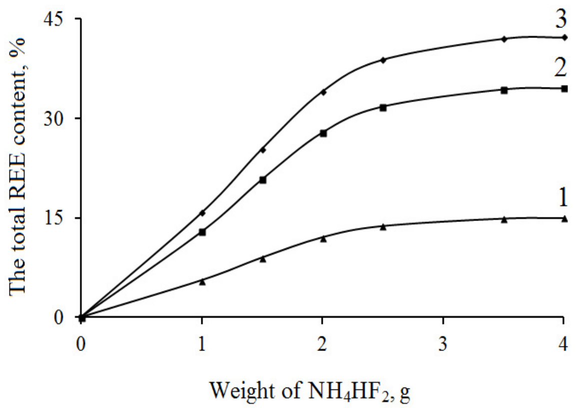

Fig.2. The degree of extraction or total REE from the mass of NH_4HF_2 in varying amounts of H_2SO_4 (1:1): 1 – 2 ml; 2 – 4 ml; 3 – 6 ml

Fig. 3 shows the X-ray fluorescence spectra, which were recorded using the X-ray fluorescence spectrometer Quant'X. Semi-quantitative analysis performed using X-ray fluorescence methods showed that at least 97% of total REE, 70% of thorium and all uranium underwent leaching and went into the solution.

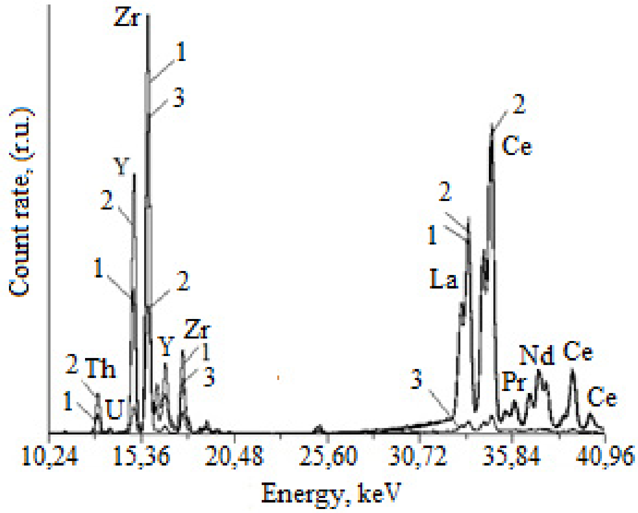

Fig.3. X-ray fluorescence spectra: 1 - monazite concentrate; 2 - solution after leaching; 3 - the solid residue after sulfuric acid leaching in the presence of NH_4HF_2

According to the X-ray diffraction analysis of the sinter, which is formed by heating a mixture of monazite concentrate and NH_4HF_2 with H_2SO_4 for 1 hour at a temperature of 160 °C, it contained phases of $Zr_3(PO_4)_4$ (PDF 00-048-0146), $(NH_4)_2SO_4$ (PDF 00-008-066), NH_4PF_6 (PDF 00-051-1741), $Th(SO_4)_2$ (PDF 00-053-0644) and $Nd_2(SO_4)_3{\cdot}(NH_4)_2SO_4$ (PDF 000-009-0283). Diffractograms were obtained on the diffractometer D8 DISCOVER (CuKα-radiation, λ = 1,54056 Å). The infrared (IR) spectra of the sinter obtained at 160 °C contained vibrations of sulfate ion, hydrogen sulfate ion, phosphate ion and ammonium ion. IR-spectra of a sample were recorded on potassium bromine tablets with IR spectrometer Nicolet 6700 in the range of 400 to 4000 cm^{-1} at room temperature.

Dissolution of NH_4HF_2 in H_2SO_4 and interaction between major components of monazite concentrate and H_2SO_4 in the presence of NH_4HF_2 at 160 °C proceeded according to the following reactions:

$$H_2SO_4 + 2NH_4HF_2 \rightarrow (NH_4)_2SO_4 + 4HF \quad (1)$$
$$2LnPO_4 + 3H_2SO_4 + (NH_4)_2SO_4 \rightarrow Ln_2(SO_4)_3{\cdot}(NH_4)_2SO_4 + 2H_3PO_4 \quad (2)$$
$$ThPO_4 + H_2SO_4 \rightarrow Th(SO_4)_2 + H_3PO_4 \quad (3)$$

$6HF + H_3PO_4 \rightarrow HPF_6 + 4H_2O$ (4)
$2HPF_6 + (NH_4)_2SO_4 \rightarrow 2NH_4PF_6 + H_2SO_4$ (5)

Heating of the sinter to a temperature of 300 °C led to the removal of NH_4HF_2 and degradation of some leachate production. In the sinter phase, $Nd_2O_2SO_4$ (PDF 00-041-0680), $Pr_2O_2SO_4$ (PDF 00-041-0679), $(LaO)_2SO_4$ (PDF 00-058-0526) and $Zr_3(PO_4)_4$ (PDF 00-048-0146) were found. In the IR spectra, vibrations of sulphate ion and phosphate ion are present. Decomposition of leachate production proceeds according to the following reactions:

$Ln_2(SO_4)_3{\cdot}(NH_4)_2SO_4 \rightarrow Ln_2O_2SO_4 + 2NH_3 + 3SO_3 + H_2O$ (6)

Table 1 shows the results for the contents of some elements in the leaching solution after sintering when heating to 300 °C.

Table 1. Elemental composition of solutions

Element	Content In The Solution,%		Element	Content In The Solution,%	
	After leaching	After absorption		After leaching	After absorption
Ce	8.34	0.018	P	0.11	13.81
Dy	0.54	-	Pr	1.12	-
Er	6.45	0.01	Sm	7.05	0.025
Eu	0.06	-	Tb	0.05	-
Fe	0.68	-	Th	3.08	0.01
Gd	0.54	-	Tm	0.045	-
Ho	0.12	-	U	0.34	-
La	4.51	-	Y	9.18	-
Lu	0.04	-	Yb	0.25	-
Nd	3.99	0.02	Zr	0.92	-

The considerable amount of phosphorus in the absorption solution indicates that heating has decomposed NH_4PF_6, and the resulting PF_5 can be absorbed with solutions of NH_4OH to give the following ammonium phosphates:

$NH_4PF_6 \rightarrow PF_5 + NH_4F$ (7)
$PF_5 + 4NH_4OH \rightarrow (NH_4)_3PO_4 + NH_4F + 4HF$ (8)

3. Conclusion

1. It follows from the experiments that the addition of NH_4HF_2 to H_2SO_4 increases the degree of leaching of monazite concentrate and allows the separation of phosphorus from the mixture of REE and radioactive elements.
2. In paper showed that at least 97% of total REE, 70% of thorium and all uranium underwent leaching and went into the solution.

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