

EFFECT OF MECHANICAL ACTIVATION ON THE STRUCTURE OF FLUORAPATITE AND DISSOLUTION OF RARE EARTH ELEMENTS IN ESFORDI CONCENTRATED PHOSPHATE OF PROCESSING PLANT

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Abstract: Esfordi phosphate concentrate with a total of 1.2% rare earth elements, is one of the richest sources of REE in Iran. In order to investigate the effect of mechanical activation on dissolution of rare earth elements, planetary ball mill with 20 mm steel balls, with ball to powder ratio of 2:1 and 15:1 was used for 90 minutes in dry mode at standard pressure. Due to the high solubility of fluorapatite and low solubility of REE-containing minerals in nitric acid, a two-stage leaching method was used. The first phase leaching residue, containing more than 99% of the rare earth elements in the initial concentrate, was mechanically reactivated with a ball to powder ratio of 12:1, then it was leached. Results showed that mechanical activation successfully improved the dissolution of rare earth elements from phosphate concentrate, from almost 1 percent (for initial concentrate) to 35.79, 42, and 34.33 percent for Ce, La, and Nd, respectively.

Keywords: Phosphate concentrate, rare earth elements, mechanical activation, leaching.

INTRODUCTION

Rare earth elements include 15 elements of the lanthanide group (from lanthanum to lutetium) with two other elements, yttrium and scandium- a total of 17 elements having similar properties and ionic radius. The main ore minerals of the rare earth elements include monazite and bastnasite minerals, and secondary mineral resources include minerals such as xenotime, apatite, and clays containing rare earth elements, allanite, zircon and loparite. Currently, the conventional method of extracting rare earth elements from phosphate ore is to use a mixture of sulphuric acid and produced phosphoric acid from the process. The phosphogypsum resulting from this process captures some of the rare earth elements in its network. Another part is precipitated in form of phosphate and fluoride. The presence of rare earth elements in refractory minerals shows that the dissolution of rare earth elements in phosphate concentrate requires high temperatures (about 270 °C). In high-temperature processes, in addition to economic and energy issues, there are environmental issues like toxic release of SO₂ and HF gases.

Mechanical activation is a high-energy ball milling process in which particles are powdered due to multiple stresses between ball and pot; ball-ball and ball-pot. Structural changes of the crystallites reduce the activation energy and increase the dissolution rate. By reducing the crystallite size and increasing the micro-strain and the degree of amorphization, the reactivity of activated minerals increases. The amorphization absorbs the largest portion of applied mechanical energy. In this paper, mechanical activation of Esfordi phosphate concentrate has been investigated in order to increase the dissolution of rare earth elements under conventional condition (temperatures below 100 °C).

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METHODS

A 250 kg sample of Esfordi's phosphate concentrate with a d80 value of 67 microns was prepared. Analysing polished and thin sections, XRD, ICP-MS and EPMA were used in the characterization step.

The phosphate concentrate samples were mechanically activated by a planetary ball mill (Pulverisette 6, FRITSCH, Germany) at 500 rpm, in the dry mode and at standard pressure, for 90 min. Stainless steel balls (20 mm diameter) and steel pot were used for milling, with a ball to powder ratio of 15:1 and 2:1. Winfit software was used to fit the XRD peaks and the Williamson-Hall method was utilized to investigate crystallite size and micro-strain variations. For dissolution tests, concentrated nitric acid (65% grade- Merck Company) and distilled water at 60 and 85 °C were used.

FINDINGS AND ARGUMENT

Leaching with 32% nitric acid at 60 °C, within 120 minutes, only dissolved about 1% of the total rare earth elements in the phosphate concentrate. According to Table 1, in conventional leaching conditions, the amount of rare earth element dissolution is low and increasing the concentration of nitric acid has a greater effect on dissolution, compared to increasing the temperature.

Table. 1 Conditions and results of distillation of phosphate concentrate in nitric acid 32 and 65% and temperatures of 60 and 85 °C.

Sample weight (gr)	Leaching agent weight (gr)	Acid concentration %	Time (min)	temperatur °C	Residual weight (gr)	Leaching %	
100	300	32	120	60	9	Ce	0.94
						La	1.2
						Nd	0.84
100	300	65	120	60	7.3	Ce	27.09
						La	32.05
						Nd	23.83
100	300	32	120	85	8.25	Ce	20.94
						La	24.46
						Nd	18.31

In Fig. 1, the peak of the XRD analysis index is shown before and after mechanical activation. After activation with a ball to powder ratio of 15 for 90 minutes, the XRD pattern of fluorapatite has been wider and shorter in comparison with the initial sample, indicating changes in the crystalline structure, amorphous phase production and activating these minerals.

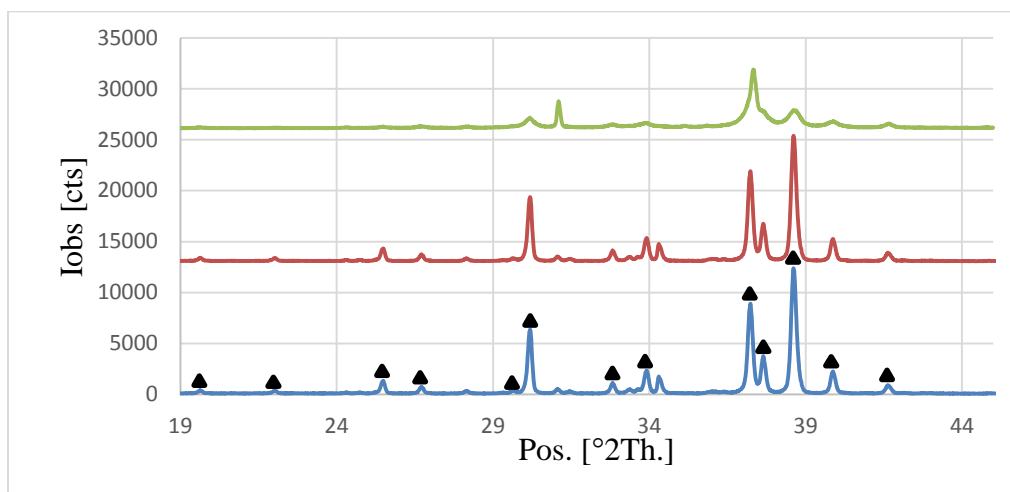


Fig. 1 Changes of XRD pattern of fluorapatite (▲) before and after mechanical activation. Green line: ball to powder ratio=15, red line: ball to powder ratio=2, blue line: initial sample

According to the results of the Williamson-Hull method (Table 2), using mechanical activation with low intensity (ball to powder ratio of 2), the energy applied by mill was used only for crushing and increasing the specific surface area of sample, while crystallite size, micro-strain, and the degree of amorphization of fluorapatite crystallites were not changed before and after mechanical activation. Using mechanical activation with high intensity (ball to powder ratio of 15), in addition to the obvious decrease in particle size, and increase in specific surface area of phosphate concentrate, crystallite size, micro-strain and amorphization degree of fluorapatite crystals, changed from 225 nm, 0.09% and 0% in the initial sample, to 81.8 nm, 0.63% and 57% in the activated sample, respectively. Therefore, it can be concluded that the increased solubility was due to the high intensity mechanical activation, and the increase of the specific surface was not the only factor improving the leaching process.

Table. 2 Results of crystallite size, micro-strain, and amorphization degree of fluorapatite crystallites measurements using the Williamson-Hall method.

Activation time (min)	Ball to powder ratio	Crystallite size (nm)	Micro-strain (%)	Amorphization degree (%)
0	0	225	0.08	0
90	2	225	0.09	1.2
90	15	81.8	0.63	57

Increasing the ball to the powder ratio from 2:1 to 15:1, the crushing ratio and particle-specific surface area were not changed significantly, but in general, it is not possible to separate the specific surface area increase from the mechanical activation process, because it is one of the inherent results of such processes. The results of laser diffraction showed that the specific surface area of phosphate concentrate increased from 1.14 m²/gr in the initial sample to 1.8 and 2.2 m²/gr in the activated samples with a ball to powder ratio of 2:1 and 15:1, respectively.

Leaching of the activated concentrate was performed with 32% nitric acid and solid to liquid ratio of 3 at 60 °C for 120 minutes

According to the leaching results, mechanical activation caused structural and superficial changes, thus had a significant role in increasing the dissolution rate of rare earth elements. Changes in

micro-strain, crystallites size, amorphization, active sites production and appearance of new surface groups are possible changes. The combination of these factors leads to a reduction in the stability and activation energy of mechanically activated phosphate concentrate to participate in subsequent reactions, such as dissolution, therefore, high-intensity mechanical activation is the reason for increasing the dissolution rate.

Mechanical activation of the waste produced from leaching of phosphate concentrate with nitric acid and the dissolution of rare earth elements from activated waste

The weight of the phosphate concentrate leaching residue (at 60 °C, for 120 minutes, with 32% nitric acid) was about 9% of the initial weight, containing about 99% of the rare earth elements in the initial sample. Therefore, the effect of mechanical activation on the dissolution of rare earth elements in the waste was investigated. The mechanical activation conditions included the ball to powder ratio of 12:1, the activation time of 90 minutes in dry mode, and at standard pressure. Leaching of the activated sample was carried out at 60 °C, 30% solids and with 32% nitric acid for 120 minutes. Mechanical activation caused a significant increase in the solubility of rare earth elements. Considering that hematite was the dominant phase in the waste sample, comparison of the XRD spectrum obtained from the activated and initial residual samples showed that the hematite crystalline structure has been changed significantly, and the intensity of the peaks has decreased, while they are wider. The decrease in intensity of the peaks indicates that the crystallites are amorphous, while the increase in width is an indicator of increasing micro-strains and reducing crystallites size. Considering that in the initial phosphate concentrate, the amount of refractory minerals containing rare earth elements (monazite and xenotime) was less than 1%, it was not possible to detect them by XRD analysis. The results of XRD analysis showed that due to the initial dissolution of the phosphate concentrate, fluorapatite, which is the main constituent of monazite and xenotime, has been dissolved and their inner pores have been released. Increasing the concentration of refractory minerals in the waste has led to their identification by XRD analysis, which was previously shown by EMPA analysis.

Conclusion

- Leaching of phosphate concentrate in 32% and 65% acid nitric, at 60°C and 85 °C, showed that the increase in temperature and concentration of acid can highly affect dissolution rate.
- Results showed that the recommended operation is to produce phosphoric acid and pre-concentrate rare earth elements in two-stage leaching, then proceed to mechanical activation and leaching of activated waste.
- According to the results of the dissolution and structural changes of the activated samples (Ball to Powder ratio of 15), and then comparison with the results of the dissolution of the initial sample, it was found that activation had the most effect on the dissolution of rare earth elements from phosphate concentrate and its effect is more than the increase in temperature and acid concentration.
- The dissolution of rare earth elements increased from about 1% (initial sample) to 35.79%, 42.61%, and 34.3% for cerium, lanthanum, and neodymium (after activation), respectively.
- Mechanical activation alters the crystalline structure and increases the number of free atoms ready to take part in reactions.
- Reduction in particles size and increase in their specific surface area are the only reasons of improved dissolution rate in refractory minerals, in fact, the use of mechanical activation alters the crystalline structure, which is proved to be the most important factor on degree of solubility.

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