

Article

The Occurrence States of Rare Earth Elements Bearing Phosphorite Ores and Rare Earth Enrichment Through the Selective Reverse Flotation

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Abstract: The reserve of rare-earth element-bearing phosphorite ores in Guizhou province in western China is huge. Increased demand for the different products manufactured from rare-earth elements has resulted in an extreme need for reasonable and comprehensive extraction of rare-earth elements. An improved understanding of rare-earth element occurrence states in single minerals of ores is important for their further processing. In this paper, rare-earth element contents were analyzed by inductively coupled plasma (ICP), and the occurrence states in single minerals were further investigated through SEM-EDS and focused ion beam-scanning electron microscope (FIB-SEM) methods. The results indicate that rare-earth element contents of apatite are far more than that of dolomite. No independent mineral of rare-earth elements exists for the studied sample. Rare-earth elements are present in the form of ions in the lattices of apatite. Based on the analysis of occurrence states and properties in single minerals, the distribution of rare-earth elements in the flotation process was investigated by reverse flotation technology. It shows that rare-earth elements are mainly concentrated in apatite concentrate. Under the optimized conditions, the P₂O₅ grade increases from 11.36% in the raw ore to 26.04% in the concentrate, and the recovery is 81.92%, while the total rare-earth oxide grade increases from 0.09% to 0.21% with the recovery of 80.01%, which is similar to P₂O₅ recovery. This study presents the feasibility of extracting rare-earth elements from rare-earth element-bearing phosphorite ores through the flotation of apatite.

Keywords: phosphorite ores; rare earth; apatite; occurrence states; froth flotation

1. Introduction

Phosphorite ores are vital nonrenewable resources and essential components in phosphorous-based chemicals and agricultural fertilizers [1]. One of the major products of phosphorite ore plants in China is a large composite ore deposit with apatite concentrate containing rare-earth elements (REEs). Recent data have estimated that total rare-earth oxide (TREO) production worldwide averages 110 Mt, with not less than 80% of production from China [2]. Several economically important phosphorite deposits occur in Guizhou Province, China. These deposits are noted for their greatly abundant REE reserves, but considerably low rare-earth oxides (REO) grade. The phosphorite ores in Guizhou hold an important position in explored apatite and rare-earth reserves of China [3].

The term REEs consists of the lanthanide series of elements, coupled with the chemically similar yttrium, and occasionally, scandium [4]. REEs and compounds are critical for a range of rapidly expanding industrial applications embracing renewable energy, agriculture, textiles, petroleum, metallurgy, catalysis, and specialty materials that rely upon their special chemical, optical, magnetic,

and electrical properties [5]. The challenge of the REE supply due to the scarcity of mineral deposits is aggravated by the fact that the elements are never found in an equal or even predictable distribution [6]. Therefore, reasonable and comprehensive extraction of REEs is important. Many researchers have identified the organic or mineral phases in which P and REEs are encountered and their distribution in the geological record [7]. These studies are more about the ore characteristics, but the investigations on REE contents and the existing state in single minerals of ores were reported little. In addition, the key constraining factors of exploitation of the single minerals are occurrence states of the P and REEs in the phosphorite ores [8]. To aid in industrial separation of ores, it is necessary to find out the occurrence states of P_2O_5 and REO in independent minerals or isomorphism.

Leaching is one of the chemical methods for the beneficiation of the REEs from the phosphorite ores. Leaching is often conducted using sulfuric acid, which breaks down the crystal structure of the mineral [9]. However, in this process, large amounts of toxic byproducts are produced. Various physical separation methods, such as gravity, magnetic and electrostatic separations, and most critically, froth flotation [10], are widely applied for enrichment of apatite [4]. In particular, the method of reverse flotation dolomite to enrichment apatite is the most popular one [11]. Nonetheless, flotation of REO involves several challenges owing to the discrepancies in REEs occurrence states and the considerably low-grade [12].

In this work, the mineral compositions and REE contents of the phosphorite ores were evaluated using X-ray diffraction (XRD), X-ray fluorescence (XRF), inductively coupled plasma (ICP), and scanning electron microscope-energy dispersive X-ray spectrometer (SEM-EDS) methods. The single apatite as the main phosphoric valuable mineral and the single dolomite mineral as the main gangue mineral in phosphorite ores were separated from ores using a manual method, respectively. The existing REE states in them were measured with focused ion beam-scanning electron microscope (FIB-SEM) technology. Moreover, the rougher reverse flotation experiment was carried out to see the distribution of REE in concentrate and its corresponding tailing product. While there have been many investigations on the flotation of apatite from the phosphorite ores, there has been little reported study about the flotation of REEs from REE-bearing phosphorite ores, to the knowledge of the authors. The objectives of the present work are to provide a theoretical basis for the comprehensive development and utilization of Guizhou REE-bearing phosphorite ores and REE enrichment in this process.

2. Experimental

2.1. Mineral Samples

Phosphorite ores originating from Guizhou province in China were crushed to 90% passing 74 μm . Based on the XRD (D8-FOCUS, BrukerAXS, Karlsruhe, Germany, Cu-K α radiation) analysis, the compositions of the phosphorite ores are apatite (24–26%), dolomite (55–57%), quartz (15–16%), feldspar (3–4%). XRF (PANalytical-AxiosMAX, Almelo, The Netherlands) chemical analysis indicated that the samples contained 11.36% P_2O_5 , 10.87% MgO, 17.59% SiO_2 , 33.52% CaO, and 1.76% Fe_2O_3 (Table 1). The REE compositions of the phosphorite ores detected by ICP (DGS-III, Shanghai, China) were given in Table 2. It is understood from this table that yttrium, with distribution of 45.86%, is the predominant form of REEs in phosphorite ores. The ICP result also revealed the absence of radioactive elements (uranium and thorium) in the phosphorite ores. This considerably simplifies and cheapens the technology of obtaining the commodity REE products because the REEs extracted from phosphorite ores are also not radioactive and, hence, do not require decontamination or question about burying the radioactive wastes.

2.2. SEM-EDS and FIB-SEM Analysis

SEM-EDS (SU8010, Hitachi, Japan) was employed to provide morphological analysis and the composition of the apatite, dolomite, and quartz. The magnification time was fixed at 30.0 K. Prior

to the measurement, the samples were thoroughly ground, and then gold-coated using an ion coater under vacuum environment.

A FIB-SEM (FEI Helios 650, Hillsboro, OR, USA) equipped with an energy-dispersive X-ray spectrometer (EDS) was used to observe the microstructure of the material and collect elemental data with accompanying backscatter electron (BSE) images. Polished and grain-mounted samples were evaporatively coated with ~10 nm of Pd. Elemental X-ray maps for different elements were acquired by EDS and TEAM Enhance V4.5-Released software.

Table 1. Chemical composition of the feed by X-ray fluorescence (XRF) analysis (wt %).

Component	P ₂ O ₅	MgO	CaO	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	ZnO
Content	11.36	10.87	33.52	17.59	1.15	0.08	0.54	0.01
Component	Fe ₂ O ₃	MnO	CuO	PbO	SO ₃	F	Cl	CO ₂
Content	1.76	0.17	0.01	0.01	0.03	2.63	0.01	19.45

Table 2. Rare-earth element (REE) compositions of the feed by inductively coupled plasma (ICP) analysis.

Component	La ₂ O ₃	CeO ₂	Pr ₂ O ₃	Nd ₂ O ₃	Sm ₂ O ₃	Eu ₂ O ₃	Gd ₂ O ₃	Tb ₄ O ₇
Content/10 ⁻⁶	185.46	93.78	24.09	87.59	10.64	0.00	10.52	6.41
Proportion	20.62	10.43	2.68	9.74	1.18	0.00	1.17	0.71
Component	Dy ₂ O ₃	Er ₂ O ₃	Tm ₂ O ₃	Yb ₂ O ₃	Lu ₂ O ₃	Y ₂ O ₃	Ho ₂ O ₃	Total
Content/10 ⁻⁶	10.36	6.25	18.03	4.36	0.57	412.51	28.94	899.52
Proportion	1.15	0.70	2.00	0.48	0.06	45.86	3.22	100.00

2.3. Rougher Flotation Tests on a Laboratory Scale

The ores were ground to 90% passing 74 µm, and flotation tests were carried out in a flotation machine (RK, XFD-0.5L, Wuhan, China). The pulp was conditioned at 25% solids, and the impeller speed was fixed at 2000 r/pm. Analytical grade reagent H₂SO₄ was used as a pH regulator by adjusting the pulp pH around 6 and was conditioned for 5 min. A desirable H₃PO₄ (depressants, 6000 g/t) and α-sulfonic acid fatty acid soap (SFAS, collector, 1400 g/t) were added and agitated for 5 and 7 min, respectively. The floated fraction was then gathered for 5 min. The concentrate (unfloated fractions) and tailing (floated fractions) were dried separately and weighed to calculate the yield and the recovery. Each test was repeated thrice for which an average recovery was reported. The recovery was calculated using the following formula:

$$\text{Recovery}(\%) = \frac{\text{Concentrate Grade}\%}{\text{Feed Grade}\%} \times \text{Concentrate yield}\% \times 100 \quad (1)$$

3. Results and Discussion

3.1. Microstructure of the Single Minerals

According to the XRD result, the apatite is the most abundant mineral matter, and the dolomite and quartz are the main gangue minerals in the phosphorite ores studied. Therefore, it is important to further investigate the corresponding elements' contents in single minerals. The elements' contents and existing state of the main minerals (apatite, dolomite and quartz) were analyzed by SEM-EDS.

3.1.1. Apatite

The main phosphoric valuable mineral was the cryptocrystalline or extremely fine crystalline apatite [13]. SEM observation shows that the apatite was spherical or ellipsoid. The results of SEM-EDS of the single apatite are presented in Figure 1. The main elements of the apatite were Ca and P. The main REEs of the apatite were Y, La, Ce, Pr, Nd, and Ho. The concentrations of these

REEs were 1.25–2.0 wt %, 0.5–1.5 wt %, 1.0–1.75 wt %, 0.5–1.75 wt %, 0.75–2.0 wt %, and 1.00–2.25 wt %, respectively. No independent mineral of REEs was found in this investigation. Therefore, apatite was the main source of REEs for the phosphorite ores. Presumably, REEs are present in the form of ions in the lattices of apatite.

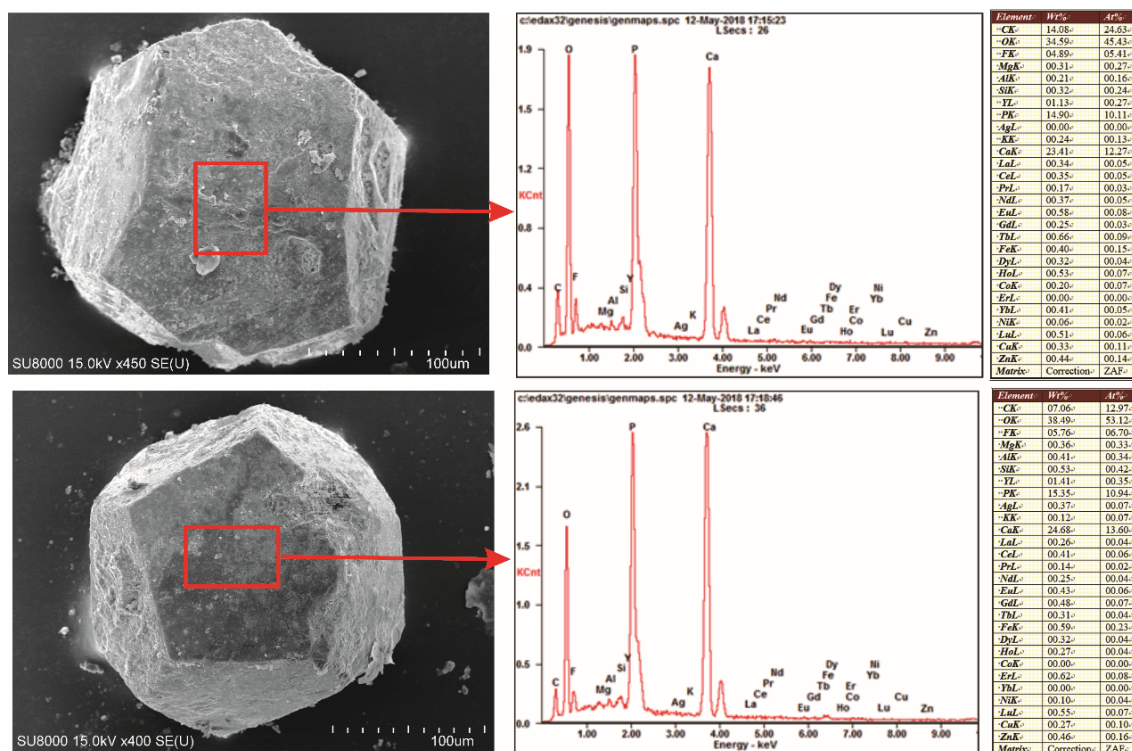


Figure 1. The microstructure and composition of apatite by using SEM-EDS analyses.

3.1.2. Dolomite

The dolomite had a crystal structure like that of calcite and was almost laminal or rhombohedron in shape. The dolomite grains were mainly distributed in the apatite in the form of cements. The results of SEM-EDS of the single dolomite are presented in Figure 2. The main elements of the dolomite were Ca, Mg, and O with an absence of REEs. After a complete survey of samples under SEM, it can be clearly seen that REEs and P contents of apatite were far more than that of dolomite.

3.1.3. Quartz

As for another gangue mineral, the quartz belonged to the trigonal system with a conchoidal breakage fracture. The results of SEM-EDS of the single quartz are presented in Figure 3. The main elements of the quartz were Si and O with little or no REEs.

3.2. Hand Specimen and FIB-SEM Analysis

Application of pretreatment in phosphorite ores was implemented in three simple steps: Desliming, dehydration, and screening. The single apatite and the paragenesis of apatite–dolomite were separated from samples using a manual method under a ZEISS-Stemi 508 electron microscope. In the hand specimen, according to the colour and hardness of these samples, typically, paragenesis was identified as combinations of apatite and dolomite (Figure 4, right). There were also some rounded grains, as single apatite (Figure 4, left) could be separated from samples using a manual method.

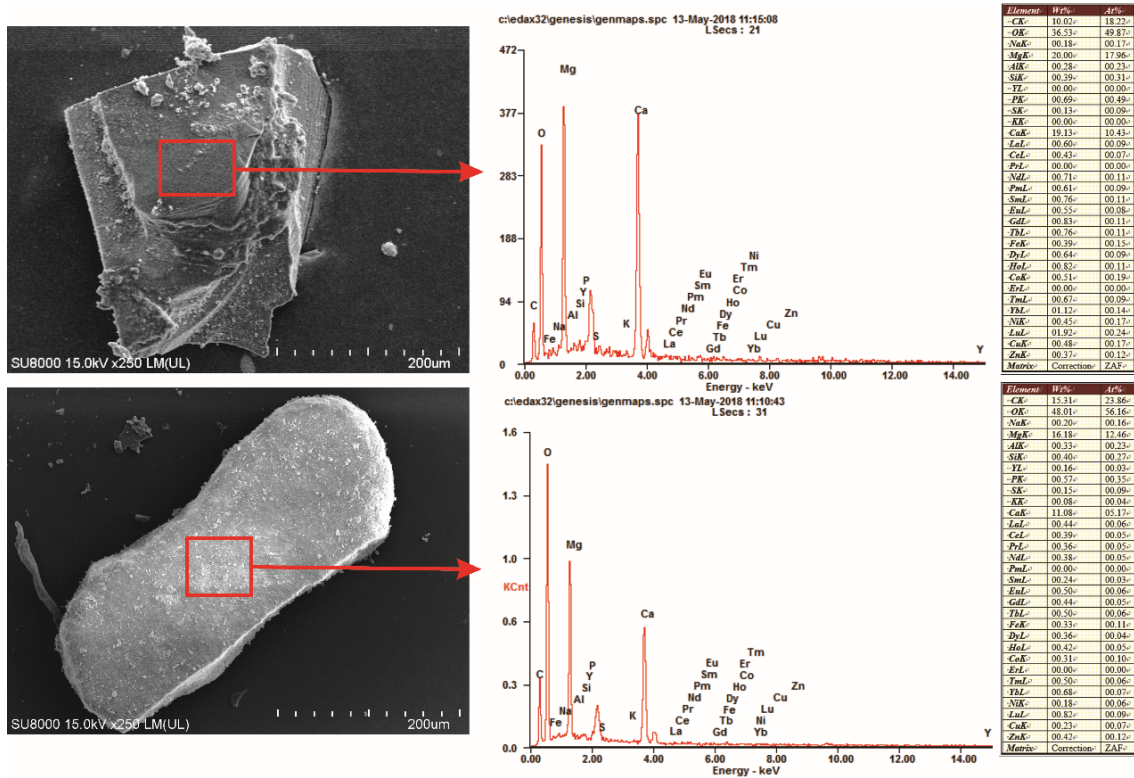


Figure 2. The microstructure and composition of dolomite using SEM-EDS analyses.

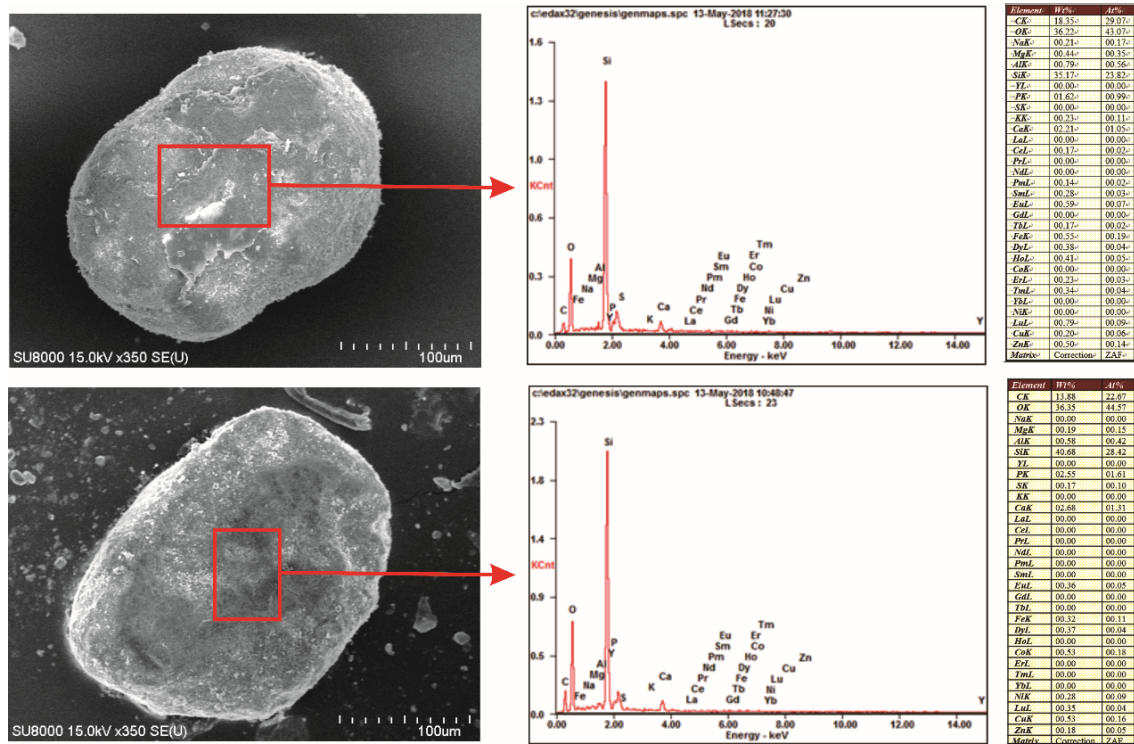


Figure 3. The microstructure and composition of quartz using SEM-EDS analyses.



Figure 4. The single apatite (**left**) and the paragenesis of apatite–dolomite (**right**).

Based on the above SEM-EDS analysis of single minerals, the REEs were mainly present in apatite. The FIB-SEM analysis was further carried out to evaluate the main elements associated with the paragenesis mineral. Figure 5 shows the BSE images of a sample from phosphorite ores. Apatite is red and includes Ca, P, and O. Dolomite is orange and includes Ca, Mg, and O. The BSE imaging shows that apatite occurs as impure laminae, lenses, and round-oval nodules and is chemically homogeneous. As can also be seen in Figure 5, there is no independent mineral of REEs, such as xenotime, cerianite, and monazite in the sample studied [14]. The elemental mapping suggests that Y and Ca, and P and O have the same sources, suggesting that REEs are tracked as impurities in apatite. The radii of REEs and the radius of Ca^{2+} are very close. REEs are supposed to be associated with apatite through replaced calcium by isomorphous [15]. Presumably, REEs are present in the form of ions in the lattices of apatite, which makes it extremely difficult to directly extract REEs from apatite. Hence, the following flotation experiment was carried out to further investigate REEs distribution in flotation products to provide valuable references for the utilization of the phosphorite ores.

3.3. REEs Distribution of Concentrate and Tailing Products

According to our single factor experiment results, the optimal experiment condition is a pulp density of 25%, flotation pH of 6, H_3PO_4 dosage of 6000 g/t, and collector dosage of 1400 g/t. The reverse flotation technology flowsheet is shown in Figure 6. A high-grade concentrate and its corresponding tailing product were analyzed by XRF and ICP to determine the recoveries and grades in the separated products. The experiment results of the reverse flotation of phosphorite ores under the optimal conditions are summarized in Tables 3–5. The collector SFAS exhibited stronger selectivity towards adsorption on dolomite. The apatite was rarely recovered by SAFS. The reverse flotation process of phosphorite ores realized the apatite concentrate with a P_2O_5 grade of 28.06 wt % and recovery of 81.92%, and the grade of MgO in the concentrate reduced from 10.87 to 0.75 wt %. From the investigations, it can be concluded that, from a selectivity (of apatite) standpoint, the use of collector SAFS and depressant H_3PO_4 has the effect of synergistic enhancement. The interaction between SAFS

and Mg on the dolomite surface strengthened the chemisorption effect [16]. Owing to the considerable Mg content of dolomite and the lack of Mg in apatite, SFAS was selectively chemisorbed onto the dolomite surface. That is the reason why the floatability of dolomite was higher than that of apatite.

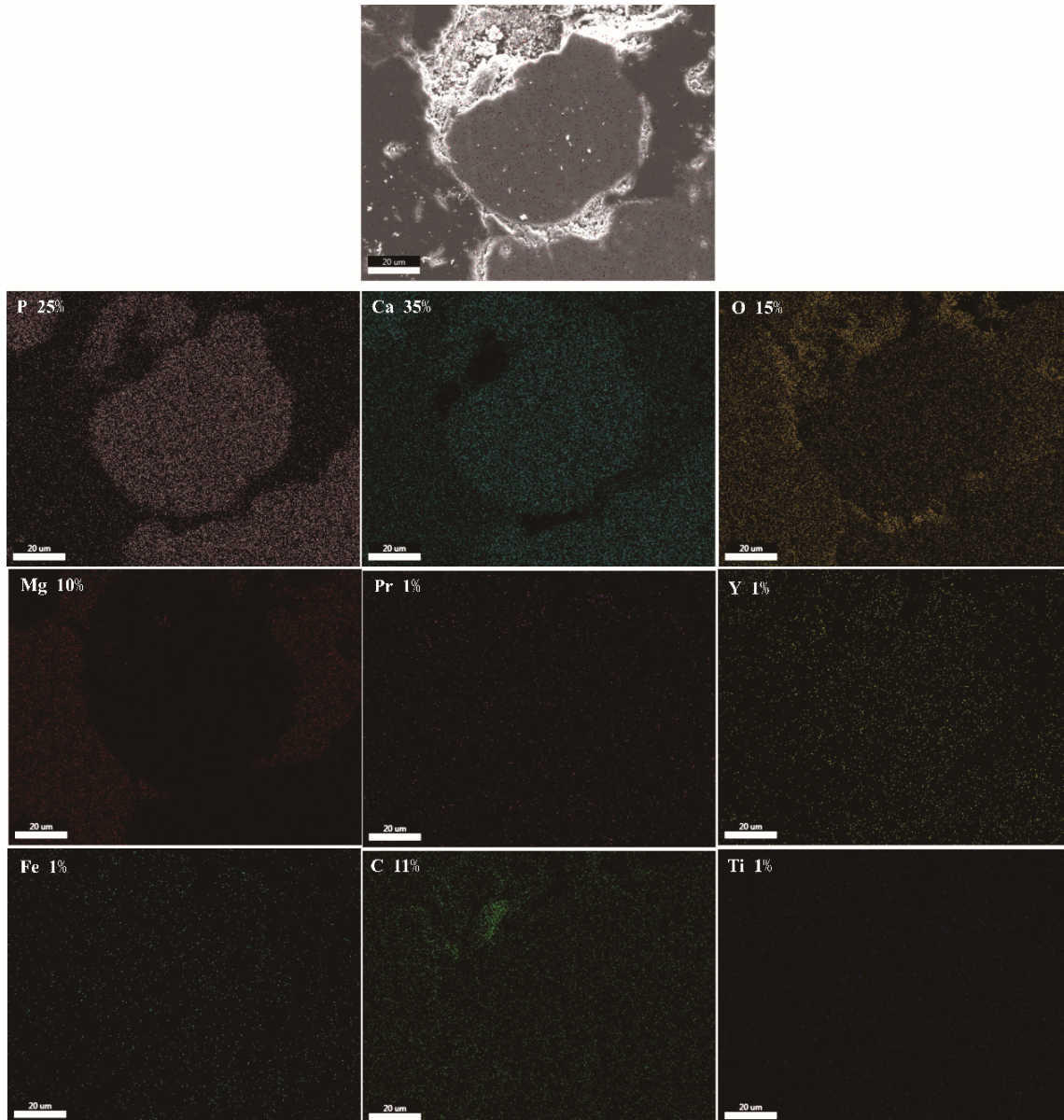


Figure 5. The backscatter electron (BSE) images of a sample from phosphorite ores using focused ion beam-scanning electron microscope (FIB-SEM) analyses.

The results of the ICP analysis (Table 4) indicated that the TREO content in the concentrate was 65.39%. The TREO grade in the concentrate was 0.21%, concentrating the REE by 2.3 times with respect to the feed (TREO feed grade = 0.09%). The results confirm that Y, La, Ce, and Nd are the major REEs in the concentrate, in the order Y > La > Ce > Nd. Among them, Y represents about 47.82% of the TREO content of the concentrate. The remaining major REE components include Pr, Gd, Sm, Tm, Tb, Dy, Er, Yb, and Ho. It can also be observed from the ICP results that 80.01% of the REO content in the feed was recovered into the final flotation concentrate, and the TREO recoveries of concentrate were similar to those of the P₂O₅ recovery.

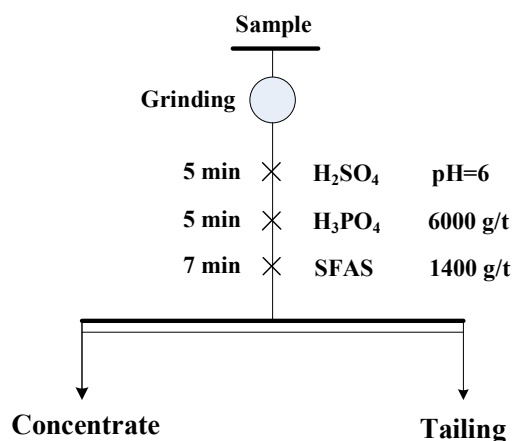


Figure 6. The rougher flotation flowsheet.

Table 3. The flotation result of P_2O_5 under the optimal flotation conditions by X-ray fluorescence (XRF) analysis.

Concentrate	Yield (%)	Grade (%)		Recovery (%)
		P_2O_5	MgO	
Content	34.12	28.04	0.75	81.92

Table 4. REE compositions of the concentrate by ICP analysis.

Component	La_2O_3	CeO_2	Pr_2O_3	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3	Tb_4O_7
Content/mg/L	417.71	224.00	54.20	189.08	23.94	0.00	23.67	14.42
Component	Dy_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	Y_2O_3	Ho_2O_3	Total
Content/mg/L	23.31	14.06	39.57	9.81	1.28	1008.15	65.12	2108.32

Table 5. The flotation result of total rare-earth oxide (TREO) under the optimal flotation conditions by ICP analysis.

Concentrate	Yield (%)	Grade (TREO, %)	Recovery (%)
Content	34.12	0.21	80.01

The results indicate that improving P_2O_5 grade and recovery of concentrate in the flotation process would result in an improvement of TREO grades and recoveries in concentrate. The result is also in accordance with research on the microstructure of single minerals, that the REEs are mainly present in apatite and existing good correlation with phosphorus. Therefore, enrichment of REEs can be achieved through the flotation of apatite.

4. Conclusions

In this paper, the microstructure of single minerals and the paragenesis mineral were analyzed, and flotation studies of the phosphorite ores were carried out to further decipher the nature of the occurrence state of REEs in apatite. The following conclusions can be drawn from the above discussion:

The P_2O_5 contents and REE compositions of the phosphorite ores were analyzed by XRF and ICP methods. The apatite was the most abundant mineral matter, and the dolomite and quartz were the main gangue minerals. The ores belonged to low-grade phosphorite ores containing REEs, low P_2O_5 content, high CaO content, and associated low REE content.

The SEM studies show that apatite is the main source of REEs for the phosphorite ores. No independent mineral of REEs was found in this investigation. The FIB-SEM analysis indicates that

Y and Ca, and P and O have the same sources, suggesting that REEs are present in the form of ions in the lattices of apatite.

In the optimized conditions, an excellent concentrate with a P₂O₅ grade of 28.04% and recovery of 81.92% was achieved after the rougher reverse flotation. The grade of MgO in the concentrate reduced from 10.87 to 0.75%. The TREO grade in the concentrate was 0.21%, concentrating the REE by 2.3 times with respect to the feed.

ICP results showed that 80.01% of the REO content in the feed was recovered into the final flotation concentrate, and the TREO recoveries of concentrate were similar to P₂O₅ recovery. The correlation between TREO recoveries and P₂O₅ recovery is also in accordance with the research on the microstructure of single minerals, that REEs are mainly present in apatite and existing good correlation with phosphorus. Therefore, enrichment of REEs can be achieved through the flotation of apatite.

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