



Study on the Rare Earth Containing Phosphate Rock in Guizhou and the Way to Concentrate Phosphate and Rare Earth Metal Thereof

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Abstract

Guizhou province is one of the main phosphate resources base in China, characterized with the co-existence of rare earth in the phosphate rock. In this work, the phosphate rock samples in Zhijin County, Guizhou province have been collected and analyzed using ICP, X-Ray diffraction, Scanning microscope, Infrared spectra and X-ray photoelectron spectroscopy. It is found that the total content of rare earth elements in the phosphate rock is about 0.1 wt%, amongst which Y, La, Ce, Pr, Nd and Sm are the main rare-earth components and co-sit the lattice of the apatite. The phosphate content in the as-collected rock is more than 20 wt%, and impurities such as quartz, calcite and clay are also present. The raw phosphate rock physically was treated with flotation to remove the impurities such as quartz and calcite; a refined phosphate with rare earth elements of more than 0.1 wt%. The refined phosphate rock is then treated with excessive H₃PO₄ to dissolve the apatite; the residue from the dissolution gives an earth enriched precipitation, which contains up to 2 wt% rare earth elements.

Compared to the conventional way to use H₂SO₄ to extract phosphate, the treatment of the refined phosphate with phosphoric acid leads to significantly improved rare earth oxide extraction.

Keywords: Phosphate; Rare earth; Calcite; Quartz; Apatite

Introduction

A vast phosphate rock sedimentary reserve has been discovered in Guizhou province, south west of China, which is named as Kaiyang Phosphate Rock Reserve [1,2]. The characteristics of the phosphate reserve are that its phosphate content is relatively low, but it has some heavy rare earth elements such as yttrium and light rare earth such as lanthanum and cerium. Therefore this reserve is regarded as a vast phosphate reserve as well as a resource for rare earth oxides. However, the phosphorus content is in the range from 17 wt% to 24 wt%, which is poor to medium grade phosphate rock reserve [3-5].

It is estimated that there is about 1.248 billion tons of phosphorus deposit in the region which also contains about 1.446 million tons of rare earth oxide. The phosphorus deposit is distributed in 3 layers concurrence siliceous apatite deposit layer, siliceous phosphorus rock deposit, layering apatite deposit.

In terms of composition, the phosphorus rock reserve can be classified into agglomerate siliceous phosphate, phosphate rock containing dolomite and bioclast. The phosphate rock is mainly composed of calcite fluoroapatite, which is present in the form of non-crystalline, cryptocrystalline and colloid rock. Their main gangue is calcite, dolomite, and ankerite [5-7].

The impurities in the reserves include dolomite, calcite, quartz, clay, sphalerite and pyrite. The key feature of Kaiyang Phosphorite reserve is that it contains some amount of rare earth elements especially yttrium and light rare earth such as La, Ce, however, the content is lower [8-10].

Up to now, there has been lots of research into upgrading and extracting phosphate from the rock, which normally adopts the milling, flotation followed by acid leaching approach. This is a general processing adopted for all the phosphate rock [2], which mostly enriches the phosphate, but the rare earth element may be lost with the gangue. There has been little detailed structure and characteristic analysis on the Kaiyang phosphorus rock and the way to benefit both phosphate and rare earth has not been reported.

In this work, we have employed various analytical techniques to characterize the composition and structure of the Kaiyang phosphate sedimentary. The state of phosphate and rare earth elements in it has been analysed. Also a way to extract phosphate and rare earth elements has been developed.

Experimental

The feed used in this study was Guizhou Kaiyang medium grade carbonaceous siliceous phosphate. Chemical analysis was conducted by inductive coupled plasma spectroscopy (ICP) and ICP-MS.

The crystalline structure and phase component of the samples were determined by X-ray diffraction (XRD) using a Philips X-PeRT Pro Alpha 1 diffractometer operating with Cu K α radiation ($\lambda=1.5406 \text{ \AA}$) at a tube current of 40 mA and a voltage of 45 kV. Data were collected over 2θ values from 20° to 80° at a speed of $1^\circ/\text{min}$.

The X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Perkin-Elmer RBD upgraded PHI-5000C ESCA system with monochromatic Mg K α excitation and a charge neutralizer. All bonding energies were calibrated to the C 1s peak at 284.8 eV of the surface adventitious carbon.

Fourier transform infra-red (FTIR) spectra were carried out

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by diffused reflectance using a Bruker Vertex-70. The geometry and morphology of the phosphate rock at different stages were investigated by JSM840F scanning electron microscopy (SEM), and the element analysis were determined by energy dispersive X-ray (EDX) in the scanning SEM mode.

A 40 mL hanging cell flotation machine is applied to conduct pure phosphate rock flotation tests. The rock sample of each test is 1.5 g, adding 25 ml distilled water, the action times of modifier and collector are kept for 1 minute in both cases, the floated sample is collected, filtered and weighed, and the recovery yield is calculated

Results and Discussion

The Kaiyang phosphate rock sedimentary is generally low to medium grade reserve. In this research, 8 medium grade phosphate rock samples have been collected from different points and mixed evenly. The composition of the samples is given in Table 1.

It is seen that the Kaiyang phosphate reserve contains about 21.4 wt% of P_2O_5 , it also contains significant amounts of Ca, Mg, MgO and Al as the metal components. There is a small amount of F, and the total rare earth metal oxide content is about 0.089 wt%.

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Each of the rare earth elements in the Kaiyang phosphate is measured in the raw rock and the results of the metal are shown in Table 2. The low non-detectable rare earth elements are not included. The high content of rare earth elements in Kaiyang reserve are Y, and La, Ce, the level of Nd is medium, and some Sm, Dy and Gd are also detected, although the main rare earth elements are light ones. Overall, the total rare earth content is high, in agreement with the literature.

The XRD patterns of the Kaiyang phosphate rock are shown in Figure 1. The crystalline phases in the Kaiyang phosphate rock include quartz, fluorapatite which may contain La and Y even Gd in the crystallites. However the main phosphate crystalline phase is fluorapatite, which accounts for 90% of the phosphate in the rock. The gangue in the Kaiyang phosphate rock are dolomite and calcite, which are not very high, however, pure CaF_2 phase is not detected which suggests that the F is mainly in fluorapatite [11-14].

The infrared spectra of the raw Kaiyang phosphate rock are shown in Figure 2. The raw phosphate rock has the main peaks at around 1035, 602 and 501 cm^{-1} are ascribed to the apatite, maybe due to the rare earth existence in the lattice of the fluorapatite phosphate, the frequencies of the P=O vibrations tends to be lower than the ones containing no rare earth [13-15].

The bands at 1457.38, 1430.38 and 879.2 cm^{-1} are due to the vibrations of C=O in the calcite [12,14-16] the peaks are strong,

Element	P_2O_5	CaO	SiO_2	MgO	Al_2O_3	FeOx	F	total Re_2O_3
Content wt%	21.4	53.1	9.2	8.36	6.1	2.51	2.1	0.089

Table 1: the composition of Kaiyang Phosphate Rock.

Rare-Earth Element	La	Ce	Nd	Pr	Sm	Dy	Gd	Y
In the raw rock:wt% x1000	0.24	0.205	0.12	0.036	0.032	0.036	0.031	4.04

*The data are from ICP analysis

Table 2: Rare earth element* content from raw phosphate rock.

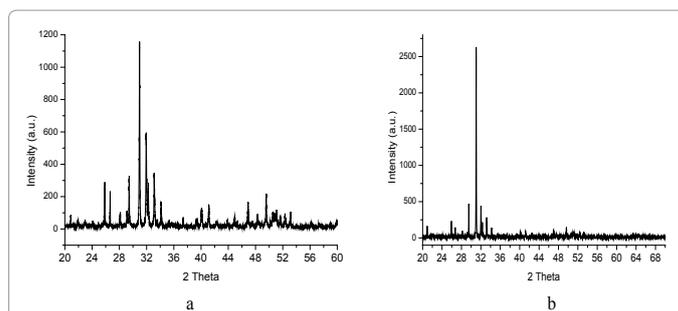


Figure 1: The XRD patterns of the medium graded phosphor rock. a. The raw phosphate rock. b. The upgraded phosphate rock through flotation.

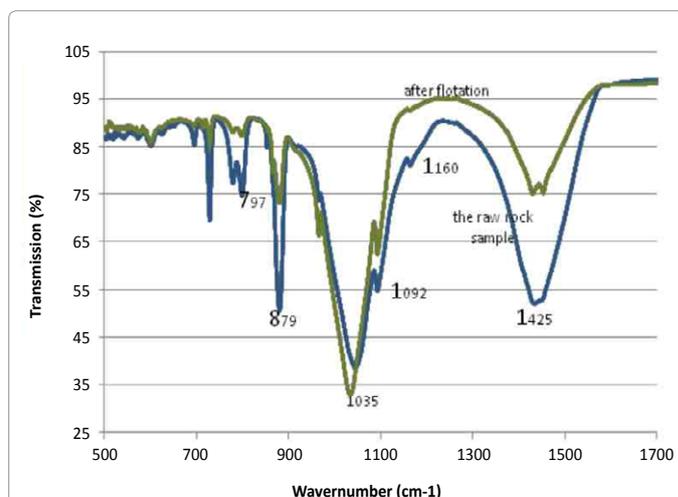


Figure 2: IR spectra of the Kaiyang phosphate rock before and after flotation.

Name	The raw phosphite rock		The floated sample		
	Position BE	%At Conc (Atomic Concentrations)	Position BE	%At Conc (Atomic Concentrations)	
P 2p	134.7	4.864	135.03	6.428	Na_3PO_4 (132 eV)
O 1s	531.8	49.661	531.95	43.721	
Ca 2p 1/2	351.56	4.347	352.03	3.588	
Ca 2p 3/2	348.1	6.508	348.41	5.414	like CaF_2 at 347.8 eV, or $CaCO_3$ (346.7 eV)
C 1s	285.54	28.018	285.88	28.478	
F 1s	684.51	2.411	684.92	2.979	Metal-F
Si 2p	104.07	3.529	103.78	3.12	Quartz
Y 3d	154.81	0.661	154.88	0.692	In forms of oxides, like Y_2O_3 , not YF_3

Calibration to O1s at 532 eV, metal oxides

Table 3: The XPS analysis results of the Kaiyang raw phosphate rock and floated sample.

which suggests that there is a significant amount of calcite in the raw phosphate rock. The peaks at 1092, 797.63, 692.89 and 516.27 cm^{-1} are from Si-O stretching attributed to quartz mineral [12]. The IR results are generally in agreement with the XRD results, which also revealed that these phases are present in the Kaiyang phosphate rock.

The X-ray photoelectron spectroscopy (XPS) is a powerful tool to analyse the states of the elements and also their surface composition in the materials. In this work we used XPS to analyse the Kaiyang phosphate sample, and the results are shown in Table 3.

It is seen that the surface of the raw Kaiyang phosphate rock is mainly covered with oxygen element, which can be understood as the phosphate, quartz, calcite and even dolomite all contain oxygen. The surface phosphorus content is only 4.68 at%, which is in the form of PO_3^- , as confirmed by XRD (Figure 1), which showed that the phosphorus is phosphite and not phosphate group. The carbon may come from calcite or the surface contained carbon. Silica content in the surface is about 3.52 at%. It is interesting to see that although there are La, Ce as evidenced by ICP-MS and XRD, the surface of the raw phosphate sample has Y, whose content is about 0.661 at%. The F is also in the form of metal fluoride attach to the Ca, but no separate CaF_2 detected in the XRD, suggesting that the F and Y may co-exist with the phosphate.

The physical floated sample to upgrade the phosphate rock

To remove the gangue in the rock, the raw phosphate rock was floated with a water solution of pH at 5.0 with fatty acid as the collector. The P_2O_5 content can be upgraded to 33.85 wt% with recovery rate of 60%.

The composition of the floated sample is given in Table 4. It is seen that the P_2O_5 increases with F and rare earth oxides while the MgO, SiO_2 and Al_2O_3 decrease significantly, this further supports the XRD results, which show that the phosphate, F and rare earth elements co-exist in the rock. The less significant change of CaO content is due to the Ca present in both the apatite and also dolomite and calcite.

The XRD pattern of the floated phosphate rock is shown in Figure 1b, it is seen that the gangue phase such as SiO_2 and $CaCO_3$ decreases significantly while the main phase, the rare earth containing calcium fluor phosphate increase in intensity, which is in agreement with the elemental analysis results.

The IR spectrum of the refined phosphate rock is also shown in Figure 2. These intensities of the bands correspond to SiO_2 and $CaCO_3$ drop while the ones arising from PO_3^- increase, in agreement with the XRD results.

The XRD and IR results give the bulk composition of the floated phosphate sample, the surface composition of the sample were analysed using XPS, and the results are shown in Table 2. It is seen that the states of the elements e.g., the binding energy position, of the P, Ca, Si, F and Re do not change compared to the raw sample, suggesting that the flotation does not change the surface property. However the composition of the element content changes. The P, F and Y content increases while the Ca and Si decrease. It is interesting that no Al or Mg is detected in XPS results, which may be covered by the phosphate, and rare earth metals.

The rare earth metal content in the residue of the acid treated floated phosphate

Phosphate rock is most often used for fertilizer or phosphoric acid production using sulfuric acid extraction into the process of phosphoric acid production. Phosphoric acid is normally produced by a wet-process, in which the phosphate rock reacts with a mixture of sulphuric acid. Calcium sulphate is the solid precipitation and aide products such as phosphogypsum and can be filtered away. In this way, the rare earth can easily get lost in the filtered precipitation. The sulfuric acid extract process is shown as follows:

P_2O_5	CaO	MgO	SiO_2	Al_2O_3	TFe_2O_3	F	Re_2O_3
33.85	45.04	4.24	3.7	4.75	1.65	3.47	0.162

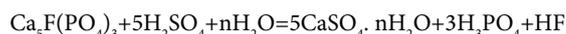
Table 4: Multi-element analysis of the floated pphosphate rock.

Rare-Earth Element	La	Ce	Nd	Pr	Sm	Y
In the raw rock:wt% x1000	0.32	0.28	0.25	0.046	0.032	20.7

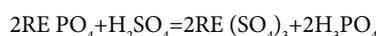
Table 5: Rare earth element* content from the residue of the H_2SO_4 treated phosphate rock.

Rare-Earth Element	La	Ce	Nd	Pr	Sm	Dy	Gd	Y	Yb
In the H_3PO_4 treated residue wt% x1000	213.5	298.4	76.3	20.6	12.1	9.3	10.4	698.6	8.1

Table 6: Rare earth element content from the H_3PO_4 treated phosphate rock residue.



The rare earth elements may react with sulfuric acid to give $Re_2(SO_4)_3$, however, the reaction may not be favored as the $RePO_4$ is much more stable than $Re_2(SO_4)_3$.



The rare earth element content in the residue of the H_2SO_4 treated phosphate rock is mainly gone with the phosphogypsum, where the rare earth element is analysed and the result is shown in Table 5.

It is seen that there is not a big difference between the rare earth element in the residue and the one in the raw phosphate rock, although the heavy re like Y is significantly concentrated in the residue. This is that the heavy Re sulfate is less soluble in the the extract system.

Here we tried to use 50% H_3PO_4 to treat floated phosphate rock at the ratio of the rock to acid ratio 1:4, we found that most rock was dissolved in the solution, which can be expressed as follows:



This is a soluble solution, while the $RePO_4$ is insoluble in the aqueous system, which is highly concentrated with the gangue such as SiO_2 and clay.

The elemental analysis of the residue in the H_3PO_4 treated system has been analysed for the rare earth content and the result is shown in Table 6.

It is noted that a significant concentration of rare earth has been achieved in the residue of the H_3PO_4 extracted system. The Y content is as high as 0.698 wt% in the residue, which can be further refined for rare earth extraction.

Conclusion

The Kaiyang phosphate rock samples have been analyzed using elemental analysis, XRD, IR and XPS for its composition and the rare earth content. It is seen that the P_2O_5 in the phosphate rock is about 25 wt%, which is mainly in fluoapatite form, while there is quartz and calcite and dolomite present in the raw rock. The rare earth elements include light, such as La, Ce and heavy rare earth like Y.

The rare earth and F co-exist in the lattice of the calcium rare fluoapatite, while the surface of the raw phosphate rock is mainly covered with Ca, O, F, P, and interestingly Y, which are mostly present in oxide form.

The flotation process can upgrade the phosphate rock and increase the P_2O_5 content to 33 wt% with more than 60% of recovery rate. The process increases the content of P, Ca, F and rare earth in the upgraded sample, suggesting that these elements exist in the same phase. The flotation removes mostly MgO, some quartz and calcite, but did not change the surface status of the elements.

The extraction of the phosphoric acid with sulfuric acid can give pure phosphoric acid, but also dissolves the rare earth elements in the phosphoric acid and the calcium lead to phosphogypsum. The rare earth element has a relatively small increase in the residue; however, extracting the calcium dihydro phosphate using H_3PO_4 can significantly increase the rare earth content in the residue which may be a way to enrich the rare earth elements.

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