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VARIOUS TECHNOLOGICAL PROCESSES

Study on the Selective Leaching of Low-Grade Phosphate Ore for Beneficiation of Phosphorus and Rare Earths Using Citric Acid as Leaching Agent[1]

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Abstract—In the study the organic/inorganic chemical leaching and enrichment technology were used for selective extraction of the dolomite which co-existed in the Zhijin low-grade phosphate ore for beneficiation phosphorous and rare earths (RE) by using citric acid as leaching agent. The effects of acid concentration, reaction time, reaction temperature, liquid/solid ratio, and particle size on P_2O_5 and rare earths grade and the recovery ratio of them were investigated. The results show that under the optimized experimental conditions (acid concentration 9%, reaction time 240 min, reaction temperature 40°C, liquid/solid ratio 50 : 1, and ore particle size 0.18–0.125 mm) the P_2O_5 grade can be increased from 15.47 to 34.82%, and P_2O_5 recovery rate comes up to 88.02%. The rare earths are mainly enriched in the leaching residues. Meanwhile, the recovery rate of rare earths is 72.08%. ΣREO grade can be increased from 978.06×10^{-4} to 1998×10^{-4}%. In addition, the reaction kinetics of the chemical reaction between citric acid and dolomite are also discussed, the results show that the leaching process is controlled by chemical reaction. The activation energy for leaching was found to be 36.6337 KJ mol^{-1} and k_0 was 3.67×10^4 s^{-1}, and the rate of the leaching based on the chemical reaction-controlled process could be expressed as $1 - (1 - a)^{1/3} = 3.67 \times 10^4 e^{-36.63/RT}t$. Compare to the conventional process, the method provided in this study not only has advantages including higher phosphate concentration and rare earth grade, and higher recovery rate, but also using less amount of chemicals. Meanwhile, the citric acid can be recycled, avoiding discharge wastewater.

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It is well-known that phosphate ore is an extremely important raw material for producing agricultural fertilizer. Over the past decades, more than 85% of the phosphate rock exploited all over the world was used to manufacture phosphate fertilizer. With the rapid growth of the world's population, the consumption of phosphate fertilizer and phosphorus ore has also increased rapidly [1–4]. After years of mining, shallow-store and high-grade phosphate rock has been reduced dramatically since it is a non-renewable resource. Hence, methods of exploitation and effective utilization of medium and low grade phosphate rock has attracting more and more attention in recent years.

The phosphate rock deposit in Zhijin area, Guizhou Province, China, is a marine sedimentary type deposit ore containing a relatively high content of light and heavy rare earth elements. According to the general planning of Zhijin Xinhua Phosphate Ore Area [5], the phosphate resources of this area have been estimated to reach upwards of 9.08 billion tons, and the average grade of P_2O_5 was approximately 24.16%. Meanwhile, the RE resources in the same area were estimated to reach 1.19 million tons, and the rare earth oxide content

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[1] The text was submitted by the authors in English.

Table 1. Chemical composition analysis results of Zhijin phosphate ore (GL-T)

Composition	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	P_2O_5	SiO_2	ΣREO (10^{-4})
Content,%	0.73	35.98	0.98	0.02	4.41	15.47	5.82	978.06

was generally 0.05–0.1%. In summary, Zhijin phosphate rock containing not only huge amounts of phosphorus, but also a great numbers of RE elements is an important source of phosphorus and RE elements in the world [6].

Previous study showed that more than 97% of RE elements bearing in the Zhijing phosphate rock were mainly in the state of isomorphism, and the partially replaced apatite crystal lattice contained calcium ion (Ca^{2+}) and magnesium ion (Mg^{2+}). Only less than 3% of RE elements were in the state of clay adsorption or ion-exchange [7]. Due to those mineralogy characteristics, it is very difficult to beneficiate and separate phosphorus and RE elements effectively and economically from Zhijin phosphate rock using conventional processes. Therefore, it is necessary to develop new methods for mining Zhijin phosphate rock.

During the past years, scientists came from various universities and research institutes have devoted a lot of efforts to develop appropriate processes for beneficiating and separating of P_2O_5 and RE elements from Zhijin phosphate rock. For instance, Li Jun Qi [8] used a kind of self-made collecting agent called WF-02 to optimize the reverse flotation process for Zhijin phosphate rock, the grade of P_2O_5 increased from 21.90 to more than 33.19%, the recovery rate of phosphorus was 89.89%, the grade of RE (sigma REO) increased from 0.07 to 0.12%, and the yield of RE was 83%. Another process for mining Zhijin phosphate rock that was researched, was the calcination-digestion method, the results showed that P_2O_5 grade can be increased from 14.07 to 28.81%. Zhou Ying etc. [9] used the combined process of stage grinding and stage selection to beneficiate Zhijin phosphate rock; P_2O_5 grade increased from 22.63 to 33.43%. Despite achieved great progress, the flotation process produced wastewater containing collecting agent, foaming agent, and other chemicals, and also increased environmental protection cost. The calcination-digestion process need more capital investment on the expensive equipment, and the high energy consumption was inevitable. In some studies, it has been proven to be using of organic acid solution as leaching agent to extract impurities selectively out from the rock is a novel and competitive and promising technology for beneficiating P_2O_5 and RE elements from low-grade phosphate rock. This technology is generally called selective leaching process and has advantages including higher beneficiating efficiency, lower investment on equipment, lower energy consumption, lower wastewater discharge, and so on [10].

Up to now, to the best of our knowledge, there is little research on beneficiating of Zhijin RE-containing phosphate ore via selective leaching process. In the paper, we first report the study on beneficiation of P_2O_5 and RE from Zhijin low-grade phosphate ore using citric acid solution as selective leaching agent. The effects of various experimental conditions on leaching and enrichment results were investigated in details. The results demonstrated that citric acid solution could be used as a potential leaching agent for beneficiating Zhijin low-grade phosphate ore, which not only could reduce obviously the leaching of impurities, but also could keep a high beneficiation efficiency of P_2O_5 and RE elements. In addition, the reaction kinetics of the chemical reaction between citric acid and impurities (dolomite) were also preliminarily discussed in this paper.

EXPERIMENTAL

Materials and Characterization

The experimental phosphate rock sample containing RE was obtained from Zhijin Gezhongwu phosphate ore area (Zhijin county in Guizhou province, China). The sample is a kind of low-grade banded dolomitic phosphate rock (apatite), and the sample number is GL-T. The chemical composition analysis result of the sample is listed in Table 1. Microscope image of apatite thin sections is shown in Fig. 1. From Fig. 1 it can be seen that apatite is distributed irregularly on a light-colored dolomite substrate, and the color of apatite is ranged from dark gray to black. The useful composition in apatite is banded structure collophanite. Optical microscope observation results show that most of the collophanite are homogeneous, only small parts of them are non-homogeneous and aphanitic. From the point of view of the morphological characteristics, collophanite is an aggregate of various shapes including granular, strip, lenticular, bone-needle,

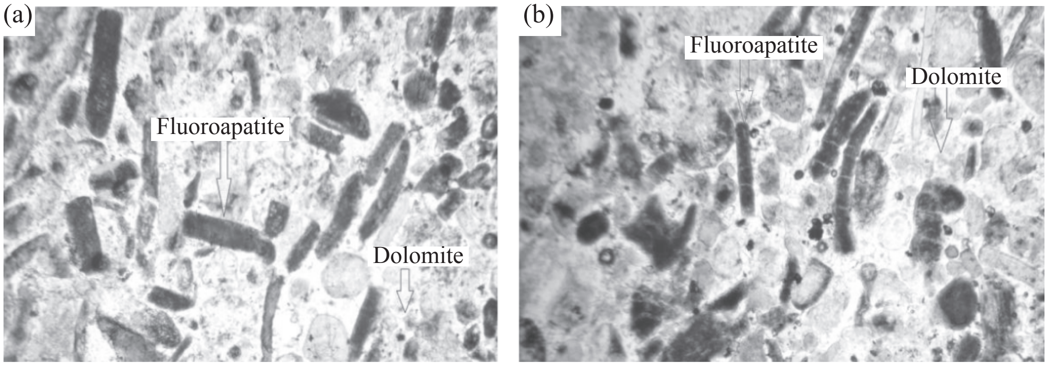

Fig. 1. Microscopic structure of Zhijin phosphate ore (GL-T). (a) Gezhongwu 2# phosphate rock GL-T: gray, bone structure of the crumb collophanite, (b) Gezhongwu 2# phosphate rock GL-T: gray strip Acicular collophanite.

and irregular-shaped, embedded in the caulking of dolomite. Generally, the organic matter is black and has the relationship of symbiosis and uneven distribution in the phosphate ore that is associated with collophanite. Dolomite is formed as a matrix of xenomorphic crystal, and its color is white, gray or light-gray.

In the analysis, after leaching, for each experiment, the recovery of P_2O_5 (%) was calculated as follow:

$$P_2O_5 \text{ recovery} = \frac{C \times c}{P \times p} \times 100\%, \quad (1)$$

where C is the weight of concentrate, c is P_2O_5 concentration (%) in the concentrate, P is the weight of original phosphate ore and p is P_2O_5 concentration (%) in original phosphate.

The chemical compositions of Zhijin phosphate rock sample (GL-T) were identified by X-ray diffractometry (XRD, Rigaku D/Max-2200, CuK_α at 40 kV, and 60 mA at 6 min^{-1} scan rate) and Polarized electron microscope. XRD analysis results (Table 2) indicated that the fluorapatite content in the Zhijin phosphate ore is 45.5%; the content of dolomite and quartz, 44.6% and 9.9%, respectively. Fluorapatite was fine particles uniformly distributed in dolomite space, the particle size ranged from 0.01 to 0.15 mm. Due to the tiny particle size of fluorapatite, it is necessary to grind the ore sample to a certain particle size to separate fluorapatite and dolomite effectively.

Laboratory Equipment and Analytical Instruments

X-ray fluorescence spectrum analyzer (XRF, Axios Max4^{KW}, PANalytical manufactured by Netherlands); inductively coupled plasma mass spectrometer (ICP-MS, HK-9600, Tiancheng Technology Co., Ltd. Beijing Branch); X-ray diffractometer (XRD, PANalytical B.V., Rigaku D/Max-2200, X Pert pro); XZM-100 vibration mill prototype, Wuhan prospecting machinery plant); Polarizing microscope (Olympus BX51-P and Nikon-D7000 Camera, Japan); PZ-40×80F jaw crusher (Jilin Province prospecting Machinery Plant).

Chemical agent: citric acid of analytical pure, provided by Tianjin Yongda chemical reagents Ltd.

EXPERIMENTAL

In this study, the influence of leaching agent (citric acid) concentration, reaction time, liquid/solid ratio, reaction temperature, and particle size on selective leaching results were investigated in details.

Firstly, the samples were crushed and grinded to a certain particle size and were dried at 105°C

in an electric oven for 8 h. After cooling to ambient temperature, the dried samples were further grinded to get the required size fraction, using a mortar grinder. Secondly, the selective leaching experiments were carried out in a 500-mL open glass reactor. A certain volumes of citric acid solution with various concentration was

Table 2. Mineralogical compositions of Zhijin phosphate ore (GL-T) analyzed by XRD

Composition	Fluorapatite	Dolomite	Quartz
Content,%	45.5	44.6	9.9

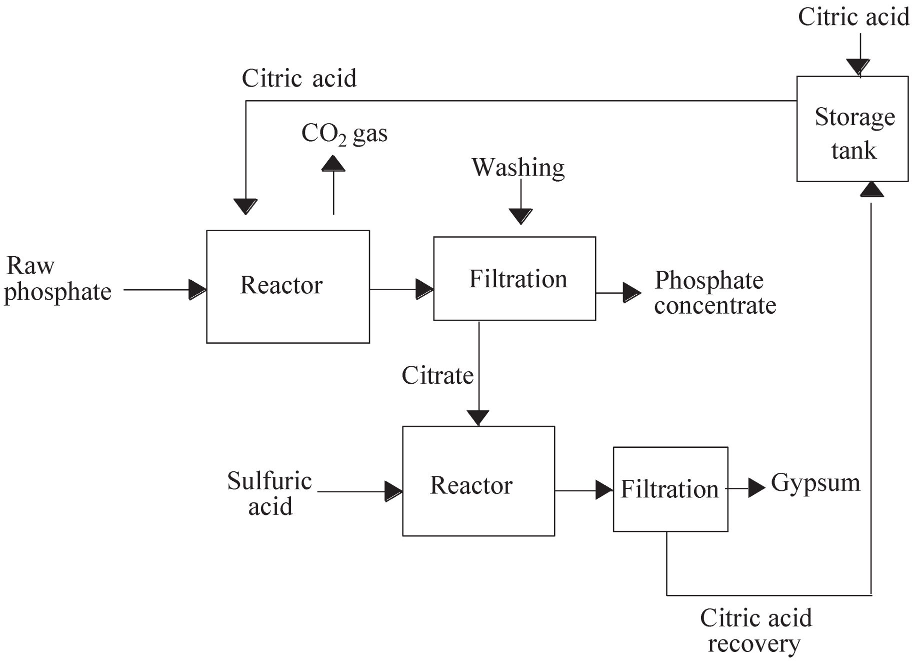

Fig. 2. Schematic diagram of the leaching process.

pour into the reaction glass and was heated to reaction temperature, using a constant-temperature water bath. Then the phosphate ore sample powder was added slowly into the reaction glass under stirring and the leaching reaction was beginning. During the experiments, the stirring speed was fixed at 300 rpm because the pulp can be stirred evenly under this condition, and no obvious sediment accumulated at the bottom of the reaction flask. Finally, the reaction was stopped by placing the reactor in an ice bath at the end of reaction. The solid phase was separated from the reaction solution by filtration and dried at 105°C to a constant weight.

The P_2O_5 content of the solid phase, i.e., leaching residues, was analyzed by X-ray fluorescence spectrum analyzer (XRF) and RE elements were determined by inductively coupled plasma mass spectrometer (ICP-MS). The mineralogical compositions of the leaching residues were identified by X-ray diffractometry. The schematic diagram of the leaching process is shown in Fig. 2.

RESULTS AND DISCUSSION

The selective leaching of phosphate rock using citric acid as leaching agent was considered from theoretical point of view. Previous studies have showed that H^+ ion played a leading role in the process of selective dissolving dolomite from phosphate rock using organic acid solution as leaching agent. In other words, the main control factors of the leaching process were the ionization constant and concentration of organic acid. Hence, choosing appropriate organic acid and acid concentration would help to obtain higher reaction rate and higher dissolving ratio of dolomite, meanwhile it would help to avoid the dissolution of apatite [11].

Citric acid is a strong organic acid and it has three acid group and can be ionized; the ionization constant is $pk_1 = 3.13$, $pk_2 = 4.76$, $pk_3 = 6.40$, respectively. When dolomite contact with citric acid solution, its calcium and magnesium carbonate components are dissolved selectively, producing two kinds of soluble salts: calcium citrate and magnesium citrate, with releasing carbon dioxide gaseous. There is no any solid product formed in the reaction system. So, citric acid has a good potential to be an ideal leaching agent for selective leaching of dolomite. Therefore, in this study, citric acid was chosen as the leaching agent for the selective leaching of dolomite in Zhijin low grade phosphate rock.

The reaction between citric acid and dolomite is a solid/liquid interfacial reaction, in this reaction system a high concentration citric acid solution does not directly react with dolomite, since it has a strong O–H polarity. Therefore, citric acid is preferentially adsorbed onto the surface of the ore particles and decomposed fluorapatite [12]. In dilute citric acid solution, water, citric acid molecules affects the polarity of the O–H bond, so its

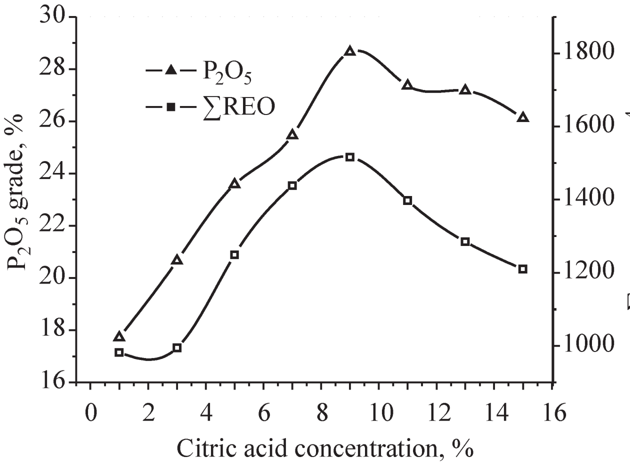

Fig. 3. Effect of citric acid concentration on P_2O_5 and ΣREO grade.

polarity becomes less strong, thereby increasing the degree of ionization. Such dilute citric acid is used as leaching agent, due to the increased degree of ionization, prompting citric acid leaching reaction selectivity with the dolomite component.

The chemical reaction between dolomite and citric acid is represented as the following formula:

$$3CaCO_3+2C_6H_8O_7 \rightarrow Ca_3(C_6H_5O_7)_2 + 3CO_2\uparrow + 3H_2O, \quad (2)$$

$$3MgCO_3 + 2C_6H_8O_7 \rightarrow Mg_3(C_6H_5O_7)_2 + 3CO_2\uparrow + 3H_2O, \quad (3)$$

Effect of Citric Acid Concentration

Under the experimental condition of reaction temperature 40°C, liquid/solid ratio 40 : 1, reaction time 60 min, and ore particle size –0.075 mm the effect of acid concentration on leaching result was investigated in details. The acid concentrations used in experiment were 1, 3, 5, 7, 9, 11, and 13%. Experimental results are shown in Fig. 3. It can be seen that the grade of P_2O_5 and RE elements increase with the increase in acid concentration while acid concentration varies from 1 to 9%. In the case of acid concentration 9%, the grade of P_2O_5 and ΣREO reach the maximum value, 28.65 and 1516×10^{-4}%, respectively. When the concentration of citric acid used for leaching was higher than 9%, the grade of P_2O_5 and ΣREO decreased with the increase in acid concentration due to the fact that fluorapatite in the ore can be dissolved in high concentration organic acid solution.

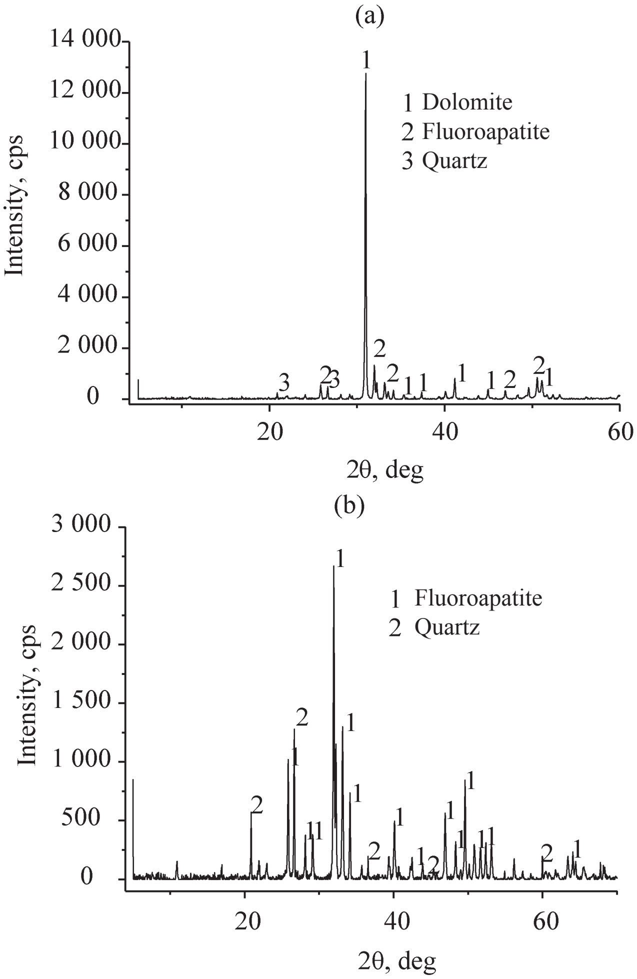

Fig. 4. XRD analysis results of phosphate rock (a) before and (b) after the acid leaching.

The XRD analysis results of the original phosphate rock and the GL-T ore sample leached by 9% citric acid solution are shown in Fig. 4. From the results in Figs. 4a and 4b it can be seen that the diffraction peaks of dolomite completely disappear (Fig. 4b), only the diffraction peaks of quartz and apatite can be seen, and no any other new substance's peaks are observed.

The result in Table 3 further show that after the GL-T ore sample was leached by 9% citric acid solution, the content of fluorapatite increases from 45.5 to 86%, yet the content of dolomite decreases from 44.6% to 0. Due to quartz cannot be dissolved by dilute citric acid its relative content in the leaching residues increases from 9.9 to 14% because of the decreasing of dolomite.

The combined results of Fig. 4 and Table 3 indicate that during the leaching process, only dolomite has been dissolved selectively, while fluorapatite and quartz have not been dissolved by citric acid.

Effect of Reaction Time

Under the conditions of citric acid 9%, liquid/solid ratio 40 : 1, reaction temperature 40°C, ore sample particle size –0.075 mm a series of experiments was carried out to investigate the effect of reaction time on the beneficiation results. The experimental results are shown in Fig. 5. In the initial stage of the reaction the concentration of citric acid and dolomite is relatively high, so the reaction rate is relatively fast, the dolomite component is decomposed quickly and release of CO_2 gas occurs violently, resulting that P_2O_5 and Σ REO content in the leaching residues increased obviously. With increasing of reaction time, citric acid and dolomite content becomes less and less, and the increase in P_2O_5 and ΣREO content becames less and less obvious. When reaction time increases to 240 min, dolomite is dissolved completely, and the grade of P_2O_5 and ΣREO in the leaching residues reaches to the maximum value, i.e., P_2O_5 grade 32.61% and that of ΣREO 1551 × 10^{-4}%, respectively. After that, with the prolonging of reaction time, collophanite is dissolved gradually by the excessive citric acid resulting in the decrease in P_2O_5 and Σ REO grades.

Effect of Liquid/Solid Ratio

With the condition: citric acid 9%, reaction time 240 min, reaction temperature 40°C, and ore sample particle size –0.075 mm, the effect of liquid/solid ratio on leaching result was investigated, using different liquid/solid ratio as 20 : 1, 30 : 1, 40 : 1, 50 : 1, 60 : 1. The experimental results are shown in Fig. 6. It was found that liquid/solid ratio is an important influence factor on the enrichment of phosphorus and RE elements. Liquid/solid ratio affects the concentration of ore slurry and the chemical reaction between citric acid and dolomite, thus, it affects the grade and recovery rate of P_2O_5 and ΣREO. Figure 6 shows that in the range of 20 : 1 to 50 : 1, the grade of P_2O_5 and ΣREO are increase with the increase шт liquid/solid ratio. At the liquid/solid ratio of 50 : 1 the grade of P_2O_5 and ΣREO reaches to the maximum value, i.e., P_2O_5 grade is 33.36% and that of ΣREO, 1673 × 10^{-4}%. When the liquid/solid ratio further increases to 50 : 1, there occur negligible changes in the amount of dolomite removed. The reason could be consisted in the higher liquid/solid ratio, the dolomite was dissolved more sufficient.

Table 3. XRD result of samples before and after leaching by citric acid

Ore characteristic	Fluorapatite, %	Dolomite, %	Quartz, %
GL-T (raw ore)	45.5	44.6	9.9
GL-T (after leaching)	86	0	14

Effect of Reaction Temperature

Under the condition: acid concentration 9%, liquid/solid ratio 50 : 1, reaction time 240 min, and ore sample particle size –0.075 mm, the effect of reaction temperature on leaching results was investigated at various temperatures 20, 30, 40, 50, 60°C. From the experimental result (Fig. 7) it can be seen that, with

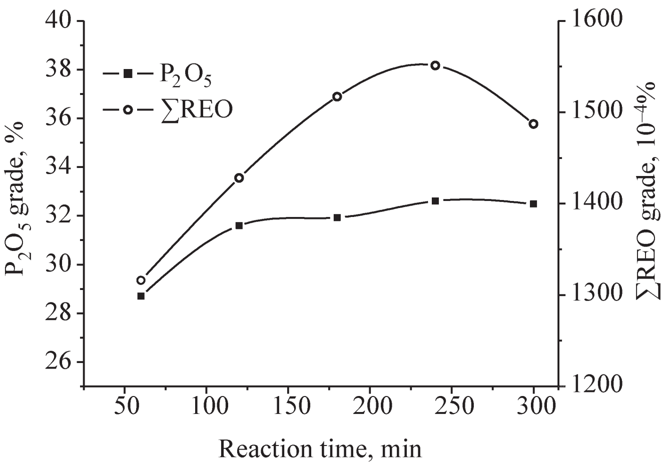

Fig. 5. Effect of reaction time on P_2O_5 and ΣREO grade.

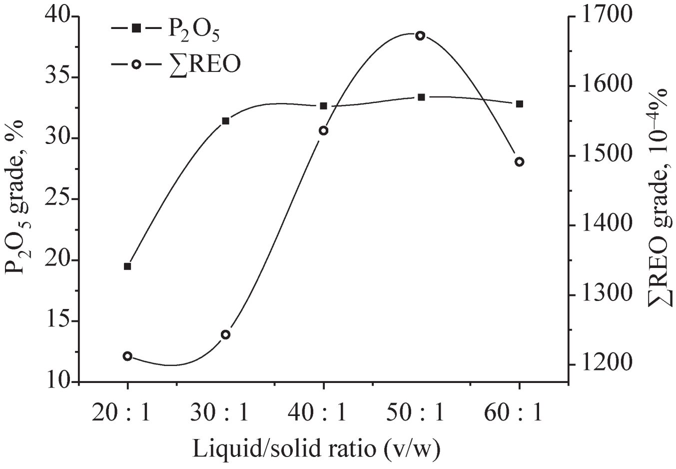

Fig. 6. Effect of liquid/solid ratio on P_2O_5 and ΣREO grade.

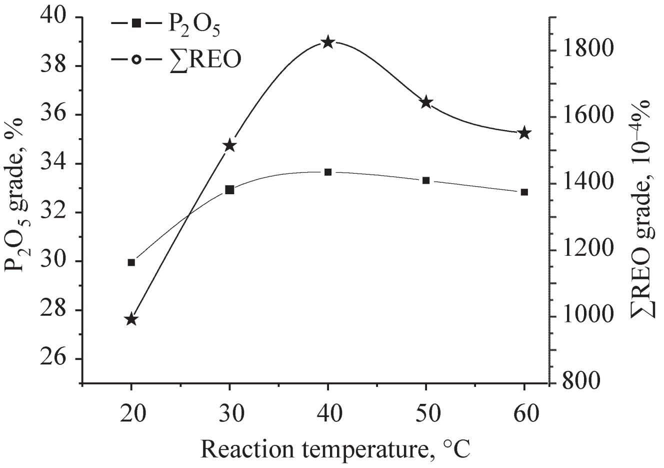

Fig. 7. Effect of temperature on P_2O_5 and ΣREO grade.

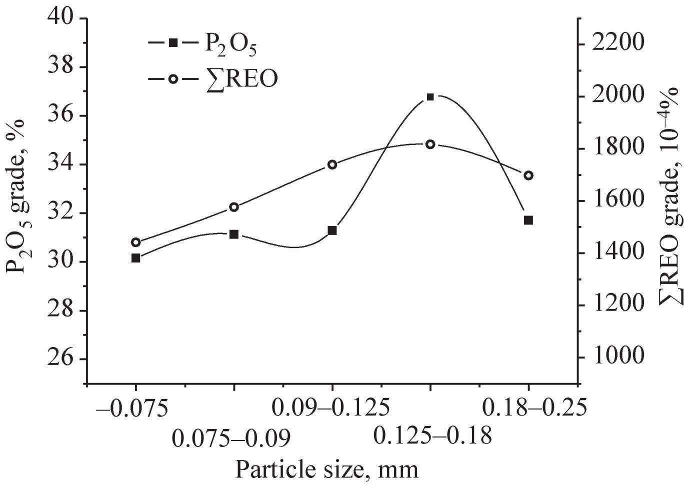

Fig. 8. Effect of particle size on P_2O_5 and ΣREO grade.

increasing reaction temperature the grade of P_2O_5 and ΣREO increases accordingly. When leaching experiment was carried out at 40°C, the grade of P_2O_5 and ΣREO was as high as 33.65% and 1824 × 10^{-4}%, respectively. It was also found from Fig. 7 that after the temperature higher than 40°C the increase in P_2O_5 grade becomes not so obvious that can be attributed to the fact that higher temperature may tend to a decrease in the solubility of citric acid along with the contamination of CO_2 gas with water and citric acid vapors. The similar result was obtained by Zafar and Ashraf etc. [13].

Effect of Particle Size

Particle size has a significant impact on the process of dissolving ore: the granularity is smaller, the specific surface area is larger; thus, it improves the dissolving capacity in citric acid. The optimum range of particle size mainly depends on the ore types and the disseminated relationship of the useful minerals and gangue minerals. If the particle after grinding was not sufficiently small, fluorapatite fine-grained dissemination in dolomite, hindering the selective dissolving of dolomite, effects on the enrichment ratio of P_2O_5 and ΣREO. On the contrary, if the ore samples have been grinded too fine, it also tend to result in the increase in pulp viscosity, hindering the liberation of dolomite reaction with citric acid. As well as it causes the extra cost of filtration and prolong the filtration time.

Due to the reasons mentioned above, it is necessary to find out what is the most appropriate ore particle size for leaching process. In order to make clear how the particle size of ore effects on the beneficiation degree of P_2O_5 and ΣREO, the raw ore (GL-T) sample was grinded to different particle size ranges before the leaching experiments, i.e., particle size ranges (mm) was <0.075, 0.075–0.09, 0.09–0.125, 0.125–0.18, and 0.18–0.25. Then a series of experiments was carried out in the conditions of acid concentration 9%, reaction time 240 min, liquid/solid rate 50 : 1, and reaction temperature 40°C. The results of experiments are shown in Fig. 8 indicating that when particle size range from 0.125 to 0.180 mm, the P_2O_5 grade reaches the maximum value and raises up from 15.47 (raw ore) to 34.82% (leaching residues); the recovery is as higher as 88.02%, the ΣREO grade improves from 978.06 × 10^{-4} to 1998 × 10^{-4}% and recovery is 72.08%. It was found that when the particle size range is from 0.125 to 0.180 mm, the grade and recovery rate of P_2O_5 and ΣREO obtained via selective leaching Zhijin phosphate rock using citric acid can meeting the market demand.

Through the above experiments and investigations, it can be summarized that the optimum process conditions for selective leaching Zhijin phosphate rock using citric acid is the following: acid concentration 9%, reaction time 240 min, liquid/solid ratio 50 : 1, reaction temperature 40°C, particle size 0.18–0.125 mm. With this optimum condition, the P_2O_5 and RE were mainly beneficiated in phosphorus concentrate. Table 4 indicates that the main REO are yttrium oxide (Y_2O_3), lanthanum oxide (La_2O_3), neodymium oxide (Nd_2O_3), and cerium oxide (CeO_2) which account for 83.62%, and the main feature consists in enrichment of the light-heavy REE, which belong to the low-grade phosphate rock containing rare earths [14].

Table 4. Rare earth oxide compositions of ore samples before and after leaching (10^{-4}%)

REO	La_2O_3	CeO_2	Pr_6O_{11}	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3	Tb_4O_7	Dy_2O_3
Raw ore	213.45	130.82	34.07	151.05	25.51	5.85	33.08	4.19	25.82
After leaching	453.87	278.84	72.01	304.43	51.95	12.74	64.78	9.16	53.25
REO	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	Y_2O_3	ΣREO	ΣLREO	ΣHREO	ΣL/ΣH
Raw ore	14.52	1.78	8.64	1.29	322.57	978.06	560.75	417.31	1.34
After leaching	28.93	2.95	14.97	1.84	637.51	1998	1173.83	824.17	1.42

The main impurities are SiO_2 and MgO. After leaching, the total rare earth enrichment is 1998×10^{-4} %. In the leaching process, phosphorus and rare earth enriched in phosphorus concentration, this result is consistent with the previous studies [15].

Leaching Kinetics Analysis

Phosphate rock leaching by organic acid solution is a typical liquid–solid heterogeneous chemical reaction; the actual dosage of low concentration organic acid should be greater than the theoretical demand. It was found in the leaching process that in the case of using a slightly insufficient amount of acid and prolonging reaction time, dolomite also can be selectively leached. Under the specific reaction conditions: temperature, pressure, and stirring speed are constant and particle size is less than 75 μm, the reaction rate depended on the contact area of mineral particles and citric acid [16].

Phosphate rock is mainly composed of granular mineral. In theory, ore particles can be regarded as spherical particles. In order to improve the reaction between mineral particles and organic acid for leaching experiment it is necessary to grind the ore to a certain particle size range fraction. To determine the kinetic parameters and rate-controlling step for selective dissolution of dolomite in low-grade phosphate rock the experimental data were analyzed on the basis of liquid–solid heterogeneous reaction models. The leaching process can be described by "a shrinking core first-order kinetics model."The leaching process is composed of the following steps: (1) Leaching liquid (citric acid) to the ore grain through passes through diffusion layer surface (spread out); (2) Leach liquor further spreads through solid membrane (diffusion); (3) Chemical reaction of leach liquor with calcium ion of ore grain. (4) Generated insoluble associated material makes the solid membrane thickening.

A number of experiments were carried out to study the effect of temperature on the dissolution of dolomite. The experiments were carried out at various reaction temperatures of 30, 40, 50, and 60°C with the other experimental condition unchanged. The validity of the experimental data into the integral rate was tested by statistical and graphical methods. The results indicated that using the conversion values for various reaction temperature, the apparent rate constants k can be evaluated by plotting $1-(1-a)^{1/3}$ vs. t. These results indicated that the dissolution rate of dolomite was controlled by surface chemical reaction. The kinetic analysis results for the leaching process were found to consistent with a chemical controlled reaction and the integral rate expression was determined to obey the following rate equation:

$$1-(1-a)^{1/3} = kt. \tag{4}$$

Using the Arrhenius equation, the activation energy can be evaluated from the plot of ln k vs. $1/T$ as shown in Fig. 9. Reducing core model for linear regression, the linear slope gives the reaction rate constant k. In order to determine the kinetic parameters and rate controlling step, the experimental data were analyzed based on Eq. (4). For the linear equation: $y = -4.406x + 10.51$, the coefficient value was calculated as 0.994. In the acid leaching reaction, the reaction rate is a function of temperature, the acid concentration under known percent solid for different temperature is shown in Fig. 9. Effect of temperature on the reaction rate constants using the Arrhenius equation can be expressed as:

$$k = k_0 \exp(-E_a/RT), \tag{5}$$

$$\ln k = \ln k_0 + (-E_a/RT), \tag{6}$$

where k is kinetic constant; k_0 is frequency factor; E_a is the activation energy; R is universal gas content (8.314510 J mol^{-1} K^{-1}); T is the reaction temperature.

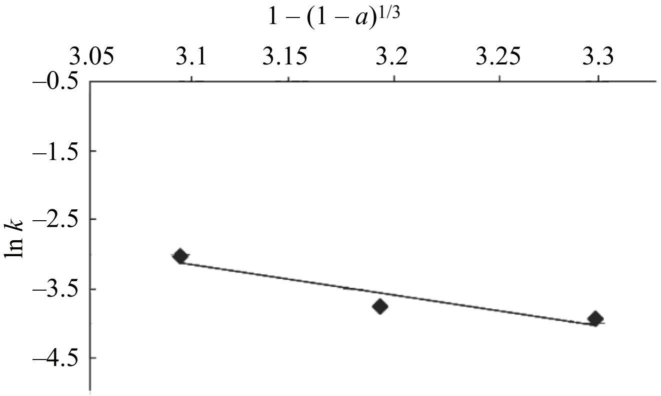

Fig. 9. Curve of ln k vs.1/*T.*

Combining Fig. 9 with Eq. (6) the activation energy E_a = 36.6337 KJ mol^{-1} was calculated (k_0 is 3.67 × 10^4 s^{-1}). A similar result was obtained by *T.* Heydarpour et al. [17–19]. The value of activation energy in the dissolution process may be characterized to predict the controlling, for a chemically controlled process, it is usually from 30–85 KJ mol^{-1}. The value of the activation energy obtained in the leaching process indicates that the leaching of dolomite in the low-grade phosphate rock was controlled by chemical reaction. The chemical reaction is the following:

$$1 - (1 - a)^{1/3} = 3.67 \times 10^4\ e^{-36.63RT}t. \tag{7}$$

The chemical reactions between organic acid and dolomite in phosphate rock was controlled by mineral interface chemical reaction as well as by mineral surface functional group, mineral structure type, surface chemical composition, surface morphology, and a variety of inorganic and organic ions or molecules in the medium of reaction type and reaction ability [20, 21]. Hence, at the present time in our lab, further research is in progress to find out the general rule of enrichment of P_2O_5 and ΣREO via selective leaching technology, using organic acid as leaching agent. The research results will play important roles in developing the organic acid selective leaching theory and novel methods for exploitation and utilization of RE-containing low grade phosphate resources.

CONCLUSIONS

(1) The mineralogical constituent of Zhijin GL-T phosphate rock (low-grade phosphate) is fluorapatite, dolomite, quartz and some clay material, and the fluorapatite (amorphous gel aggregate, 45.5%), dolomite (44.6%), and quartz (9.9%). After being selective leaching by citric acid solution, the content of P_2O_5 and RE elements were upgrade effectively, P_2O_5 content raised up from15.47% (raw ore) to 34.82%, recovery rate is as high as 88.02%; the content of RE element increases from 978.06×10-4% (raw ore) to 1998 × 10-4% (phosphate concentrate), recovery rate is as high as of 72.08%. The grade and recovery rate of phosphate concentrate can meet the market demand. The findings of the current work are significant to the effective use of low-grade phosphate rock which containing RE elements in Zhijin county of Guizhou province.

(2) After leaching, the phosphate and RE elements mainly enrichment in leaching slag, and the REE content increase with the increase of P_2O_5 content. It was found that the enrichment ratio, the recovery rate of P_2O_5 and REE were raised at the same time. The results indicated that there is a positive correlation between phosphorus ore and RE elements description in this type phosphate.

(3) The leaching of dolomite in the phosphate rock is controlled by chemical reaction, and the apparent activation energy of the leaching process is 36.6337 KJ mol^{-1} and k_0 is 3.67 × 10^4 S^{-1}. The rate of the leaching based on a chemical reaction-controlled process could be expressed as $1 - (1 - a)^{1/3} = 3.67 \times 10^4\ e^{-36.63RT}t$.

(4) Compare with the conventional process, the method provided by this study not only have advantages including higher phosphate concentrate and rare earth grade, higher recovery rate, but also use less chemicals. Meanwhile, the citric acid can be recycling use, avoiding discharge wastewater.

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