UDC 53.091+547.953

DOI: 10.15372/KhUR20180503

Study on Structures and Leaching Property of Phosphate Ore after Mechanical Activation

CHEN WANG[1,2], XIN-RONG MO[1], CHENGMIN WANG[1], and HONG GAO[1]

[1]School of Materials Science and Engineering, Dalian Jiaotong University, Dalian (China)

E-mail: wangchen19870913@126.com

[2]Liaoning Geology Engineering Vocational College, Dandong (China)

Abstract

A high-energy planetary mill was used to conduct the mechanochemical activation treatment of phosphorite powders and increase the phosphate leaching rate. Laser particle analysis, X-ray diffractometry, and scanning electron microscopy were applied to study the influence of this treatment on the phosphate leaching rate. The kinetics and mechanisms of the mechanical activation of phosphorite powders was preliminarily analyzed on the basis of a solid-phase reaction kinetic model. Results show that the mechanochemical activation of phosphorite powders can effectively reduce the degree of crystallinity and improve their reactivity. The phosphate leaching rate can reach as high as 56.19 % after phosphate is activated eight times at a rotational speed of 1000 r/min of the planetary mill. The solid-phase reaction of activated phosphorite includes two processes: diffusion and interfacial reaction. The kinetic constant continuously changes with the reaction.

Key words: mechanical activation, phosphorite powder, leaching degree, kinetics

INTRODUCTION

Phosphate fertilizer is one of the fertilizers urgently needed by plants. It is traditionally produced through chemical and microbiological methods by using high-grade phosphate ores. However, phosphate ore belongs to a scarce and non-renewable resource. As such, the increasing demand cannot be satisfied by simply relying on high grade phosphate ores and maximizing the use of medium and low grade phosphate ores has become a crucial problem. Nowadays, the utilization of medium and low grade phosphate ores is limited by difficult mineral separation, high energy consumption, high cost, serious environmental pollution, and other drawbacks [1]. The direct processing of medium and low grade phosphate ores through mechanochemical methods has been widely explored. This method is practical, affordable, and environmentally friendly. Ying *et al.* [2] used reduced the powder limit by changing the ball milling mode during mechanical activation to process phosphate ores directly and improve the leaching rate of available phosphorus. Mo *et al.* [3] increased the leaching rates of water-soluble phosphorus and potassium through the joint activation method of phosphate ore and potassium ore. However, previous studies did not examine the kinetics and mechanism of mechanical activation.

In this experiment, mechanically activated phosphorite powders were utilized, and leaching was applied to examine the influences of mechanical activation on the granularity, crystalline structure, and leaching rate of phosphorite powders. A solid-phase reaction kinetic model was used to calculate and analyze the kinetics of the mechanically activated phosphorite powders and provide an economical and environmentally friendly method for leaching phosphorus from medium and low grade phosphate ores.

TABLE 1

Basic components of phosphate ore (mass %)

Components	P_2O_5	CaO	SiO_2	F	Al_2O_3	Fe_2O_3	K_2O
Mass fraction	28.142	36.652	21.826	1.747	6.834	2.842	1.067

EXPERIMENTAL

Experimental raw materials

Phosphate ore (D_{90} = 0.94 mm) was obtained from Yunnan, China, and its main components are listed in Table 1.

Methodology

Mechanical activation. A high energy planetary mill AGO-2 (Russia) was adopted in this experiment. The ball to powder mass ratio was 20 : 1. For each grinding experiment, the samples (10 g in each batch) were added into a stainless steel chamber with stainless steel milling balls (d = 4 mm, m = 0.8 g), then the samples were subjected to dry milling and no other additives were used during the milling. Ball milling was discontinuous (compared with continuous ball milling to explore the rules of intermittent operation of large ball mills and the rules of addition in ball milling process), and each ball milling time lasted 30 s. The rotational speed of the ball mill was set at 200, 1000, and 1400 r/min, and activation frequency was set at one, four, eight, and ten times. The concrete ball milling conditions and process are shown in Table 2.

Leaching. Quinoline phosphomolybdate gravimetric method was used in the experiment to determine the available phosphorus content in the sample. Detection was based on the standard GB/T8573–2010 *Determination of Available Phosphorus Content in Compound Fertilizers*. Phosphomolybdate gravimetric method was applied to detect the available phosphorus content. According to the determination principle, orthophosphate ions chemically react with a quimociac reagent in an acidic medium, thus generating yellow quinoline phosphomolybdate sediments.

TABLE 2

Factors influencing the grinding process

Influencing factor	Process variable
Rotational speed (r/min)	200, 1000, 1400
Activation frequency	1, 4, 8, 10
Activation process	Dry milling

RESULTS AND DISCUSSION

Granularity analysis

Figure 1 indicates that the sample D_{50} changes after mechanical activation under different ball milling times at different rotational speeds. When the rotational speed of the planetary mill is 200 r/min, D_{50} declines from 17.91 to 12.21 μm from the first to the tenth milling process. When the rotational speed increases to 1000 and 1400 r/min, D_{50} decreased after it is activated once. However, it fairly increases as the ball milling frequency increases mainly because mechanical energy increases, and granular agglomeration is greater than granular crushing as the rotational speed increases. To reduce system energy, we can easily agglomerate the grains, resulting in an increase in D_{50}.

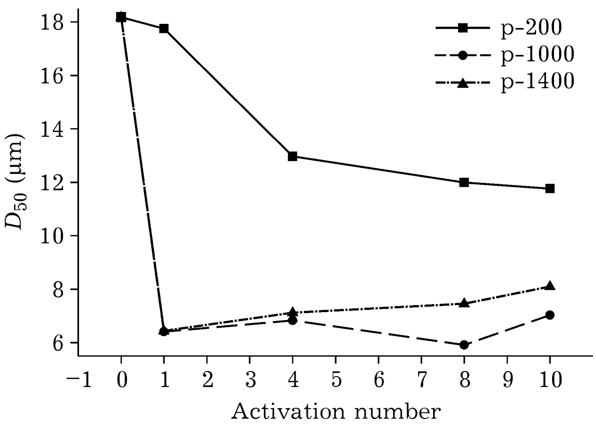

Fig. 1. Median diameter (D_{50}) distribution map of activated phosphate ore.

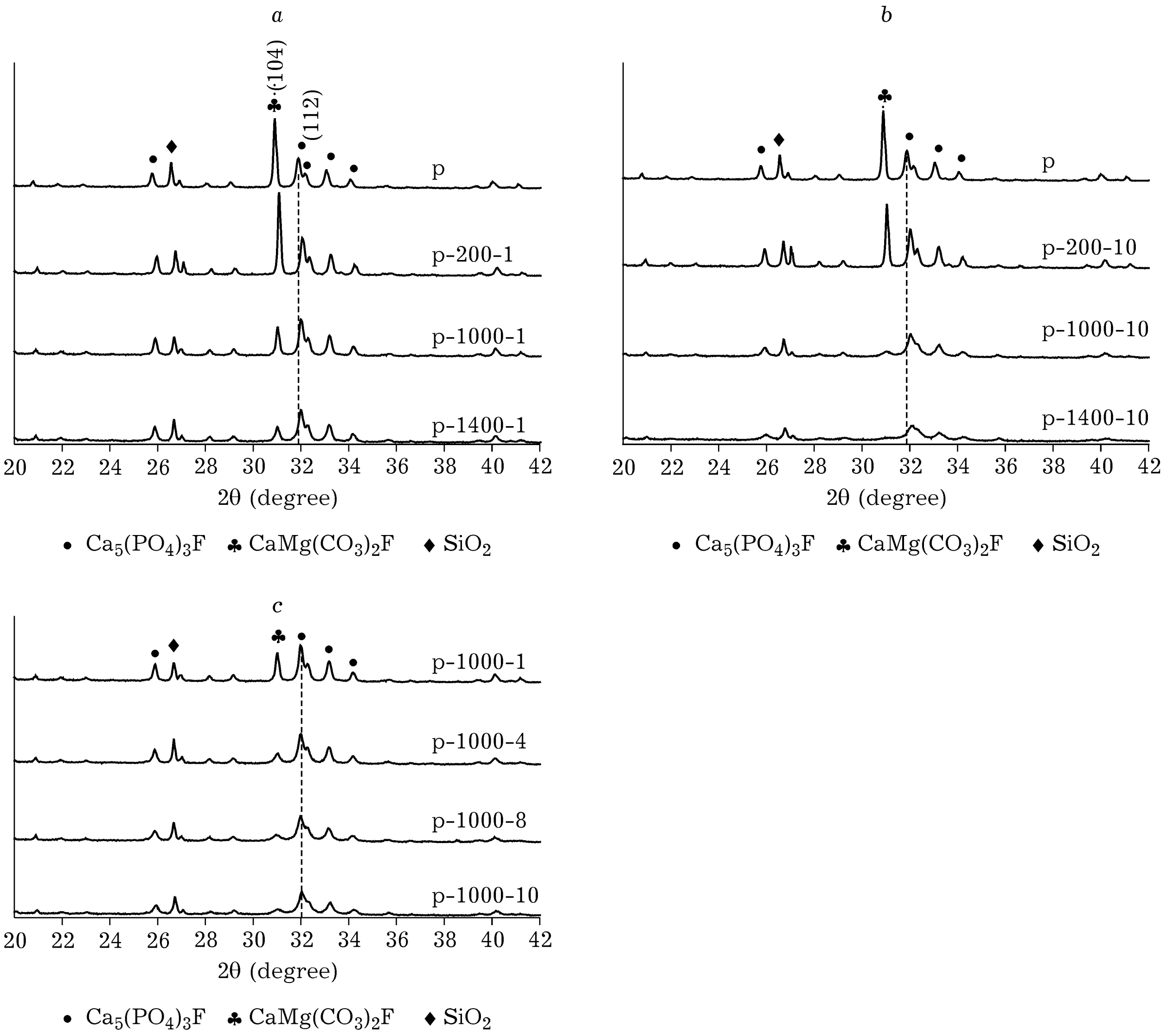

Fig. 2. XRD patterns of activated phosphate ore: *a* – one time, *b* – ten times, *c* – 1000 r/min.

X-ray diffraction (XRD) analysis

Figure 2 shows the XRD patterns of phosphorite powders obtained under different ball milling conditions. The phosphorite powder contains three crystalline phases, namely, $CaMg(CO_3)_2$, quartz, and fluorapatite with obvious diffraction peaks and high crystallinity degree. The intensity of $CaMg(CO_3)_2$ diffraction peaks after one-time mechanical activation at 1400 r/min decreases as the peak width increases, and this finding is consistent with 2.89–11.51 μm granularity. In Fig. 2, *b*, the diffraction peaks of quartz and fluorapatite decrease after ten activation processes at 1000 r/min, and they even disappear in the tenth activation process at 1400 r/min. The decrease in peaks and the increase in their width can indicate amorphous condition and size of the lattice parameter reduction. Figure 2, *c* illustrates the influence of mechanical activation frequency on XRD. The intensity of the diffraction peak of phosphorite weakens as the activation frequency increases at 1000 r/min. When the tenth activation frequency is reached, no obvious diffraction peak of the (112) crystal face of fluorapatite can be observed, suggesting that the higher the rotational speed of the ball milling is, and the greater the activation frequency will be. The clearer the widening and weakening of

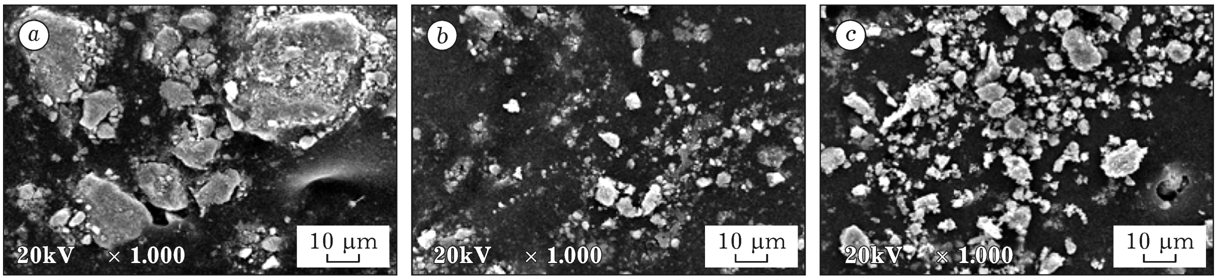

Fig. 3. SEM images of phosphate ore activated once (r/min): *a* – 200, *b* – 1000, *c* – 1400.

the main diffraction peak of fluorapatite are, the more sufficient the mechanical activation will be. Likewise, the clearer the lattice distortion is, and the more the lattice imperfections will be. Subsequently, the degree of crystallinity declines and even turns into an amorphous state.

Scanning electron microscopy (SEM) analysis

Figure 3 presents the SEM pictures of one-time mechanical activation of phosphorite powders at different rotational speeds. In Fig. 3, *a*, phosphate ore is first activated at 200 r/min to crush phosphorite grains with large granularities and clear mineral boundaries. During phosphate ore activation at a low rotational speed, large grains are crushed into small grains because of low rotational speed, short activation time, slight mechanical force effect, and insufficient mineral crushing, but granularity reduction is visibly unclear. In Fig. 3, *b* and *c*, when the initial activation occurs at 1000 and 1400 r/min, mineral grains are small and fine, but small grains agglomerate into large grains, so agglomeration is obvious between small grains, indicating that the higher the rotational speed is, the more beneficial the granularity reduction of mineral grains will be. As a result, agglomeration occurs between mineral grains and slightly enlarged granules. This finding is consistent with the granularity analysis result.

P_2O_5 leaching degree analysis

Figure 4 shows the influence of mechanical activation frequency on the phosphorus leaching degree. The leaching degree of available phosphorus in non-activated phosphorite powders is 20.03 %. When the phosphate ore is activated using a planetary mill at 200 r/min, the available phosphorus content slowly increases as the activation frequency increases. Its content reaches the maximum of 25.91 % in the tenth activation process. The available phosphorus content first increases and then decreases with the activation frequency at 1000 r/min. The leaching degree of available phosphorus reaches the maximum value of 58.42 % in the eighth activation process, increases rapidly at the initial activation, increases slowly with the activation process at 1400 r/min, and achieves the maximum value of 56.19 % in the tenth activation process. These results demonstrate that the optimal time to increase the leaching degree of available phosphorus is the eighth activation at 1000 r/min. Crystal stability is closely related to mineral crystal structure and granularity. The higher the crystal chaotic degree is, the higher the amorphous degree and the higher the leaching degree of available phosphorus will be. The granularity analysis reveals that the higher the

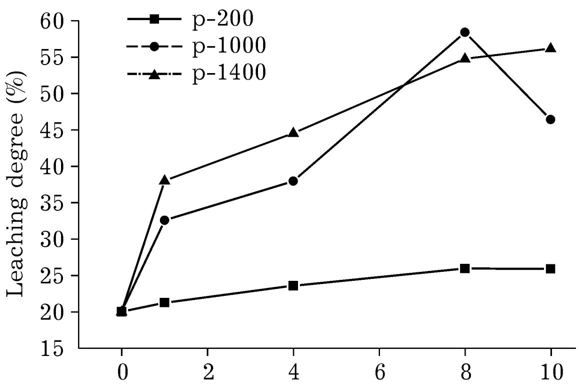

Fig. 4. Effect of activated phosphate ore on the leaching degree of available phosphorus.

rotational speed is, the greater the activation frequency and the more obvious the reduction in phosphate ore granularity will be. The XRD analysis shows that the crystal chaotic degree and the amorphous degree increase with rotational speed and activation frequency, thereby contributing to the increase in the leaching degree of the available phosphorus.

Kinetic study

Mechanical activation is a process of solid-phase reaction that involves diffusion and interfacial reaction. A kinetic model is selected on the basis of the experimental data. Graphic comparison integral method [4] is applied to determine the mechanical activation mechanism. The common integral formula (1) of solid-phase reaction kinetic equation can be summarized as follows [5]:

$$g(\alpha) = kt + c \quad (1)$$

$$f(\alpha) = k(t / t_{0.5}) \quad (2)$$

where $t_{0.5}$ is the time needed for 50 % conversion rate; α is the reaction degree; $f(\alpha)$ is a function representing the reaction model; $g(\alpha)$ is the integral form of the reaction model $f(\alpha)$.

The experimental data cannot be completely consistent with the standard curve. The comparison of the kinetic reaction models reveals that the curve matches the 2D diffusion model [6] before the fourth activation, and the curve with an activation frequency of greater than 4 coincides with the 2D interfacial reaction curve.

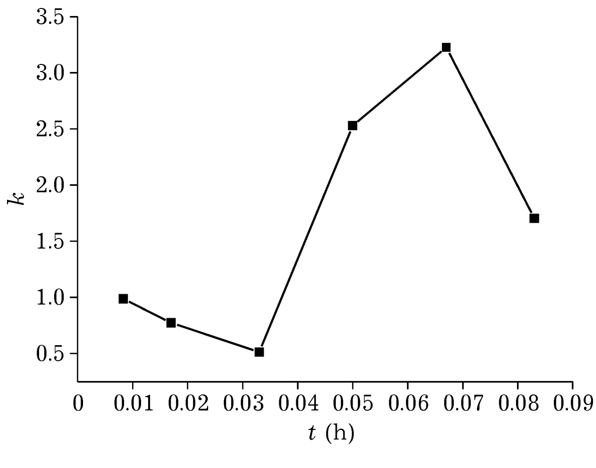

Fig. 5. Relationship between time and reaction constant.

Figure 5 displays the relationship between the kinetic solid-phase reaction constant and the reaction time. The kinetic reaction of the mechanically activated phosphate ore does not have a constant value; that is, it is always changing. The reaction rate continuously decreases during diffusion as the reaction proceeds. It first increases and then decreases during the interfacial reaction, indicating that the interfacial reaction rate at the beginning is lower than that as the reaction proceeds in the later phase or during the reduction of reactants.

CONCLUSIONS

A planetary mill was used in this study to investigate the influences of high energy activation on the leaching degree of phosphorite powders and the solid-phase reaction kinetics. The main conclusions were drawn as follows.

– The granularity distribution curve of phosphorite powders before and after the mechanical activation consists of three peaks that correspond to three principal crystalline phases in an ascending order: fluorapatite, $CaMg(CO_3)_2$, and quartz.

– The P_2O_5 leaching degree of phosphorite powders can increase from 20.03 to 58.42 % after eight times of activation compared with that of non-activated phosphorite powders.

– The variable value analysis of the mechanically activated reaction kinetic constant reveals that the mechanical activation of phosphorite powders comprises two reaction processes: diffusion and interfacial reaction. The reaction constant of diffusion continuously declines as the activation frequency increases, whereas the interfacial reaction constant initially increases and then decreases.

REFERENCES

1 Fang N. N. and Liu W. // J. Liaoning Agricultural Sci. 2016. No. 3. P. 15.
2 Ying Y. F. and Chen M. L. // J. Dalian Jiaotong University. 2015. No. 2. P. 80.
3 Mo X. R. and Gao H. // J. Chinese Ceram. Soc. 2016. No. 8. P. 2660.
4 Blum S. L. // J. Am. Ceram. Soc. 1961. Vol. 42, No. 12. P. 611.
5 Frade J. R. and Cable M. // J. Mater. Sci. 1997. Vol. 32. P. 2727.
6 Chung H. S. // J. Mater. Sci. 1998. No. 8. P. 17.