

## Kinetics of the removal of magnesium from phosphate ore with diluted acid \*

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**Abstract** The kinetics of magnesium removal from phosphate ore with diluted sulfuric acid was studied. The experimental results showed that hydrogen ion concentration, temperature, reaction time and particle size distributions of phosphate ore have different effect on the phosphorus removal and magnesium removal. A kinetic database of magnesium and phosphorus removals from ore was set up. The three-dimensional graphs of phosphorus and magnesium removals versus time and reaction conditions were drawn by a computer. The kinetic equations were developed.

**Keywords:** phosphate ore, magnesium removal, kinetics.

China has tremendous phosphate resources of about 15.158 billion tons of deposit<sup>[1]</sup>. However, the quality of phosphate ore is relatively poor because of its high magnesium content. Furthermore, with the exploitation, the magnesium content becomes higher and higher. The magnesium plays a very important role in the formation of phosphate ore<sup>[2]</sup>, so its content is closely related to the quality of phosphate ore. But the magnesium has undesirable effect on the processing of phosphate ore<sup>[3-5]</sup>. It causes the loss of phosphate, the decrease of productivity and inferior product, etc., so the removal of magnesium from the phosphate ore is of major concern. The physical dressing is an option, but it is difficult to separate the magnesium from the phosphate ore because the particles of dolomite are too small to be depleted. To solve this problem, we studied the kinetics of magnesium removal from the ore with diluted sulfuric acid, by which a kinetic database of magnesium and phosphorus removal from the ore was established.

### 1 Theoretical

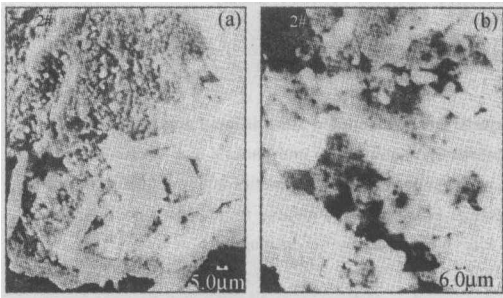
From the results of our experiments, the following factors should be considered in the kinetic equations. The pretreatment of phosphate ore with weak acids is a heterogeneous reaction because it takes place on the surfaces of the ore particles. There is a liquid film adhered on the surface of the particles. If  $H^+$  ions react with the ore particles, they must pass the film of liquid. According to Fick's law of diffusion and Arrhenius equation<sup>[6]</sup>, we have

$$\frac{dn}{d\tau} = K' e^{-\frac{E}{RT}} [H^+]^\beta, \quad (1)$$

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where  $\frac{dn}{d\tau}$  is the mass of dissolved substance through the solid surface in unit time ( $\text{kg}/\text{M}^2 \cdot \text{s}$ );  $E$  the activation energy ( $\text{J}/\text{mol}$ );  $R$  the molar gas constant ( $8.314 \text{ J}/\text{K} \cdot \text{mol}$ );  $T$  the reaction temperature ( $\text{K}$ );  $A$  the area of surface ( $\text{m}^2$ );  $K'$  a constant and  $\beta$  a function of diameter of ore's particle.

Figure 1 is the photo of scanning electron microscope (SEM) of a demagnetized ore particle's surface. Analysis of energy dispersive spectrum, shows that the black part is dolomite and the white part is phosphorite in graph (a), and some crystals of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  have formed on the surface of the ore particle (white part in graph (b)).



We found that surface area of particles is changing with the reaction time. So the surface area is a function of time. The relationship between surface area of particles and time may be expressed as the following equation when the temperature and pH of solution are invariable:

$$A = A_0 \tau^\alpha, \quad (2)$$

Fig. 1. SEM photo of demagged phosphate ore.

where,  $A_0$  is area of original ore ( $\text{m}^2$ ) and  $\tau$  reaction time (s).

On the other hand, the particle size will effect the surface area. We take the average diameter of the original particles to represent the particle size.

The effect of particle size on the surface area may be expressed as

$$A_0 \propto r^{-1}, \quad (3)$$

where  $r$  is diameter or original ore's particle.

The effect of particle size on  $\beta$  of eq. (1) and on  $\alpha$  of eq. (2) may be assumed by the following equations:

$$\beta = \sum_i^n \beta_1 r^i, \quad (4)$$

$$\alpha + 1 = \sum_i^n \alpha_1 r^i. \quad (5)$$

From eqs. (1) to (5), we get

$$\eta = K_1 (\alpha + 1)^{-1} e^{-E/RT} r^{-1} [H^+]^{\beta} t^{\alpha+1}, \quad (6)$$

$$\frac{dn}{d\tau} = K_2 e^{-E/RT} r^{-1} [H^+]^{\beta} t^{\alpha}. \quad (7)$$

Equations (6) and (7) are the kinetic equations for the removal of phosphorus and magnesium respectively, where  $\beta = \sum_i^n \beta_i r^i$ ;  $\alpha + 1 = \sum_i^n \alpha_i r^i$ ;  $\eta$  is portion of removal;  $K_1$  and  $K_2$  are constants;  $t$  is time (s).

## 2 Experimental

### 2.1 Materials

The experimental materials are 98% sulfuric acid, phosphate ore and water. The composition of the phosphate ore is given in table 1.

Table 1 Main composition of the phosphate ore

Composition/%			Average diameter/ $\mu\text{m}$
P <sub>2</sub> O <sub>5</sub>	MgO	CO <sub>2</sub>	
24.23	6.96	14.62	39-127

### 2.2 Method

The ore and water were mixed in the reactor and continually stirred at a fixed temperature. Sulfuric acid was added into the reactor to maintain pH value. A series of samples (ore) were taken out at regular time intervals, and were analyzed. Then the data were processed by a computer. The relationship between phosphorus or magnesium removal and time at fixed temperature and fixed particle size of ore was obtained.

## 3 Results

All experiments were carried out at 40–80°C with the particle sizes of 39–137  $\mu\text{m}$ , and with pH values of 2.5–3.0. A kinetic database of magnesium and phosphorus removal from ore was established. Figs. 2 and 3 are the three-dimensional graphs demonstrating the dependence of phosphorus or magnesium removal on the reaction time and other conditions.

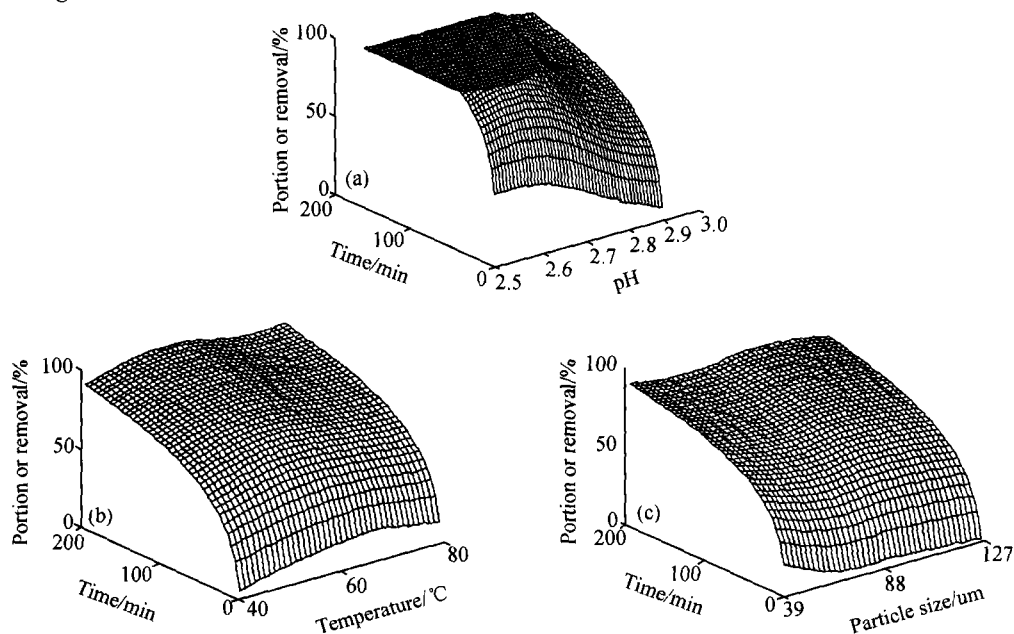


Fig. 2. Dependence of magnesium removal on pH and time ( $T = 80^\circ\text{C}$ , particle size =  $91 \mu\text{m}$ ) (a), on temperature and time (pH = 3.0, particle size =  $91 \mu\text{m}$ ) (b), and on particle size and time ( $T = 80^\circ\text{C}$ , pH = 3.0) (c).

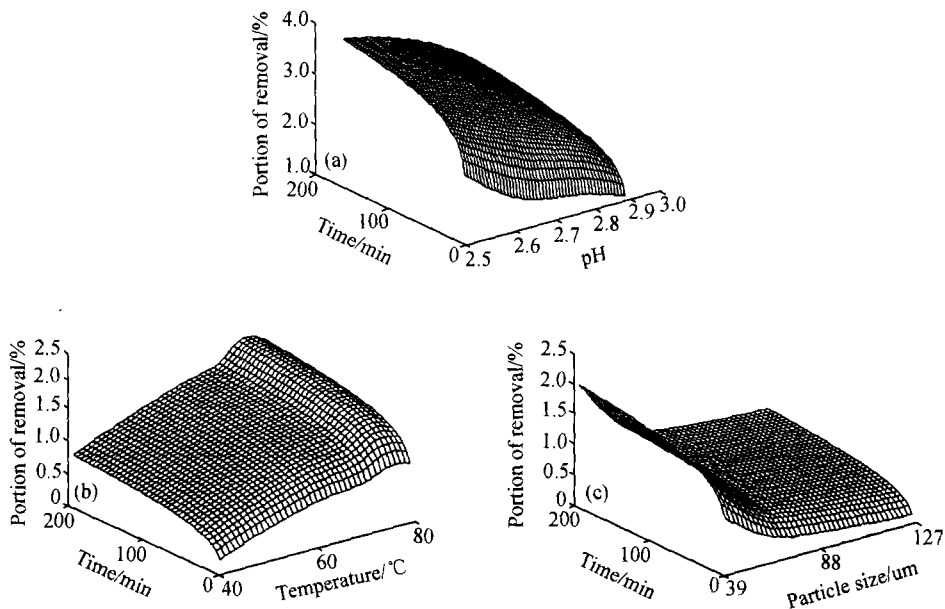


Fig. 3. Dependence of phosphorus removal on pH and time ( $T = 80^{\circ}\text{C}$ , particle size =  $91\ \mu\text{m}$ ) (a); on temperature and time ( $\text{pH} = 3.0$ , particle size =  $91\ \mu\text{m}$ ) (b); and on particle size and time ( $T = 80^{\circ}\text{C}$ ,  $\text{pH} = 3.0$ ) (c).

In addition, the kinetics of reaction can also be described by the mathematical equations derived from the theory mentioned in sec. 1. In order to avoid the nonlinear problem, the functions for  $\alpha$  and  $\beta$  are simplified. The calculated result using kinetic equation for phosphorus removal is in accordance with the experimental data, but the calculated result using kinetic equation for magnesium removal is not fully in accordance with the experimental. So the reaction of magnesium removal is described by three kinetic equations for different contents of MgO and the calculated results are consistent with the experimental data.

The kinetic equation for phosphorus removal is

$$R_p = 1.259 \times 10^5 r^{-1} e^{-2945/T} [H^+]^{\beta} t^{\alpha}. \quad (8)$$

The kinetic equations for magnesium removal can be expressed as

$$R_{\text{MgO}1} = 3.591 \times 10^4 r^{-1} e^{-810.8/T} [H^+]^{\beta_1} t^{\alpha_1} \quad (\text{MgO}\% > 3.5\%), \quad (9)$$

$$R_{\text{MgO}2} = 1.153 \times 10^3 r^{-1} e^{-193.6/T} [H^+]^{\beta_2} t^{\alpha_2} \quad (\text{MgO}\%, 3.5\% - 1.4\%), \quad (10)$$

$$R_{\text{MgO}3} = 2.160 \times 10^{-2} r^{-1} e^{-136.3/T} [H^+]^{\beta_3} t^{\alpha_3} \quad (\text{MgO}\% < 1.4\%), \quad (11)$$

where  $\alpha, \beta, \alpha_1, \alpha_2, \alpha_3, \beta_1, \beta_2$  and  $\beta_3$  are the functions of the particle size of ore, namely

$$\beta = \sum_i^n \beta_i r^i, \quad \alpha = \sum_i^n \alpha_i r^i - 1. \quad (12)$$

From fig. 2(a) and fig. 3(a) it can be seen that both the rates of magnesium and phosphorus removals increase rapidly with the increase of pH. From fig. 2(b) and fig. 3(b) it can be seen that the effect of temperature on magnesium removal is not significant, but on phosphorus removal is obvious. The phosphorus removal increases when the temperature rises. There is a peak in fig. 3(b). Actually, this peak means the optimal temperature for the reaction of phosphorus with sulfuric acid. From fig. 2(c) and fig. 3(c) it can be seen that the particle size of ore has slight influence on the magnesium removal, but has significant influence on the phosphorus removal (especially  $r < 80 \mu\text{m}$ ).

#### 4 Conclusions

From the above results and discussion, the following conclusions can be drawn.

(i) The impetus of magnesium removal is  $\text{H}^+$  ion concentration. It is necessary to keep the pH value stable to reduce the phosphorus loss.

(ii) In the reaction, the phosphorus loss increases with the rising of temperature, while the magnesium removal is only slightly effected by temperature. So it is better to put the reaction at lower temperature.

(iii) The effect of particle size of ore on the phosphorus loss is significant but is not for magnesium removal. So larger particle size should be used in the reaction for reducing phosphorus loss and it is also easier to separate ore.

(iv) The kinetics of magnesium removal from phosphate ore is not in good accordance with the classical kinetics<sup>[7]</sup>. It seems that it is in accordance with the kinetics of the fractal substrate<sup>[8]</sup>. To clarify this, further study is needed.

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