Leaching and Kinetic Modeling of Pyrite Cinder in Sulphuric Acid

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Pyrite cinder has often been utilized for the preparation of pigments, water purification materials and other materials including sponge iron powder, recovering iron, iron oxide red, ferrous sulfate and even bricks. In this work, orthogonal experiments were carried out to optimize the leaching conditions of pyrite cinder containing 48.94 % Fe, 13.9 % acid insoluble substance, 0.64 % Al₂O₃, 0.35 % Cu, 1.3 % S and 3.6 % CaO and then the corresponding kinetic equation was proposed. Effects of sulphuric acid concentration, excess coefficient, reaction temperature and reaction time on the leaching ratio were investigated. Statistical analysis indicates that the influence of the four factors on the leaching ratio is in the following sequence: reaction temperature, reaction time, excessive coefficient and sulphuric acid concentration. Furthermore, the optimized reaction conditions are obtained as reaction temperature 100 °C, reaction time 3 h, excessive coefficient 1.05 and sulphuric acid concentration 8 M. We also explored the reaction kinetics and the corresponding kinetic equation has been proposed. The reaction of pyrite cinder in sulphuric acid medium fits the surface chemical reaction model. The kinetics equation was obtained with apparent activation energy of 38.69 kJ/mol.

Key Words: Pyrite cinder, Sulphuric acid, Orthogonal experiment, Leaching kinetics.

INTRODUCTION

Pyrite cinder is the residual of the production of sulphuric acid from pyrite, which mainly contains iron oxide (Fe₂O₃ and Fe₃O₄). A great deal of pyrite cinder has been produced in the world. For example, in China the average annual production of pyrite cinder is more than ten million tons. However, pyrite cinder has been rarely used directly as the raw materials for iron making because it contains only low grade iron oxide as well as sulfur and other impurities. The utilization of pyrite cinder generally involves the preparation of pigments and water purification materials. Recently, the preparation of sponge iron powder, recovering iron, iron oxide red, ferrous sulfate and bricks from pyrite cinder has been widely reported¹⁻¹¹.

It is important to investigate the reaction kinetics of leaching pyrite cinder. Previously some researchers have proposed some related kinetic equations. Yang *et al.*¹² studied the reaction kinetics of calcine bearing high silicon in the H₂SO₄-H₂O system. They suggested that the leaching ratio is consistent with the shrinking core model, which was expressed as $1+2(1-x)-3(1-x)^{2/3} = kt$ with an apparent activation energy of 55.469 kJ/mol. Hou *et al.*¹³ explored the kinetics of acidolysis pyrite cinder and their results indicated that the acidolysis reaction is chemical reaction controlled with a

kinetic equation of $1-(1-x_B)^{1/3} = kt$ and an apparent activation energy of 51.755 kJ/mol. However, Zhan *et al.*¹⁴ insisted that the leaching kinetics of pyrite cinder is a diffusion controlling reaction with a kinetic equation of $1-(1-x_B)^{2/3} = kt$ and an apparent activation energy of only 6.936 kJ/mol. It is clear that the reported results are inconsistent.

Herein, orthogonal experiments were performed to optimize the leaching conditions of pyrite cinder. And then a kinetic equation was proposed.

EXPERIMENTAL

Sulphuric acid (AR, 98 %), hydrochloric acid (AR, 36.5 %), stannous chloride (AR), methyl orange (AR) and diphenylamine sulphuric acid sodium salt (AR) was purchased from Sinopharm Chemical Reagent Co. Ltd. (China). Phosphorus mixture was prepared by dumping 150 mL of concentrated sulphuric acid into 700 mL of deionized water and then mixing with 150 mL of phosphoric acid after cooling. Pyrite cinder was supplied by Anhui Tongling Chemical Industry Co. with mass fractions of 48.94 % Fe, 13.9 % acid insoluble substance, 0.64 % Al₂O₃, 0.35 % Cu, 1.3 % S and 3.6 % CaO. Size distribution of the provided pyrite cinder is shown in Table-1.

TABLE-1
SIZE DISTRIBUTION OF PYRITE CINDER

Size (mm)	>0.300	0.300-0.200	0.200-0.125	0.125-0.075	<0.075
Faction (wt %)	2.66	14.80	20.90	58.19	3.45
Fe (%)	—	44.23	47.98	49.35	—

Treatment of pyrite cinder: To reuse the pyrite cinder, 30 g of pyrite cinder was added into a 250 mL three-necked bottle followed by the addition of sulphuric acid. The reaction was allowed at designed temperature under a stirring speed of 400 rpm. Then the reactants were collected by filtration and washing with deionized water for three times. The residues were dried for 2 h at $110 \pm 2^\circ\text{C}$ and then weighted (mg). The weight fraction of iron was determined and the leaching ratio was calculated according to the following equation:

$$\text{Leaching rate (\%)} = \frac{m \times \text{Fe \%} - M \times \text{Fe' \%}}{m \times \text{Fe \%}} \times 100 \quad (1)$$

where, m is the weight of feed pyrite cinder (g); $\text{Fe \%}$ is the weight fraction of iron in pyrite cinder; M is the weight of residual solid after reacting with sulphuric acid (g); $\text{Fe' \%}$ is the weight fraction of iron in the residual solid.

Determination of the weight fraction of iron: Pyrite cinder (1 g) was accurately weighted and placed in a 250 mL beaker followed by 20 mL of concentrated hydrochloric acid. The pyrite cinder was heated to boiling and kept for 1 min. The solution was transferred to a 250 mL volumetric flask after cooling to ambient. Then 25 mL of the prepared solution was transferred into a 250 mL conical flask followed by the addition of 8 mL of concentrated hydrochloric acid. Afterward, the solution was also heated to boiling and 6 drops of methyl orange was added. Then stannous chloride was slowly added dropwise. During this process, the conical flask was shaken severely. When redness of the solution exactly fades, the conical flask was cooled rapidly. After that, 50 mL of deionized water and 20 mL of phosphorus mixture were added. At the end, the mixture was titrated by 0.05 M $\text{K}_2\text{Cr}_2\text{O}_7$ to stable fuchsia as terminal point using diphenylamine sulfonic acid sodium salt as the indicator.

RESULTS AND DISCUSSION

Leaching of pyrite cinder in sulphuric acid is a reaction at liquid/solid interface. The main influencing factors include ratio of liquid to solid, stirring speed, sulphuric acid concentration, excess coefficient, reaction temperature and reaction time. Zhan and Zheng¹⁴ systematically investigated the effects of stirring speed and the ratio of liquid to solid, showing the optimized stirring speed is 400 rpm. In previous work, it was proposed that the ratio of liquid to solid has little influence on the reaction when it is less than 4.7¹². In the present work, we focused on the effects of sulphuric acid concentration, excess coefficient, reaction temperature and reaction time. An orthogonal array with four factors in four levels was employed to evaluate each factor and the results are summarized in Table-2.

According to the statistical analysis, the range results indicate that the influence of the four factors on the leaching ratio is in the following sequence: reaction temperature (0.212), reaction time (0.0755), excessive coefficient (0.0625) and sulphuric acid concentration (0.0577). It could be seen that

reaction temperature is the most significant factor affecting the leaching ratio whereas other factors show similar effects. Therefore, the optimized reaction conditions are: reaction temperature is 100°C , reaction time is 3 h, excessive coefficient is 1.05 and sulphuric acid concentration is 8 M. In practice, it is difficult to control the temperature at 100°C and hence reacting under pressure may be preferable.

TABLE-2
EFFECTS OF EXCESS COEFFICIENT (E), SULFURIC ACID CONCENTRATION (C, M), REACTION TEMPERATURE (T, $^\circ\text{C}$) AND REACTION TIME (t, h) ON THE LEACHING RATIO (RL)

No.	E	C/M	T ($^\circ\text{C}$)	t (h)	RL
1	1.05	5.0	70	1.5	0.3925
2	1.05	6.0	80	2.0	0.4442
3	1.05	7.0	90	2.5	0.5615
4	1.05	8.0	100	3.0	0.7334
5	1.10	5.0	80	2.5	0.4732
6	1.10	6.0	70	3.0	0.4440
7	1.10	7.0	100	1.5	0.5326
8	1.10	8.0	90	2.0	0.5737
9	1.15	5.0	90	3.0	0.5476
10	1.15	6.0	100	2.5	0.7265
11	1.15	7.0	70	2.0	0.4771
12	1.15	8.0	80	1.5	0.5103
13	1.20	5.0	100	2.0	0.6349
14	1.20	6.0	90	1.5	0.5239
15	1.20	7.0	80	3.0	0.5481
16	1.20	8.0	70	2.5	0.4616
K1	2.1316	2.0482	1.7797	1.9593	
K2	2.0235	2.1386	1.9758	2.1299	
K3	2.2615	2.1193	2.2067	2.2228	
K4	2.1685	2.2790	2.6274	2.2731	
k1	0.5329	0.5121	0.4449	0.4898	
k2	0.5059	0.5347	0.4940	0.5325	
k3	0.5654	0.5298	0.5517	0.5557	
k4	0.5421	0.5698	0.6569	0.5683	
R	0.0625	0.0577	0.2120	0.0755	

Fig. 1 shows the effects of reaction time on the leaching ratio. The reactions were conducted for different time of 1, 1.5, 2, 2.5 and 3 h under the condition of excess coefficient of 1.05, sulphuric acid concentration of 6 M and reaction temperature of 60°C . Then the experiments were carried out at 70, 80 and 90°C . It could be seen from Fig. 1 that leaching ratio increases with reaction time at the initial stage and levels off after 150 min. Besides, the leaching ratio obviously increases with reaction temperature.

Fig. 1. Effects of reaction time on the leaching ratio at different reaction temperatures. (Origin 7.0)

Effects of sulphuric acid concentration on the leaching ratio at different reaction temperatures are shown in Fig. 2. The experiments were operated with the condition of excess coefficient of 1.05, reaction time of 2 h. Results show that reaction ratio was enhanced with the concentration of sulphuric acid. However, considering the physical properties of the reaction slurry, the concentration of sulphuric acid should be avoided to be too high.

Fig. 2. Effects of sulfuric acid concentration on the leaching ratio at different reaction temperatures. (Origin 7.0)

Effects of reaction temperature on the leaching ratio were also investigated and the results are shown in Figs. 3 and 4. At the same concentration of sulphuric acid, the leaching ratios increase sharply with temperature, which are consistent with the results from orthogonal array experiments. It means that effects of reaction temperature on the leaching ratio are remarkable. The results shown in Fig. 4 have a similar tendency with those in Fig. 3.

Fig. 3. Effects of reaction temperature on the leaching ratio under different sulfuric acid concentrations. (Origin 7.0)

Based on the above mentioned optimized reaction conditions, the reaction kinetics was explored. Pyrite cinder leaching in sulphuric acid medium is a reaction at liquid/solid interface without solid products. During the reaction, the size of pyrite cinder particles decreases continuously during the reaction process. The shrinking core model considers that the leaching process is controlled either by the diffusion of reactant through the solution boundary, or through a solid product layer, or by the surface chemical reaction rate. Assuming that

Fig. 4. Effects of reaction temperature on the leaching ratio at different reaction time. (Origin 7.0)

pyrite cinder particles have a spherical geometry and surface chemical reaction is the slowest step, the following expression of the shrinking core model can be used to describe the dissolution kinetics¹⁵:

$$1-(1-x_B)^{1/3} = k't \quad (2)$$

Besides, there is not any gas reactant or products in this process. Similarly, when the diffusion between the solid phase and liquid phase is the rate controlling step, the following expression can be used¹⁶:

$$1-(1-x_B)^{2/3} = k't \quad (3)$$

Based on the analysis of the effects of reaction time on the leaching ratio, the above-mentioned two kinetics equations were fitted and the correlation coefficients (f) were summarized in Table-3. It could be found that the correlation coefficients of surface chemical reaction controlling kinetics eqn. (2) were slightly higher than those of kinetics eqn. (3), which indicates surface chemical reaction controlling kinetics model is more appropriate.

T (°C)	t (min)	x_B	$1-x_B$	$1-(1-x_B)^{1/3}$	f	$1-(1-x_B)^{2/3}$	f
60	60	0.3115	0.6885	0.1170		0.2203	
	90	0.3271	0.6729	0.1237		0.2321	
	120	0.3432	0.6568	0.1308	0.9875	0.2441	0.9870
	150	0.3672	0.6328	0.1415		0.2629	
	180	0.3724	0.6276	0.1438		0.2670	
70	60	0.3505	0.6495	0.1340		0.2500	
	90	0.3768	0.6232	0.1458		0.2704	
	120	0.3885	0.6115	0.1512	0.9452	0.2796	0.9331
	150	0.4026	0.5974	0.1578		0.2907	
	180	0.4213	0.5787	0.1667		0.3056	
80	60	0.3694	0.6306	0.1425		0.2646	
	90	0.4127	0.5873	0.1626		0.2987	
	120	0.4616	0.5384	0.1865	0.9690	0.3382	0.9673
	150	0.4737	0.5263	0.1926		0.3481	
	180	0.4907	0.5093	0.2014		0.3623	
90	60	0.3944	0.6056	0.1540		0.2842	
	90	0.5067	0.4933	0.2099		0.3757	
	120	0.5381	0.4619	0.2270	0.9170	0.4025	0.9107
	150	0.5613	0.4387	0.2402		0.4226	
	180	0.5723	0.4277	0.2466		0.4323	

On the basis of eqn. (2), curves of $1-(1-x_B)^{1/3}$ vs. reaction time was plotted in Fig. 5 and the slope is the reaction rate constant k' .

$$k' = \frac{k c_{H_2SO_4}^{n_1}}{R_s^{n_2}} \quad (4)$$

$$k = k_0 \exp(-E_a/R_g T) \quad (5)$$

Equation (5) was substituted to eqn. (4):

$$\ln k' = \ln k_0 - \frac{E_a}{R_g T} + n_1 \ln c_{H_2SO_4} + n_2 \ln \frac{1}{R_s} \quad (6)$$

Fig. 5. Plots of $1-(1-x_B)^{1/3}$ vs. reaction time at different temperatures. (Origin 7.0)

Based on eqn. (6), curve of $\ln k'$ vs. $1/T$ was plotted in Fig. 6. The slope of the fitted line is $-(E_a/R_g)$, which equals to -4654 . Hence, the activation energy E_a is calculated as 38.69 kJ/mol and $k_0 = 250$.

Fig. 6. Plot of $\ln k'$ vs. $1/T$. (Origin 7.0)

Equation (6) was substituted to eqn. (2):

$$\ln[1-(1-x_B)^{1/3}] = \ln k_0 - \frac{E_a}{R_g T} + n_1 \ln c_{H_2SO_4} + n_2 \ln \frac{1}{R_s} + \ln t \quad (7)$$

Curves of $\ln[1-(1-x_B)^{1/3}]$ vs. $\ln c_{H_2SO_4}$ were plotted in Fig. 7 in accordance with eqn. (7). It could be calculated that n_1 equals to 0.4947 , 0.4832 , 0.5376 and 0.4500 at 60 , 70 , 80 and 90 °C, respectively and the average value is 0.4914 . Curves of

$\ln[1-(1-x_B)^{1/3}]$ vs. $\ln[1/R_s]$ were also plotted (Fig. 8) on the basis of eqn. (7). Accordingly, the following parameters were obtained: n_2 equals to 0.1759 , 0.2035 and 0.1250 at 70 , 80 and 90 °C, respectively and the average value is 0.1681 .

Fig. 7. Plot of $\ln[1-(1-x_B)^{1/3}]$ vs. $\ln c_{H_2SO_4}$. (Origin 7.0)

Fig. 8. Plot of $\ln[1-(1-x_B)^{1/3}]$ vs. $\ln[1/R_s]$. (Origin 7.0)

The obtained parameters were substituted to eqn. (2) and the kinetics equation can be obtained as following:

$$1-(1-x_B)^{1/3} = 250 \times \exp\left(-\frac{38690}{R_g T}\right) \times c_{H_2SO_4}^{0.49} \times \left(\frac{1}{R_s}\right)^{0.17} t \quad (8)$$

Under the reaction temperature of 70 °C and sulphuric acid concentration of 6 M, the values of x_B at different reaction time were calculated according to eqn. (8) and compared with the experimental results (Fig. 9)¹⁷. F test indicated that the model can be used to describe the reaction kinetic of pyrite cinder leaching in sulfuric acid.

Conclusion

(1) The orthogonal experiments have shown that reaction temperature is the most significant factor affecting the leaching ratio of pyrite cinder and the influence of sulphuric acid concentration, reaction time and excessive coefficient decreases in sequence. The optimized reaction conditions are as following: reaction temperature is 100 °C, reaction time is 3 h, excessive coefficient is 1.05 and sulphuric acid concentration is 8 M.

Fig. 9. Comparison of x_B from calculation and experiments. (Origin 7.0)

(2) The reaction of pyrite cinder in sulphuric acid medium fits the surface chemical reaction model.

(3) The kinetics equation can be expressed as:

$$1 - (1 - x_B)^{1/3} = 250 \times \exp\left(-\frac{38690}{R_g T}\right) \times C_{\text{H}_2\text{SO}_4}^{0.49} \times \left(\frac{1}{R_s}\right)^{0.17} t$$

F test indicated that this equation can be used to describe the reaction kinetic of pyrite cinder leaching in sulfuric acid.

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