IMPROVED LEACHING METHOD AND

KINETICS OF MANGANESE CARBONATE

ORE AT ROOM TEMPERATURE[①]

Yuan Mingliang, Mei Xiangong, Chen Jin, Zhuang Jianming
Department of Mineral Engineering,
Central South University of Technology, Changsha 410083

ABSTRACT　　Up to now, the leaching of manganese carbonate ore was usually performed at high temperature up to 363 K but leaching rate was lower than 90%. Even in laboratory test, the leaching rate was only about 90%. Therefore an improved method for more effective leaching of manganese carbonate ore was introduced, that is a certain amount of ammonium salt was added to the pulp to raise the solubility of Mn^{2+} and reduce the adsorption quantity of Mn^{2+} on the ore surface. Experimental results showed that a leaching rate over 95% could be obtained at the temperature 273 K. The activation energy was calculated to be 7.15 kJ/mol, which is lower than that of normal leaching technique. Meanwhile a kinetic model was deduced, and verified with experiments, showing that the model could describe the leaching process successfully.
Key words　leaching　manganese ore　kinetics　model

I INTRODUCTION

Leaching of manganese ore is a key problem in the manganese salt production, which can be divided into two parts, i. e. leaching manganese dioxide ore and manganese carbonate ore. The emphasis of the leaching of manganese dioxide ore was put on the reduction technique and reducing agent[1-3]. The leaching process of manganese carbonate ore is relatively simpler than that of manganese dioxide ore. The ore is usually leached with sulphuric acid at 363 K. Although a leaching rate of 80%~90% can be achieved by using SO_2 solution to leach the ore at 293~303 K, the high SO_2 pressure and longer reaction time are necessary[4]. The efficiency of recovery of Mn from a lump ore was increased by a technology of leaching and impact pulverizing grinding simultaneously[5]. It has been reported that manganese carbonate ore could be leached with the leaching rate about 90% at 303 K[6].

All these facts mentioned above imply that the leaching rate could be increased usually by raising reaction temperature while pretreating leaching process, however which will result in operation difficult and decrease productivity. Therefore, it is necessary to enhance the studies of leaching technique on manganese carbonate ore. In the meantime, most of the current kinetic models studied were based on the reaction, in which concentration of the reaction agent was constant, and the kinetic model of solid-liquid intermittent heterogeneous reaction of leaching process was rarely full discussed. It should be stressed to meet the need of many manganese salt plant.

2 EXPERIMENTS AND DISCUSSION

2.1 *Leaching Process*

Tests were carried out in a glass vessel(2 L). Ore sample of 100 g was added in the di-

lute sulphuric-acid. The temperature of leaching process was controlled by a thermostat.

In the leaching process, Mn^{2+} and Fe^{2+} produced from a reaction form a dense layer of sulphate on the surface of the leaching ore, preventing the reactant from diffusing[7], and resulting in a limited increase of the leaching rate by raising reaction temperature. However, the possibility to raise the leaching rate by decreasing the surface energy has been proved by tests. On the basis mentioned above, it is discovered that certain ammonium salt PL adding in the pulp can increase the solubility of Mn^{2+} and reduce the adsorption quantity of Mn^{2+} and destroy the dense layer of sulphate on the ore surface. These will result in speeding the diffusion of reactant and quicken the leaching step.

2.2 Test Results

The chemical composition of the sample of manganese carbonate ore from Guizhou is given in Table 1. Sample 1 was added in the dilute sulphuric-acid solution in the absence of PL. The acid concentration was 1.93 mol/L, stirring speed 1 000 r/min, pulp density 160 g/L. The process was performed at constant temperature, using thermometry to control the reaction temperature. The tests results are given in Fig. 1, where ε represents the leaching rate.

Table 1　Chemical composition of manganese carbonate ore

Item	Mn	Fe	SiO_2	Al_2O_3	CaO	MgO	Cu
Content /%	19.54	5.78	15.71	3.63	10.20	3.12	0.012

Sample 2 was leached in the presence of PL about 1.5%. Other reaction conditions were similar to that of sample 1. The tests results (as shown in Fig. 2) indicated that the leaching rate is increased by using PL.

The relationship among reaction rate constant K, activation energy E and temperature T_k is expressed as:

$$K = A \exp^{-E/RT_K} \qquad (1)$$

The reaction velocity can be expessed as:

$$d\varepsilon/dt = KC^n \qquad (2)$$

The values of $d\varepsilon/dt$ at different temperatures can be calculated by processing the data of Fig. 1 and Fig. 2. The curves of $(\ln(d\varepsilon/dt) \sim 1/T_K)$ are shown as Fig. 3. The slope of the curve is considered as the apparent activation energy:

$$E_1 = 7.15 \text{ kJ/mol}; \quad E_2 = 12.09 \text{ kJ/mol}$$

where E_1 is the apparent activation energy of leaching reaction in the presence of PL; E_2 is the apparent activation energy in the absence of PL. Therefore, in the absence of PL, raising reaction temperature from 298 K to 363 K, the increased magnitude of the reaction rate
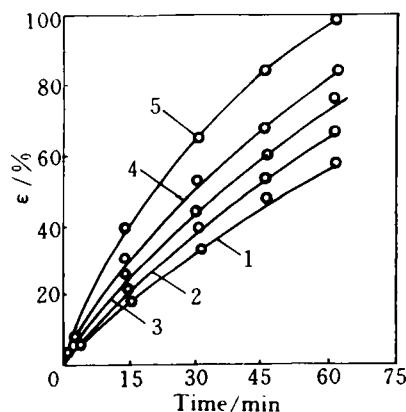
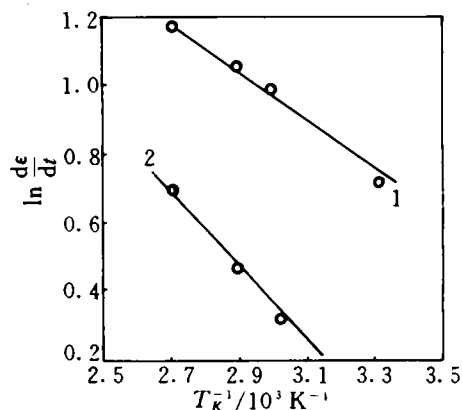**Fig. 1　Test result of sample 1**
1—30 ℃; 2—50 ℃; 3—60 ℃; 4—70 ℃; 5—90 ℃
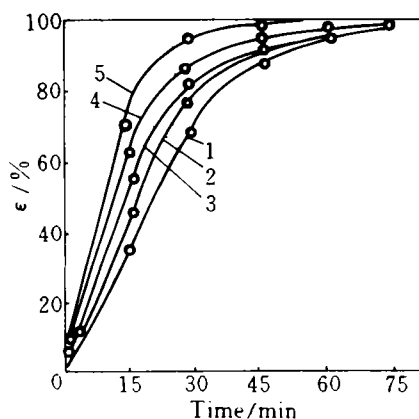
Fig. 2　Test result of sample 2
1—30 ℃; 2—50 ℃; 3—60 ℃; 4—70 ℃; 5—90 ℃

is:

$$\frac{K_{363}}{K_{298}} = \exp\left[\frac{12\,090}{8.\,314}\left(\frac{1}{298} - \frac{1}{363}\right)\right] = 2.\,40 \quad (3)$$

However at 298 K, because of adding PL, the increased magnitude of the reaction rate is:

$$\frac{K'_{298}}{K_{298}} = \exp\left[\frac{1}{8.\,314 \times 298}(12\,090 -\right.$$
$$\left. 7\,150)\right] = 7.\,34 \quad (4)$$

Fig. 3   Effect of temperature on reaction rate

1—in the presence of PL;
2—in the absence of PL

Hence, the addition of PL can decrease the activation energy of the leaching reaction remarkably and the effect of temperature decreases greatly. The leaching at room temperature can be realized by adjusting other conditions. The effects of particle size, agitating speed, concentration of acid, and pulp density on the leaching rate were tested and the optimum conditions are: particle size $< 0.\,25$ mm, agitation speed > 960 r/min, $H_2SO_4 : MnCO_3 > 1.\,2$, pulp density $150 \sim 250$ g/L, respectively.

3   THE KINETIC MODEL

3.1   *Model Selection*

The studies on the leaching speed and the model of leaching process of manganese carbonate ore exhibit that the leaching rate controlling steps embrace diffusion in the porous residue layers and reaction within the mineral

grains[1]. The size distribution of the raw material and residue after leaching was measured and shown in Table 2.

**Table 2   Particle size composition of the raw mineral and dregs after leaching**

Particle size /μm	Raw ore /%	Leaching dregs /%
2.5~5.5	29.4	25.5
5.5~11	20.8	26.4
11~22	6.3	19.2
22~44	21.5	21.4
44~88	21.3	7.2
88~125	0.4	0
Average size/μm	19.06	13.3
Leaching rate/%	96.3	96.3

Note: Reacting time 60 min; temperature 358 K.

The data in Table 2 indicate that the particle size of the residue decreases slightly as compared with that of the raw ore, when the leaching rate is high up to 95%. Scraping of the particle during leaching can be considered as the cause of the decreasing in size. The test results explained that the composition of the ore that did not dissolve in acid wrapped the non-reacting pit to form a structure of remaining layer and did not peel off. The leaching agent must diffuse through the remaining layer for further leaching. The reaction will occur on the slide interface of the non-reacting pit and the remaining layer. The tests of agitating speed vs leaching rate indicated that the effect of external diffusion was eliminated when agitating speed > 950 r/min. Therefore, the leaching process can be describe with a model, in which the process is controlled by chemical reaction and internal diffusion.

3.2   *Development of the Model*

The leaching reaction of manganese carbonate ore can usually be expressed as:

$$A(aq) + bB(s) = cC(aq) + dD(g) \quad (5)$$
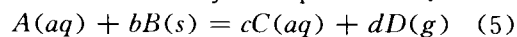
This kind of heterogeneous reaction can be considered as irreversible reaction of first order. The diffusion amount of reactant A

through remaining layer is:

$$J_A = -4\pi r_C^2 D_e \frac{dc_A}{dr_C} \tag{6}$$

where J_A is the diffusion amount of A; r_C is the radius of non-reacting pit; D_e is the diffusion coefficient of A; C_A is the concentration of A. Integrate Eq. (6):

$$\int_{C_{Ac}}^{C_{Ab}} dC_A = \frac{J_A}{4\pi D_e} \int_{r_0}^{r_C} \frac{1}{r_C^2} dr_C \tag{7}$$

where C_{Ac} is the concentration of A at the solid-solid interface; C_{Ab} is the concentration of A in the pulp; r_0 is the initial particle size of B. Eq. (8) can exist, when the reaction is in a stable state:

$$C_{Ab} - C_{Ac} = \frac{J_A}{4\pi D_e}\left(\frac{1}{r_c} - \frac{1}{r_0}\right) \tag{8}$$

The chemical reaction is:

$$\frac{dG_A}{dt} = K \cdot S \cdot C_{Ac} = 4\pi r_C^2 \cdot K \cdot C_{Ac} \tag{9}$$

where G_A is the amount of A reacted; K is the reacting rate constant; S is the diffusion area. When the reaction is in stable state, the chemical reaction rate is equal to the diffusion speed:

$$J_A = -\frac{dG_A}{dt}$$

$$4\pi D_e\left(\frac{r_0 r}{r_0 - r_c}\right)(C_{Ab} - C_{Ac}) = 4\pi r_c^2 C_{Ac} \tag{10}$$

Eq. (11) can be obtained from Eq. (5):

$$-\frac{dG_A}{dt} = -\frac{1}{b}\frac{dG_B}{dt} = -\frac{\rho_B}{bM_B}4\pi r_C^2\frac{dr_c}{dt} \tag{11}$$

where ρ_B is the density of B and M_B is its molecular weight. Let x denote leaching rate, whose value is equal to reacting fraction of B:

$$C_{Ab} = C_{A0}(1 - x) \tag{12}$$

where C_{A0} is the initial acid concentration.

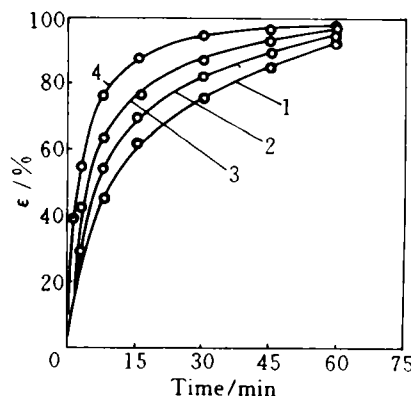The x can also be expressed as:

$$x = 1 - \left(\frac{r_C}{r_0}\right)^3 \tag{13}$$

Rearrange Eqs. (9)~(13), Eq. (14) can be achieved:

$$t = \frac{r_0^2 \rho_B}{De \cdot C_{A0} \cdot bM_B}[(1-x)^{-1/3} - 1 + \ln(1-x)^{1/3}] + \frac{r_0 \rho_B}{2K \cdot C_{A0} \cdot bM_B}[(1-x)^{-2/3} - 1] \tag{14}$$

3.3 *Verifying of the Model*

The manganese carbonate ore used for confirming tests is given in Table 1($\rho_B = 3.4$ g/cm^3, particle size 125~170 mesh, average size 0.1 mm). Leaching results of the ore is shown in Fig. 4.

Fig. 4 Leaching result of the manganese carbonate ore

1—30 ℃; 2—50 ℃; 3—70 ℃; 4—90 ℃

Rearrange Eq. (14) as follows:

$$\frac{t}{(1-x)^{-1/3} - 1 + \ln(1-x)^{1/3}}$$
$$= \frac{r_0^2 \rho_B}{De \cdot C_{A0} \cdot bM_B} + \frac{r_0 \rho_B}{2K \cdot C_{A0} \cdot bM_B}$$
$$\cdot \frac{(1-x)^{-2/3} - 1}{(1-x)^{-1/3} - 1 + \ln(1-x)^{1/3}} \tag{15}$$

Suppose:

$$y = \frac{t}{(1-x)^{-1/3} - 1 + \ln(1-x)^{1/3}} \tag{16}$$

$$x = \frac{(1-x)^{-1/3} - 1}{(1-x)^{-1/3} - 1 + \ln(1-x)^{1/3}} \tag{17}$$

$$e = \frac{r_0^2 \rho_B}{De \cdot C_{A0} \cdot bM_B} \tag{18}$$

$$f = \frac{r_0 \rho_B}{2K \cdot C_{A0} \cdot bM_B} \tag{19}$$

Then Eq. (15) is reformed as:

$$y = e + fx \tag{20}$$

The values of e and f can be obtained by regressing the data of Fig. 4, based on Eq. (20), K and D_e at different temperatures can be calculated from Eqs. (18) and (19). Meanwhile, the relationship of K, D_e to tempera-

ture T would be:

$$K = K_0 \cdot e^{-\frac{E_k}{RT}} \qquad (21)$$

and

$$D_e = D_0 \cdot e^{-\frac{E_D}{RT}} \qquad (22)$$

K_0, D_0, E_K and E_D can be obtained by substituting K, D_e and the corresponding T into Eqs. (21) and (22) and make regression just as above process.

$K_0 = 1.94 \times 10^{-2}$, $E_K = 20.60 \, \text{kJ/mol}$

$D_e = 6.93 \times 10^{-6}$, $E_D = 13.59 \, \text{kJ/mol}$

Substitute the parameters into Eq. (14):

$$t = \frac{r_0^2 \cdot \rho_B}{6.93 \times 10^{-6} \cdot e^{\frac{-13590}{RT}} \cdot C_{A0} \cdot b \cdot M_B} \cdot [(1-x)^{-1/3} - 1 + \ln(1-x)^{1/3}] +$$
$$\frac{r_0 \cdot \rho_B}{3.88 \times 10^{-2} \cdot e^{-\frac{20640}{RT}} \cdot C_{A0} \cdot b \cdot M_B} \cdot [(1-x)^{-2/3} - 1] \qquad (23)$$

Eq. (23) has been verified with the data of experimental leaching as Fig. 5.

Curves in Fig. 5 are calculation results of Eq. (23). Points "○" and "●" are the actual test results at 333 K and 293 K, respectively.
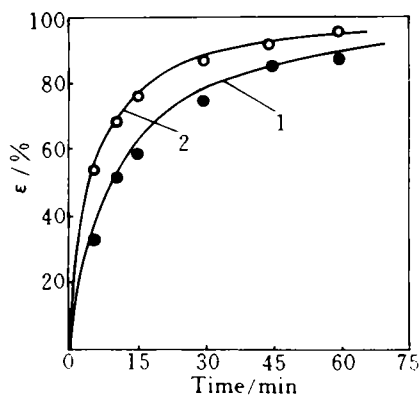

Fig. 5 Verified results of the model
1—293 K; 2—333 K

Fig. 5 expresses that the non-reacting core shrinking model can describe the leaching process of manganese carbonate ore properly.

4 CONCLUSIONS

(1) The leaching rate of the manganese carbonate ore is increased tremendously due to the addition of PL. The activation energy is calculated to be 7.15 kJ/mol. Consequently the effect of reaction temperature is decreased. The leaching rate over 95% at room temperature can be obtained under the following optimal condition: stirring speed > 960 r/min, particle size < 0.20 mm, reaction time 90 min, H_2SO_4: $MnCO_3 > 1.2$, pulp density 150 ~205 g/L.

(2) It would be inexact to describe the leaching process of manganese carbonate ore with the kinetic model in which the important effect of the change in acid concentration is neglected and a constant concentration is considered instead. Test results showed that the process is controlled by the chemical reaction and the diffusion through remaining layer when stirring speed > 960 r/min. The non-reacting shrinking kinetic model of changing concentration for leaching of manganese carbonate ore was deduced and verified with the leaching tests of manganese carbonate ore from Guizhou by adding PL, which explains that the non-reaction core shrinking model can describe the leaching process properly.

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