International Journal of Minerals, Metallurgy and Materials
Volume 20, Number 3, March 2013, Page 221
DOI: 10.1007/s12613-013-0716-5

Fluidized roasting reduction kinetics of low-grade pyrolusite coupling with pretreatment of stone coal

*Ya-li Feng*1), *Zhen-lei Cai*1), *Hao-ran Li*2), *Zhu-wei Du*2), *and Xin-wei Liu*1)

1) School of Civil and Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, China

2) State Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

(Received: 26 May 2012; revised: 26 June 2012; accepted: 28 June 2012)

Abstract: Based on the fluidized roasting reduction technology of low-grade pyrolusite coupling with pretreatment of stone coal, the manganese reduction efficiency was investigated and technical conditions were optimized. It is found that the optimum manganese reduction efficiency can be up to 98.97% under the conditions that the mass ratio of stone coal to pyrolusite is 3:1, the roasting temperature of stone coal is 1000°C, the roasting temperature of pyrolusite is 800°C, and the roasting time is 2 h. Other low-grade pyrolusite ores in China from Guangxi, Hunan, and Guizhou Provinces were tested and all these minerals responded well, giving ∼99% manganese reduction efficiency. Meanwhile, the reduction kinetic model has been established. It is confirmed that the reduction process is controlled by the interface chemical reaction. The apparent activation energy is 36.397 kJ/mol.

Keywords: pyrolusite; ore roasting; ore reduction; fluidized beds; kinetics; stone coal

1. Introduction

Manganese plays an important role in many fields, such as steel production, preparation of dietary additives, fertilizers, cells, and fine chemicals [1-2]. More than 90% of manganese ores are used in the iron and steel industry, of which manganese dioxide ores almost account for 60% [3]. Due to the ever-increasing demand of manganese resources and the exhaustion of high-grade manganese ores, utilizing and exploiting low-grade manganese ores become increasingly important.

It is well-known that manganese extraction from manganese dioxide ores should be conducted under the reduction conditions [4]. Two main alternatives have been proposed to recover manganese from pyrolusite: roasting reduction and hydrometallurgical reduction. Compared with the hydrometallurgical reduction process, which proceeds mainly with reductants such as sodium sulfite [5], iron powder [6], ferrous sulfate [7], hydrogen peroxide [8], sulfur dioxide [9], molasses [10], methyl alcohol [11], sawdust [12], cornstalk [13], oxalic acid [4], pyrite [14], sphalerite [15], and galena [16], the roasting reduction process was widely employed due to its easily controlled conditions and good applicability.

Paixdo *et al.* [17] studied the effect of CO-H_2 gas mixtures on the manganese reduction efficiency and the results indicated that almost all manganese dioxide in the ore could be reduced in the temperature range of 700-800°C for 2 h. De Bruijn *et al.* [18] and Jerez *et al.* [19] studied the reduction of pyrolusite in hydrogen atmosphere in the temperature range of 275-400°C and the experimental results revealed that the reduction product was Mn_3O_4. Chen *et al.* [20] found out that the microstructure of solid phase reduction on manganese oxide ore fines containing coal is one of the important conditions of influencing microwave heating and MnO_2 phase was entirely changed into MnO. Biomass roasting reduction of low-grade manganese dioxide ores is popular in recent years [1, 3]. Biomass straw

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Corresponding author: Ya-li Feng E-mail: ylfeng126@126.com

was investigated as a reductant and fuel for reducing manganese oxide ores at low temperatures of up to 600°C and the activation energy could be calculated at different temperature ranges [21]. Cai *et al.* [22] achieved the results that the maximum manganese reduction efficiency could be optimized to nearly 100% using biogas residual as a reductant. The results of the above research are convincing but the reduction roasting kinetics of low-grade pyrolusite remains to be investigated and studied.

The total reserve of vanadium in stone coal is 1.18×10^8 t in terms of V_2O_5 in China, which accounts for >87% of the total reserve of vanadium nationwide [23]. Therefore stone coal is the main vanadium resource in China. But utilizing the carbon components in stone coal has been rarely reported. The pretreatment of stone coal, which is to oxidizing roast the carbon components, usually generates a lot of harmful gases such as CO and SO_2 and the efficient exploitation of carbon components in stone coal becomes one of the most important parts in cleaner production for vanadium extraction.

In this paper, a novel fluidized roasting coupling technology, which is to couple the pretreatment of stone coal with the reduction roasting process of low-grade pyrolusite, was presented. The main purpose was to investigate the effects of different variables such as the mass ratio of stone coal to pyrolusite, the roasting temperature of stone coal, the roasting temperature of pyrolusite, and the roasting time on the manganese reduction efficiency of low-grade pyrolusite to determine the rate-controlling step of the reduction roasting process. Meanwhile, the reduction kinetic model was established to strengthen the reduction roasting effect and improve the economic applicability of this technology.

2. Experimental

2.1. Materials

The sample of stone coal was obtained from Guangxi Province, China. The ore sample was crushed and ground into powder with a particle size smaller than 0.074 mm. Chemical multi-elemental analysis showed that the stone coal used contained 6.72wt% Al, 23.88wt% Si, and 17.75wt% C, as listed in Table 1. The mineralogical composition of the ore sample was defined by powder X-ray diffraction (XRD). The XRD pattern (Fig. 1) showed that the main minerals included quartz, muscovite, and phlogopite.

Table 1. Chemical multi-elemental analysis results of stone coal wt%

V	Al	Si	C	S	Ca	Mg	Fe
0.62	6.72	23.88	17.75	2.25	3.44	5.58	0.11

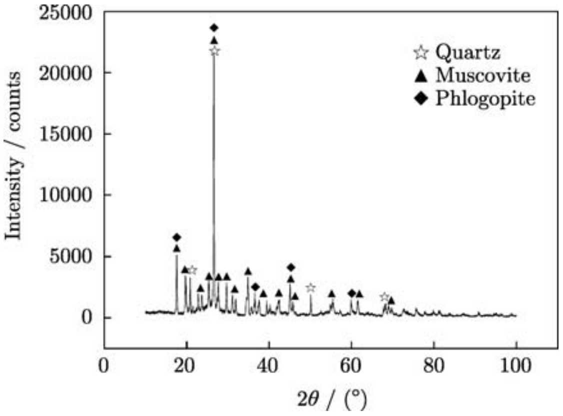


Fig. 1. XRD pattern of stone coal.

The sample of low-grade pyrolusite was obtained from Yunnan Province, China. The ore sample was crushed and ground into powder with a particle size smaller than 0.147 mm. Chemical multi-elemental analysis showed that the pyrolusite used contained 21.43wt% Mn, 36.36wt% SiO_2, and 8.11wt% Fe_2O_3, as listed in Table 2. XRD analysis showed that manganese was mainly in the form of manganese dioxide in the pyrolusite, and the main gangue minerals included quartz and feldspar, as shown in Fig. 2.

Table 2. Chemical multi-elemental analysis results of low-grade pyrolusite wt%

Mn	SiO_2	Fe_2O_3	Al_2O_3	CaO	Na_2O	MgO	S	P
21.43	36.36	8.11	7.79	5.31	2.79	1.93	0.2	0.02

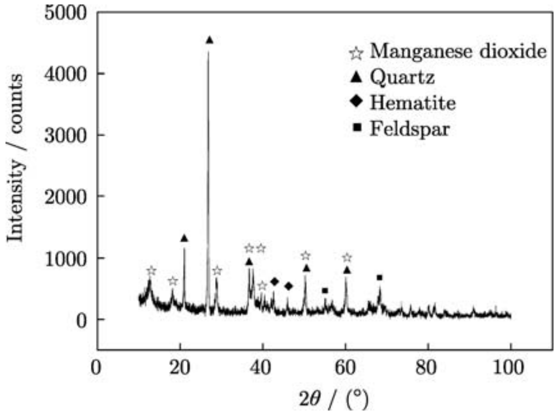
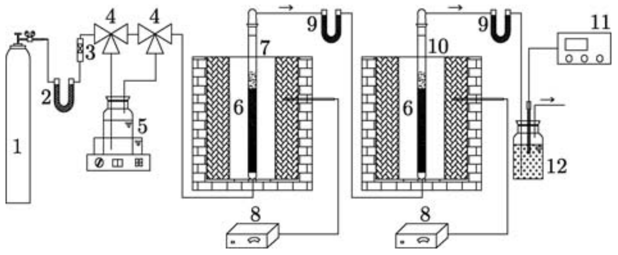


Fig. 2. XRD pattern of low-grade pyrolusite.

2.2. Experimental equipment

Fig. 3 shows the experimental equipment designed by ourselves. It consisted of two quartz fluidized bed reactors, a nitrogen cylinder, a rotameter, a steam generator, a crucible resistance furnace, and an acidometer. Nitrogen used in the experiment was of industrial grade. All other chemicals were of analytical grade and used without further purification.



1—nitrogen cylinder; 2—dryer; 3—rotameter; 4—three-way valve; 5—steam generator; 6—crucible resistance furnace; 7—quartz fluidized bed reactor I (stone coal); 8—electronic thermo-controllers; 9—absorber; 10—quartz fluidized bed reactor II (low-grade pyrolusite); 11—acidometer; 12—alkali liquor bottle

Fig. 3. Schematic diagram of the fluidized roasting coupling reactor.

2.3. Experimental procedure

After crushing, rod milling, screening, and drying, 10 g of stone coal and a certain amount of pyrolusite were added into the quartz fluidized bed reactor I and II, respectively, according to the mass ratio of stone coal to pyrolusite. Before the roasting experiment started, the oxidizing atmosphere of the system was removed by inert gas. When both the stone coal and pyrolusite were roasted at the designated temperature, N_2 was fed into the steam generator at 80°C by switching the three-way valve and it loaded steam into the fluidized bed reactor I to react with the carbon components in stone coal to produce CO and H_2. The reductive gas mixture was then fed into the fluidized bed reactor II to reduce manganese dioxide in the low-grade pyrolusite. After the roasting reduction was completed, the roasted product was put into a leaching pod containing enough quantities of sulfuric acid immediately lest the reduced ore was reoxidized by oxygen in air. The solution was stirred continuously until all the manganese oxide was leached from the roasting product. After the sample was filtrated and dried, manganese in the filtrate was analyzed to calculate the manganese leaching efficiency, and it can be indicated by the manganese reduction efficiency, due to the fact that manganese dioxide cannot be dissolved by sulfuric acid. The manganese reduction efficiency can be calculated as follows:

$$\eta = \frac{V\beta}{m\alpha} \times 100\% \tag{1}$$

where η is the manganese reduction efficiency, wt%; V is the volume of the filtrate, mL; β is the manganese content in the filtrate, g/mL; m is the mass of raw pyrolusite, g; and α is the manganese content in raw pyrolusite, wt%.

The main chemical reactions related during the experiment are shown as follows.

$$\mathrm{C} + \mathrm{H_2O} \rightarrow \mathrm{CO} + \mathrm{H_2} \tag{2}$$

$$\mathrm{MnO_2} + \mathrm{CO} \rightarrow \mathrm{MnO} + \mathrm{CO_2} \tag{3}$$

$$\mathrm{MnO_2} + \mathrm{H_2} \rightarrow \mathrm{MnO} + \mathrm{H_2O} \tag{4}$$

3. Results and discussion

3.1. Effect of the mass ratio of stone coal to pyrolusite on the manganese reduction efficiency

To evaluate the effect of the mass ratio of stone coal to pyrolusite, a series of experiments was carried out by varying the mass ratio from 0.5:1 to 4:1 while fixing the roasting temperature of stone coal at 1000°C, the roasting temperature of pyrolusite at 800°C, and the roasting time at 2 h. From Fig. 4, it can be seen that the manganese reduction efficiency increased with the increase of the mass ratio. The reason was probably that the concentration of the reductive gases (CO and H_2) increased with the increase of the mass ratio, thus enhancing the reductive atmosphere and improving the manganese reduction efficiency. When the mass ratio of stone coal to pyrolusite was 3:1, the manganese reduction efficiency could be up to the maximum value of ~98.94%. Further increasing the mass ratio only resulted in a slight increase in the manganese reduction efficiency. Therefore, the following experiments took 3:1 as the preferable mass ratio.

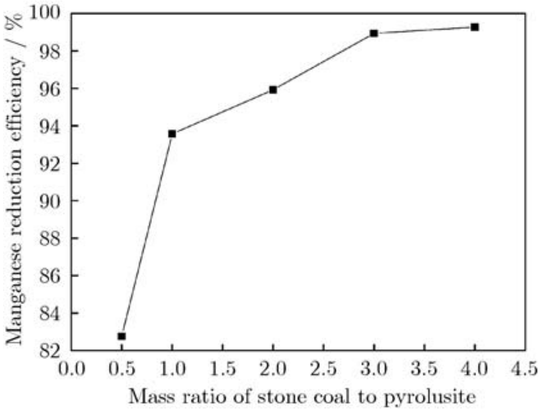


Fig. 4. Effect of the mass ratio of stone coal to pyrolusite on the manganese reduction efficiency.

3.2. Effect of the roasting temperature of stone coal on the manganese reduction efficiency

The fluidized roasting coupling experiments at roasting temperatures of stone coal from 700 to 1100°C were carried out while fixing the mass ratio of stone coal to pyrolusite at 3:1, the roasting temperature of pyrolusite at 800°C, and the roasting time at 2 h (Fig. 5). The results demonstrated that the manganese reduction efficiency increased as the roasting temperature of stone coal increased. After the roasting temperature was up to 1000°C, the manganese reduction efficiency increased slowly with the roasting temperature increasing. This was mainly because the carbon components in stone coal reacted with steam adequately at 1000°C, and the concentration of the reductive gases (CO and H_2) at this temperature was higher than that at low temperature. Hence, the optimum roasting temperature of stone coal should be 1000°C.

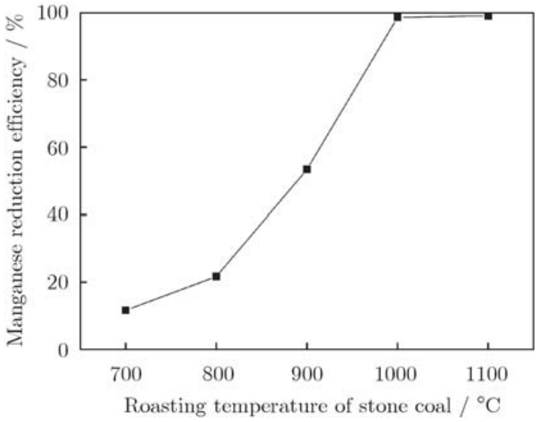


Fig. 5. Effect of the roasting temperature of stone coal on the manganese reduction efficiency.

3.3. Effect of the roasting temperature of pyrolusite on the manganese reduction efficiency

The effect of the roasting temperature of pyrolusite on the manganese reduction efficiency is presented in Fig. 6 while fixing the mass ratio of stone coal to pyrolusite at 3:1, the roasting temperature of stone coal at 1000°C, and the roasting time at 2 h. The manganese reduction efficiency increased with the roasting temperature of pyrolusite rising. When the roasting temperature was up to 800°C, no improvement could be observed with the increase in roasting temperature; besides, a small amount of sintering turned up in the roasting sample. The reason was probably that the sintered sample caused by high roasting temperature formed a barrier for the manganese components in the sample to contact and react with the reductive gases. Therefore, the roasting temperature of pyrolusite should not be higher than 800°C.

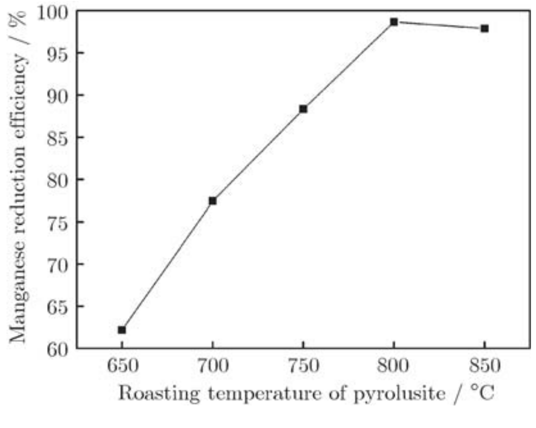


Fig. 6. Effect of the roasting temperature of pyrolusite on the manganese reduction efficiency.

3.4. Effect of roasting time on the manganese reduction efficiency

The manganese reduction efficiency also depended on roasting time (Fig. 7). The experiment was carried out while fixing the mass ratio of stone coal to pyrolusite at 3:1, the roasting temperature of stone coal at 1000°C, and the roasting temperature of pyrolusite at 800°C. When the roasting time ranged from 0.5 to 2.5 h, a longer roasting time benefited the manganese reduction efficiency. The manganese reduction efficiency increased to 98.97% when the roasting time was 2 h. Further extending the roasting time improved the manganese reduction efficiency slightly. Considering the equipment and the roasting cost, the optimum roasting time should be 2 h.

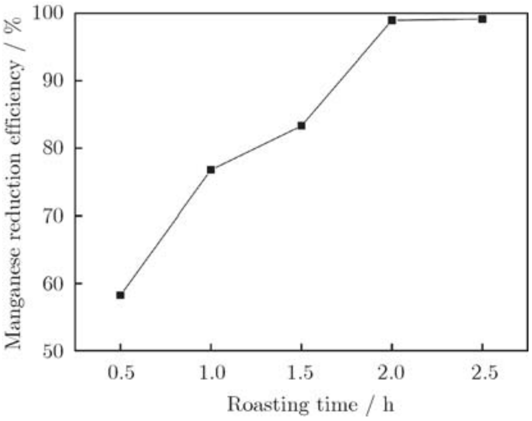


Fig. 7. Effect of roasting time on the manganese reduction efficiency.

3.5. Reduction behavior of other low-grade pyrolusite ores

Other low-grade pyrolusite ores in China from Guangxi, Hunan, and Guizhou Province were tested under the following conditions: mass of the ore sample, 10 g; roasting temperature of stone coal, 1000°C; roasting temperature of pyrolusite, 800°C. The results are shown in Table 3. The amount of stone coal for these minerals was varied to optimize the manganese reduction efficiency, and it was dependent on the manganese content of pyrolusite. The present study established the suitability of stone coal as a reductant for various low-grade pyrolusite ores.

3.6. Reduction kinetic analysis

The reduction kinetics was analyzed for the fluidized roasting of pyrolusite. Because of the reaction complexity in the fluidized bed reactor, some reaction conditions should be simplified for reduction kinetic modeling [24].

Table 3. Reduction behavior of other low-grade pyrolusite ores

Low-grade pyrolusite	Mass of stone coal / g	Roasting time / h	Manganese reduction efficiency / %
Guangxi (26.09wt% Mn)	35	0.5	63.23
		1.0	79.83
		1.5	90.15
		2.0	98.93
		2.5	99.12
Hunan (17.78wt% Mn)	27	0.5	59.27
		1.0	72.31
		1.5	85.94
		2.0	98.76
		2.5	98.95
Guizhou (21.36wt% Mn)	30	0.5	57.63
		1.0	74.62
		1.5	86.56
		2.0	98.89
		2.5	99.08

(1) The particles of the roasting sample could be approximated to sphere.

(2) As the manganese oxide in pyrolusite was reduced step by step, and several reaction interfaces may exist in particles, making the modeling of the reduction complex, the reduction process was simplified from multi-interface to single interface.

(3) The temperature inside the fluidized bed could be considered well distributed, because particles in the bed were scattered evenly and the mass and heat transfer was sufficient.

(4) The oxidative component in the reductive gases, which were produced from the excessive carbon components in stone coal at high temperature, was extremely low. Meanwhile, the gases could easily react in equilibrium with the carbon components in which particles in the bed were scattered evenly, the mass and heat transfer was sufficient, and the reaction rate was quite fast. Therefore, the reductive atmosphere of the reaction system could be considered to be basically unchanged.

(5) The exterior diffusion resistance of the steam transmission could be ignored because the flow rate of the reductive gases was relatively great, making the gas phase boundary layer of pyrolusite particles very thin. The interior diffusion resistance could also be neglected because of the small, loose, and porous particles. Therefore, the fluidized reduction process was assumed to be controlled by the interface chemical reaction. The single interface unreacted core model was taken to deal with the single reaction particles. When the restricted step is the interface chemical reaction, the interface reaction rate of the particles could be expressed as follows [25].

$$v = \frac{4\pi r^2 k(1+K)(C_0 - C^*)}{K} \tag{5}$$

where k is the interface reaction rate constant, s^{-1}; K is the reaction equilibrium constant; C_0 is the reductant concentration of the particle surface, $\mathrm{g/m^2}$; and C^* is the reductant concentration of the reaction equilibrium, $\mathrm{g/m^2}$.

The reduction rate could be expressed as follows.

$$\frac{\mathrm{d}f}{\mathrm{d}t} = \frac{3}{r_0\rho} \cdot \frac{k(1+K)}{K}(1-f)^{\frac{2}{3}} \cdot (C_0 - C^*) \tag{6}$$

where f is the reaction efficiency (%) at the moment of t(s); ρ is the oxygen content per volume of the particle, $\mathrm{g/m^3}$; and r_0 is the original particle size, m.

The relationship between the reduction efficiency f and the roasting time t could be obtained by the integration with Eq. (7).

$$f = 1 - \left[1 - \frac{k(1+K)}{K} \cdot \frac{C_0 - C^*}{r_0\rho} t\right]^3 \tag{7}$$

With the assumption that the particle size ranges from 0 to r_m, where r_m is the variation in particle size, r_0 could be expressed by xr_m and the x value ranged from 0 to 1. The beta distribution $\beta(2,2)$ could be used to describe x [24], when $\varphi(x)$ was the distribution density function of x:

$$\varphi(x) = \begin{cases} 6x(1-x), & 0 \le x \le 1 \\ 0, & \text{others} \end{cases} \tag{8}$$

Therefore, the average reduction efficiency of the whole fluidized bed was

$$\overline{f} = \frac{\displaystyle\int_0^1 \frac{4}{3}\pi r_0^3 \rho f \varphi(x)\mathrm{d}x}{\displaystyle\int_0^1 \frac{4}{3}\pi r_0^3 \rho \varphi(x)\mathrm{d}x} = 5m^3t^3 - 7.5m^2t^2 + 4.5mt \tag{9}$$

$$m = \frac{k(1+K)(C_0 - C^*)}{K r_\mathrm{m} \rho} \tag{10}$$

The Arrhenius equation is

$$k = A\mathrm{e}^{-\frac{E}{RT}} \tag{11}$$

$$\ln k = -\frac{E}{RT} + \ln A \tag{12}$$

where k is the interface reaction rate constant, s^{-1}; E is the apparent activation energy, kJ/mol; T is the reaction temperature, K; and A is the reaction constant.

The experiment about the manganese reduction efficiency changed with the roasting time was studied by varying the roasting temperature from 873 to 1173 K. Then, the relationship between the kinetic model and the roasting time at different temperatures could be obtained by substituting the manganese reduction efficiency into the kinetic model controlled by the interface chemical reaction. Consequently, the reaction rate constant k at different temperatures could be obtained.

By fitting ln$k$ to $1/T$ (Fig. 8), the regression equation between the interface reaction rate constant k and the roasting temperature T of the fluidized reduction system could be expressed as follows.

$$\ln k = 0.9135 - \frac{4377.3}{T} \tag{13}$$

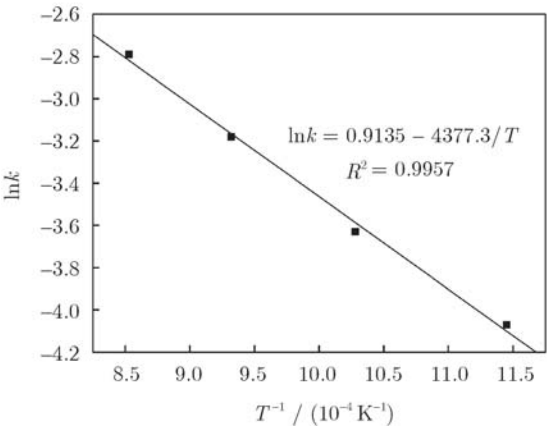


Fig. 8. Relationship between the interface reaction rate constant and roasting temperature.

Meantime, the apparent activation energy of the reduction roasting reaction could be calculated as 36.397 kJ/mol by the slope of the regression equation, which is so high that the system was controlled by the interface chemical reaction. The specific expression of m could be obtained according to the regression equation

$$m = \exp\left(0.9135 - \frac{4377.3}{T}\right)\frac{(1+K)(C_0 - C^*)}{K r_{\mathrm{m}} \rho} \tag{14}$$

For the sake of agreeing the kinetic model of the fluidized roasting reduction reaction with the experimental data, the curve of the manganese reduction efficiency changed with the roasting time was achieved when the roasting temperature of pyrolusite was 1023 K. From Fig. 9, the agreement is relatively good, which further confirms the fact that the reaction is controlled by the interface chemical reaction.

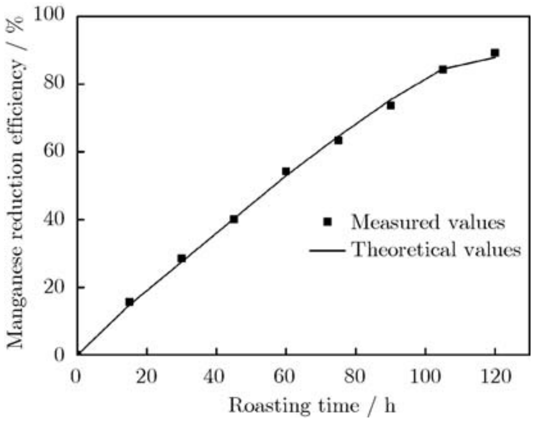


Fig. 9. Relationship between the manganese reduction efficiency and roasting time.

4. Conclusions

(1) The fluidized roasting reduction technology of low-grade pyrolusite coupling with pretreatment of stone coal for manganese exploitation and utilization is investigated. The optimum manganese reduction efficiency could be up to 98.97% under the conditions that the mass ratio of stone coal to pyrolusite was 3:1, the roasting temperature of stone coal was 1000°C, the roasting temperature of pyrolusite was 800°C, and the roasting time was 2 h.

(2) The fluidized roasting coupling technology, which is to couple the pretreatment of stone coal with the reduction roasting process of low-grade pyrolusite, is generally applicable to the extraction of various low-grade pyrolusite ores, and it is promising to be utilized widely in the manganese industry due to its high efficiency, good availability, and low cost.

(3) The reduction kinetic model has been established. It is also confirmed that the reduction process is controlled by the interface chemical reaction. The apparent activation energy is 36.397 kJ/mol.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Nos. 21176026 and 21176242), the National High Technology Research and Development Program of China (No. 2012AA062401), the National Key Technology R&D Program of China (Nos. 2012BAB07B05 and 2012BAB14B05), China Ocean Mineral resources R&D Association (No. DY125-15-T-08), and the Fundamental Reserach Funds for the Central Universities of China (No. FRT-TP-09-002B).

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