Kinetics of Reduction Roasting of Low-grade Manganese Dioxide Ore in the Novel Four-tube Reduction Finance

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ABSTRACT

The kinetics of reduction roasting of low-grade manganese dioxide ore used in this work has been established with four-tube reduction finance. XRD analysis of the as-mined ore samples affirmed the presence of manganese dioxide as the major manganese mineral in the ore. Samples with particles size ranges -5mm were treated using coal as the reductant. The effects of reduction temperature, time and mass ratio of coal to low-grade manganese dioxide ore on the rate of reduction were investigated. It was found that the optimum manganese reduction rate could be up to 93.05% under the conditions that the mass ratio of coal to manganese dioxide ore was 0.12:1, the roasting temperature was 850°C, and the roasting time was 20min. An unreacted shrinking-core model was proposed to describe the kinetics of reduction. Based on experimental results, It was confirmed that the reduction process was controlled by diffusion through the ash/inert solid layer. The apparent activation energy was determined to be 106.65 kJ /mol.1

KEYWORD

low-grade manganese dioxide ore; reduction roasting; unreacted shrinking core model; Kinetics
Manganese is an important raw material for the cells production, preparation of the steel, dietary additives and fine chemicals [1, 2]. With the ever increasing demand for manganese resources and the depletion of high grade ores, exploitation and utilization of low-grade manganese ores becomes increasingly important [3, 4]. Since MnO2 phase is stable in acid or alkaline oxidizing conditions, the extraction of manganese from manganese dioxide ores must be carried out under reducing conditions [5]. There are two kinds of reductive technologies for manganese dioxide ores at present: the roasting reduction and the hydrometallurgical reduction. Compared with the hydrometallurgical reduction process, the roasting reduction process is widely employed due to its easily controlled conditions and good applicability [6].

The conventional method of treating low-grade manganese oxide ore is the reduction roasting by coal with high temperature of over 900 ºC, and different aspects of the carbothermic reduction of manganese ores have been reported [7, 8]. Jerez et al. [9] studied the kinetics of the reaction between pyrolusite and hydrogen in the temperature range of 275-400 ºC and the activation energy for the process was calculated to be 140.0 kJ/mol. According to the investigation of Eric and Burucu [7], the rate and degree of reduction of manganese ore increased with increasing temperature and decreasing particle size. In the early stages of reduction, this stage was possibly controlled by diffusional process across the boundary layer between the solid phases. An apparent activation energy of 61.03 kJ/mol was calculated for this diffusional process. After about 30% reduction, reduction rate was possibly controlled by chemical reaction between the oxide and gaseous phases for which an activation energy of 153.32 kJ/mol was calculated.

Based on the fluidized roasting reduction technology of low-grade manganese dioxide ore with pretreatment of stone coal, Feng et al [6] found that the optimum manganese reduction efficiency can be up to 98.97% under the optimization conditions. It was confirmed that the reduction process is controlled by the interface chemical reaction. The apparent activation energy was 36.397 kJ/mol. Muriana et al. [10] established the kinetics of carbothermic reduction of manganese ore from Ka’oje deposit. Results showed that the apparent activation energy (E) of the chemical reaction controlled reduction was 19.99 kJ/mol using the diminishing area rate equation. Obtained E values for diffusion controlled reduction of the ore-minerals were 36.28 kJ/mol and 29.56 kJ/mol using Jander and Ginsthing-Brounshtein equations respectively. Gao et al. [11] found that the reduction rate of manganese ore by CO increases with increasing temperature and CO content of the reducing gas. The activation energy was determined to be 66 kJ/mol. The complete rate expression for this reduction process was developed. The rate was of first order with respect to CO partial pressure. Zhang et al. [3] carried out the reduction investigation of low-grade manganese dioxide ore pellets.
by using wheat stalk as reductant. The results showed the increase of the reduction temperature and time, biomass/ore ratio, and the decrease of particle size, heating rate and nitrogen flow rate could significantly enhance reduction efficiency. The reduction kinetic of the manganese ore was controlled by three-dimensional mass diffusion of gaseous reductive volatiles passing from the surface to the core of the ore particles. The activation energy $E$ and frequency factor $A$ were calculated to be 24.15 kJ·mol$^{-1}$ and 166 min$^{-1}$, respectively.

As stated above, a survey of the literature indicates that the mechanism of the reduction of low-grade manganese ores is divergent and still a matter for investigation. No reaction mechanism has been found which can account for all aspects of the observed behavior. This paper focuses on the kinetics of roasting reduction of low-grade manganese dioxide ore using coal as a reducing agent. The main purpose is to investigate the effects of different variables such as the mass ratio of coal to manganese dioxide ore (C/Ore), the roasting temperature, and the roasting time on the manganese reduction efficiency of low-grade manganese dioxide to establish the optimal reaction conditions and to determine the rate-controlling step of the reduction roasting process. Meanwhile, For low-grade manganese ores, the reduction kinetic model is established to strengthen the reduction roasting effect and optimize the operational parameters, and improve the economic applicability of this technology.

EXPERIMENTAL

The sample of low grade manganese dioxide ore was obtained from Hunan Province, China. The ore sample was crushed and ground into powder with a particle size smaller than 0.074mm. Chemical multi-elemental analysis showed that the manganese dioxide ore used in the experiment contained 22.3wt% Mn, 36.66wt% SiO$_2$, and 16.52wt% Fe$_2$O. The structural properties of the sample were measured by high resolution X-ray diffraction (XRD, X’pert PRO, Philips, Eindhoven, Netherlands) with Cu K$\alpha$ ($\lambda$=0.15418 nm) radiation. XRD analysis showed that manganese was mainly in the form of manganese dioxide in the raw ore, and the main gangue minerals included quartz, hematite and muscovite, as shown in Fig. 1.

Reduction roasting studies were performed using particle size of low grade manganese dioxide ore <5 mm. The reduction experiments were carried out in a vertical reduction furnace [12] in the temperature range of 750–900°C. Manganese ore and coal were thoroughly mixed, fed to reduction roasting pipe placed inside the furnace. The furnace was heated to the reduction temperature. At the end of the reduction time, the roasted samples staying in the furnace were cooled to room temperature. Finally, the cooled samples were discharge from the reaction tube and put in the desiccators. Perchloric acid oxidation-ferrous ammonium sulfate titration methods was used to determine the manganese content of low grade manganese dioxide raw ores and roasting samples in the
experiments [13]. Chloric acid-sodium thiosulfate titration analysis was used to
determine the MnO2 content of raw ores and roasting samples in the experiments
[14]. Therefore, the reduction ratio of MnO2 can be calculated. All the reagents
used were of Analytical grade.

![Figure 1. XRD patterns of raw ore(a) and its roasted ore (b).](image)

**RESULTS AND DISSUSION**

**Effect of the Mass Ratio of Coal to Manganese Dioxide Ore on the
Manganese Reduction Rate**

To evaluate the effect of the mass ratio of C/ore on the reduction rate,
experiments were conducted at four different mass ratio of C/ore between 0.06:1
to 0.15:1. Reduction temperature and time was controlled at 850 °C and 20min,
respectively. The results were presented in Fig. 2 and Fig.3. It can be observed
that the manganese reduction rate increased markedly with increasing of the mass
ratio value from 0.06:1 to 0.15:1 and then increase slowly. The reason was
probably that the concentration of the reductive gases increased with the increase
of the mass ratio, thus enhancing the reductive atmosphere, increasing the gas
diffusion across the boundary layer and improving the manganese reduction rate.
When the mass ratio of C/ore was 0.12:1, the manganese reduction rate could be
almost the maximum value. Further increasing the mass ratio only resulted in a
slight increase in the manganese reduction percentage. Therefore, the following
experiments took 0.12:1 as the preferable mass ratio of C/ore.

**Effect of the Roasting Temperature of Manganese Dioxide Ore on the
Manganese Reduction Rate**

The effect of temperature on the reduction rate of manganese dioxide ore was
studied in the range from 750 to 900 °C while fixing the roasting time at 20min
and varying the mass ratio from 0.09:1 to 0.18:1. (Fig. 4). The results, shown in
Fig.4, demonstrated that the manganese reduction efficiency increased as the roasting temperature of manganese dioxide ore increased.

Fig. 2. Reduction rate curves of low-grade manganese dioxide ore samples with different mass ratios of C/ore at various temperture (temperture: 850 °C).

Fig. 3. Reduction rate curves of low-grade manganese dioxide ore samples with different mass ratios of C/ore at various temperture (time: 20min).

After the roasting temperature was up to 850 °C, the manganese reduction efficiency increased slowly with the roasting temperature increasing, and all the corresponding curves tended to level off. Therefore, the optimum roasting temperature of manganese dioxide ore should be 850 °C.

The increase of reduction percentage with rise of temperature may be due to the increase of number of reacting moles having excess of energy which leads to the increase of reduction rate. Also the raise of temperature leads to an increase of the rate of mass transfer of the diffusion and rat of desorption [2, 15]

**Effect of Roasting Time on the Manganese Reduction Efficiency**

The manganese reduction efficiency also depended on roasting time. The experiment was carried out while fixing the roasting temperature of manganese dioxide ore at 850°C. Reduction curves were presented in Figures 5. When the roasting time ranged from 5min to 20min, a longer roasting time benefited the manganese reduction percentage. The manganese reduction rate increased to 93.05% while fixing the mass ratio of C/ore at 0.12:1 and the roasting time at 20min. Further extending the roasting time improved the manganese reduction rate slightly. Considering the equipment and the roasting cost, the optimum roasting time should be 20min.
Reduction Roasting Kinetics

Gas-solid reaction has wide application in the metallurgical and chemical industries. Mathematical modelling of gas–solid systems is usually used to interpret experimental results and to gain insight into the reaction mechanisms. Due to its importance, the modelling of these heterogeneous reactions has been of strong interest to investigators for several decades, resulting in a variety of modelling approaches [16]. The major models that have been developed for non-catalytic gas–solid reactions are the unreacted shrinking core, shrinking particle, homogeneous and grain models. The homogeneous model is applicable to a solid with a homogeneous distribution of pores, while the grain model is applicable to a solid consisting of individual dense grains compacted together [17]. When solid reactant is nonporous, shrinking particle model and unreacted shrinking core model are commonly used. For the shrinking particle model, reactions are confined at the surface of the particle and the size of the particle is reduced by gasification of the products or flaking off the solid products. The unreacted shrinking core model is applied when the reactant is converted to another solid material leaving behind the unreacted solid. The converted material, which is sometimes called “ash”, is regarded as porous and inert substance, so that the gas reactants can diffuse from the external surface of the particle to the surface of the unreacted core. Thus, the unreacted core shrinks as the reaction proceeds, but the overall particle size basically remains constant. Although the unreacted shrinking core model does not precisely represent the whole mechanism of gas–solid reactions, it is accepted as the best simple model for the majority of reacting gas–solid systems [18].

In the establishment to the unreacted shrinking core model, the solid reactant is considered to be non-porous and is initially surrounded by a gas film through which mass transfer occurs between the solid particle and the bulk of the gas. As the reaction proceeds, an ash/inert layer forms around the unreacted core. The general reaction shown in Eq. (1), is used in the development of the unreacted
shrinking core model. Detailed derivation of the shrinking core model can be found in the literatures [16, 19].

\[ aA_{(g)} + bB_{(s)} \rightarrow cC_{(g)} + dD_{(s)} \]  

(1)

It is assumed that the solid particle is spherical and it reacts with the gas isothermally. When the process is controlled by the reactant diffusion through the gas film surrounding the particle:

\[ x_B = k_m t \]  

(2)

\[ x_B = 1 - \left( \frac{r_c}{r_0} \right)^3 \]

Where \( k_m \) is apparent rate constant when gas film diffusion controls, \( X_B \) is fraction of \( B \) in solid that is converted to products at time \( t \); \( t \) is the reaction time, \( r_c \) is the unreacted core radius at given time, and \( r_0 \) is the initial particle radius.

If the reaction is controlled by product layer (inert/ash layer) diffusion, then

\[ 1 - 3(1 - x_B)^{2/3} + 2(1 - x_B) = k_d t \]  

(3)

where similarly to Eq. (2), \( k_d \) is apparent rate constant when ash/inert solid layer diffusion controls.

When the process is controlled by the chemical reaction:

\[ 1 - (1 - x_B)^{1/3} = k_i t \]  

(4)

Where \( k_i \) is apparent rate constant when chemical reaction controls.

In order to obtain kinetics rate controlling step and parameters, The experiment data about the manganese reduction rate changed with the roasting time was analyzed in the range of roasting temperature from 750 °C to 900 °C (Fig.5). Then, the relationship between the kinetic model and the roasting time at different mass ratios of C/ore could be obtained by substituting the manganese reduction rate into the kinetic model. Of all the three models tested, all the studied data were found only to fit the relation in the Eq.(3) with correlation coefficients (R2) greater than 0.97. The linear relationship between Eq.(3) and roasting time (t) shown in Fig. 6 suggested that the roasting process of manganese dioxide ore was controlled by diffusion through the ash/inert solid layer. Therefore, this reduction process was best described by Eq.(3). It is indicated that the roasting process of low-grade manganese ore in this work accords with the kinetics of reduction roasting of low-grade manganese dioxide ore pellets by using wheat stalk as reductant [3] as well as the carbothermic reduction kinetics of Ka’oje manganese ore [10].
The reaction constant \( k_d \) is given by Arrhenius equation as:

\[
\log k_d = -\frac{E}{2.303RT} + \log A
\]  

(5)

Where \( T \) is the reduction temperature, \( E \) is the apparent activation energy, \( R \) is the gas constant, \( A \) is the pre-exponential or frequency factor.

Fig. 7 showed that the temperature dependence of the reaction constant by plotting \( \log k_d \), from the data of Fig. 4, versus \( 10000/T \). The activation energy \( E \) and frequency factor \( A \) of reduction process of low-grade manganese dioxide ore in the temperature range between 750-900 °C was calculated to be 106.65 kJ.mol\(^{-1}\).and 2585.8min\(^{-1}\), respectively.

By analyzing the reduction roasting process and experimental date, it can be concluded that the mechanism of low-grade manganese dioxide ore as follows: The reaction rate mainly depends on CO diffusion through the solid product layer, so the diffusion step is restrictive step and its kinetics equation is:

\[
1-3(1-x_B)^{2/3} + 2(1-x_B) = k_d \ t
\]

\[
k_d = 2585.8 \times \exp(-106650 / RT)
\]

XRD Analysis of The Roasted Manganese Dioxide Ore

XRD analysis of the roasted manganese dioxide ore was shown in Fig. 1(b). It was clear that the main phases of the manganese in roasted ore was MnO. It is indicated by Fig. 1 that the manganese dioxide ore was successfully reduced to acid-soluble MnO with over 12% coal after reduction roasting at 850 °C and 20min.
CONCLUSIONS

1 The reduction rate of low-grade manganese ore used in this work increases with increasing temperature, time and mass ratio of C/ore. The optimum manganese reduction efficiency can be up to 93.05% under the conditions that the mass ratio of coal to manganese dioxide ore is 0.12:1, the roasting temperature is 850 °C, and the roasting time is 20min.

2 The kinetics of reduction roasting of low-grade manganese dioxide ores can be described using unreacted shrinking core model. Based on the experimental data, the reduction roasting process of manganese dioxide ore is controlled by diffusion through the ash/inert solid layer. The apparent activation energy of reductive roasting process and pre-exponential factor for Arrhenius equation is determined to be 106.65kJ/mol and 2585.8min\(^{-1}\), respectively. The complete rate expression for this reduction process is developed.

3 XRD analysis of original and roasted ore show that the major phase of manganese contained in the original ore is MnO\(_2\), and MnO\(_2\) in the as-mined ore is successfully reduced to predominantly MnO under optimization roasting conditions.

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