Kinetic study on silicon-activation reaction of sodium carbonate roasting electrolytic manganese residue

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Abstract. In order to explore the economic and comprehensive utilization of electrolytic manganese residue (EMR), the reaction kinetics of sodium carbonate roasting EMR were studied by using the model of flake structure minerals. The results showed that the initial roasting reaction was controlled by chemical reaction, while the middle and late reaction is controlled by diffusion. From the content of available silicon and the change node of the control type, the roasting reaction was basically completed in the initial stage. Therefore, chemical reaction control was the determining factor affecting the available silicon content in the process of sodium carbonate roasting EMR.

1. Introduction
Electrolytic manganese residue (EMR) is a kind of solid waste produced when producing electrolytic manganese industrially. With the increase of electrolytic manganese demand and the decrease of manganese ore quality, the total amount of EMR in China has exceeded 60 million tons, with an increase of 10 million tons every year [1]. Most of the enterprises pile it directly in the open for a long time, which will not only waste land resources, but also seriously pollute the surrounding environment. Therefore, rational resource utilization and reduction treatment of EMR have important practical significance.

In China, the area of cultivated soil lacking available silicon has reached more than 50%, and the demand for available silicon in soil is increasing. The balance of available silicon in soil cannot be maintained only by the natural weathering of silicon in soil and the return of platycodon to the field [2]. Electrolytic manganese residue (EMR) is an important silicon source. Silicon-activation with EMR as raw material can not only solve the serious shortage of available silicon resources, but also be an effective way to achieve the reduction of EMR [1]. Mineral waste residue as raw material is an...
effective way to solve the serious shortage of silicon resources. At present, the study of silicon-activation technology used in silicon-bearing minerals focused on fly ash [3], coal gangue [4], medical stone [5], magnesium-reducing residue [6] and other silicon-bearing ores and industrial wastes as raw materials.

Generally, there are relatively few studies on the recovery and utilization of silicon resources using EMR as raw material, and the activation efficiency of silicon is low, even the theoretical research on the roasting process is not in-depth enough. Therefore, reaction kinetics of sodium carbonate roasting EMR was studied in this paper, to determine the main control factors in the process of roasting, so as to reveal the activation behavior of silicon and provide new ideas for utilization and reduction processing of EMR.

2. Methods and Materials

2.1. EMR

The EMR used in this research was collected from Guangxi Dameng Manganese Industry Group Co., Ltd. The sample was dried in an electrothermal blowing drying oven (101-2AB, Tianjin Tester Instrument Co. Ltd., China), ground after cooling. Then, an omnidirectional planetary ball mill (XQM-6, Changsha Tencan Powder Technology Co. Ltd., China) was used to grind the sample for 80 min, under the conditions of mass ratio of ball to material=10:1 and rotation speed of 200 rev·min⁻¹. Finally, the EMR sample was screened (100 mesh nylon sieve) for later use. X-ray fluorescence spectroscopy (XRF) (Axios advanced, PANalytical al, Netherlands) was used to analyze the main chemical components of the raw EMR, and the results were shown in Table 1.

| Components | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO | CaO |
|------------|------|-------|-------|-----|-----|
| Content /% | 24.12| 2.46  | 8.57  | 1.24| 14.96|
| Components | MnO | SO₃ | CO₂* | K₂O|
| Content /% | 4.80| 27.58| 14.95| 0.60|

*: The burning loss of the sample was expressed by the content of CO₂)

2.2. Roasting activation in microwave sintering furnace

Weighing a certain amount of screened EMR, adding distilled water and auxiliary-sodium carbonate, stirring evenly, and then baking in the drying oven at 105°C for 12 h. After that, grinding the mixing sample when the sample was cool down, and put it in a microwave sintering furnace (XO-3KW, Nanjing Xianou Instrument Manufacturing Co., Ltd., China). Other parameters were set as follows: microwave power was 2400 W, EMR/Na₂CO₃=1/0.5 (mass ratio). After cooling and grinding, the content of available silicon in the mixing sample was determined. The determination method of available silicon referred to silico-molybdenum blue spectrophotometry [7].

2.3. Roasting kinetics

In order to draw the kinetics curve in the roasting process, the transformation law of available silicon in EMR was tested by changing the roasting time (0-120 min) and roasting temperature (400-900°C), under the premise of other experimental conditions confirmed. In our previous study, we found that the SEM morphology of EMR mainly showed needle like, columnar and flaky, and the morphology of EMR after high temperature calcination was also mainly flaky [2]. Therefore, the roasting kinetics model of flaky minerals established by Zhao was used to study the silicon-activation reaction of sodium carbonate roasting EMR [8]. Based on Fick's first law and the definition of chemical reaction rate, the kinetic equations of diffusion controlled and chemical reaction controlled flaky minerals are established. The roasting kinetics equation of flaky minerals controlled by diffusion is as follows:

\[
\dot{y} = \left( y - y^* \right) \dot{y} = k \cdot t
\]  

(1)
the roasting kinetics equation of flaky minerals controlled by chemical reaction is as follows: when \( n=1 \),
\[
F(\gamma) = -\ln \left( 1 - \gamma \right) = k t
\]
(2)
when \( n \neq 1 \),
\[
F(\gamma) = \frac{1}{1 - n} - \frac{(1 - \gamma)^{1-n}}{1 - n} = k t
\]
(3)
For the system of sodium carbonate roasting EMR, the content of available silicon represents the conversion (\( Y \)) of roasting process. However, due to the fact that there was inherent part of available silicon (0.13%), so the initial content of available silicon should be subtracted when calculating the available silicon content in the roasting process. Therefore, Eq. (1) is transformed into:
\[
F(\gamma) = (\gamma - 0.0013)^t = k t
\]
(4)
Eq. (2-3) is transformed into:
\[
F(\gamma) = -\ln \left( 1 - 0.0013 - \gamma \right) = k t
\]
(5)
\[
F(\gamma) = \frac{1}{1 - n} - \frac{(1.0013 - \gamma)^{1-n}}{1 - n} = k t
\]
(6)
The apparent activation energy is calculated according to Arrhenius formula:
\[
k = A e^{-\frac{E_a}{RT}}
\]
(7)
where \( k \) represents rate constant, \( A \) indicates pre exponential factor, \( E_a \) is apparent activation energy (kJ·mol\(^{-1}\)), \( R \) means gas constant (J·mol·K\(^{-1}\)), and \( T \) represents calcination temperature (K). Take logarithm on both sides of Eq. (7):
\[
\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \ln A
\]
(8)
3. Results and discussion

3.1. Kinetic curve of silicon-activation

![Fig. 1. Available silicon content at different roasting temperature and roasting time.](image)

In order to draw the kinetics curve of available silicon in the roasting process, the roasting time and roasting temperature were changed under certain other experimental conditions. The roasting temperature were set at 400°C, 500°C, 600°C, 700°C, 800°C and 900°C, while roasting time were set as 0 min, 5 min, 15 min, 30 min, 45 min, 60 min, 75 min, 90 min, 105 min and 120 min, respectively. The kinetic curve of roasting EMR with sodium carbonate was shown in Fig. 1.
It can be seen that the available silicon content at the same temperature had a trend of sharp rise at first and then stable with the extension of reaction time. With the increase of reaction temperature, the peak value of available silicon content in the final EMR after roasting was higher, that is, the activation effect of silicon was more ideal.

3.2. Linear fitting of roasting kinetics
The least square method in origin 9.0 was used to fit the experimental results, and the results were shown in Table 2. If the roasting process was diffusion controlled, then \((Y-0.0013)^2\) and roasting time \((t)\) should show a significant linear relationship. Fig. 2 showed the relationship between \((Y-0.0013)^2\) and \(t\) in the roasting reaction process, and Fig. 3 showed the relationship between \(F(Y)\) and \(t\).

It can be seen from Table 2 and Fig. 2 that, \((Y-0.0013)^2\) had a good linear relationship with \(t\) in the middle and later stages of roasting at different temperatures, which indicated that when the roasting time was 30-120 min at 400\(^\circ\)C, 600\(^\circ\)C, 800\(^\circ\)C, 900\(^\circ\)C, and when the roasting time was 45-120 min at 500\(^\circ\)C and 700\(^\circ\)C, the roasting stage was diffusion controlled.

![Fig. 2. Relationship between \((Y-0.0013)^2\) and \(t\) during roasting](image)

| Table 2 Linear fitting data for kinetic study in the roasting reaction process |
|-----------------------------|-----------------------------|-----------------------------|
| **Temperature (\(^\circ\)C)** | **Chemical reaction controlled** | **Diffusion controlled** |
|                             | **Time (min)** | **\(n\)** | **R\(^2\)** | **\(k\) (min\(^{-1}\))** | **R\(^2\)** | **Time (min)** | **\(k\) (min\(^{-1}\))** | **R\(^2\)** |
| 400                         | 0-30           | 0.003     | 0.9084     | 0.0134     | 0.9337     | 30-120        | 0.0025     | 0.7862     |
| 500                         | 0-45           | 0.013     | 0.8324     | 0.0329     | 0.9667     | 45-120        | 0.0258     | 0.8772     |
| 600                         | 0-30           | 0.022     | 0.9875     | 0.0650     | 0.9232     | 30-120        | 0.0959     | 0.7518     |
| 700                         | 0-45           | 0.142     | 0.9458     | 0.1084     | 0.9835     | 45-120        | 0.3774     | 0.8465     |
| 800                         | 0-30           | 0.055     | 0.8300     | 0.1808     | 0.9150     | 30-120        | 0.8882     | 0.9211     |
| 900                         | 0-30           | 0.128     | 0.9770     | 0.2343     | 0.9391     | 30-120        | 0.1645     | 0.9830     |

According to the chemical reaction controlled kinetics Eq. (5) and (6) of the roasting process, it can be seen that the reaction order \(n\) should be determined first, in order to determine whether other roasting stages are also chemical reaction controlled. The value of \(dY/dt\) is obtained by tangent to the curve of \(Y-t\), and the slope of the linear fitting of \(\ln(dY/dt)-\ln(1-Y)\) is the reaction order \(n\). The reaction stages of roasting sodium carbonate with EMR at different roasting temperatures are shown in Table 2. It can be seen from Table 2 that the reaction order \(n\) at the roasting temperature of 400\(^\circ\)C, 500\(^\circ\)C, 600\(^\circ\)C, 700\(^\circ\)C, 800\(^\circ\)C and 900\(^\circ\)C are 0.003, 0.013, 0.022, 0.142, 0.055 and 0.128 respectively. Since the \(n\) at different temperatures is not equal to 1, therefore, they all apply to the chemical reaction controlled kinetics Eq. (6). Substituting the \(n\) value at different temperatures into Eq. (6), the kinetic
equation of flake structure material controlled by chemical reaction in the roasting process can be obtained:

When roasting temperature was at 400ºC and \( n=0.003 \), the kinetic equation of chemical reaction control can be obtained after relevant values substituted into the Eq. (6):

\[
\frac{dY}{dt} = 1.003 - 1.003 \times (100.13 - Y)^{0.003} = kt
\]

When roasting temperature was at 500ºC and \( n=0.013 \), the kinetic equation of chemical reaction control can be obtained after relevant values substituted into the Eq. (6):

\[
\frac{dY}{dt} = 1.013 - 1.013 \times (100.13 - Y)^{0.013} = kt
\]

When roasting temperature was at 600ºC and \( n=0.022 \), the kinetic equation of chemical reaction control can be obtained after relevant values substituted into the Eq. (6):

\[
\frac{dY}{dt} = 1.022 - 1.022 \times (100.13 - Y)^{0.022} = kt
\]

When roasting temperature was at 700ºC and \( n=0.142 \), the kinetic equation of chemical reaction control can be obtained after relevant values substituted into the Eq. (6):

\[
\frac{dY}{dt} = 1.166 - 1.166 \times (100.13 - Y)^{0.142} = kt
\]

When roasting temperature was at 800ºC and \( n=0.055 \), the kinetic equation of chemical reaction control can be obtained after relevant values substituted into the Eq. (6):

\[
\frac{dY}{dt} = 1.058 - 1.058 \times (100.13 - Y)^{0.055} = kt
\]

When roasting temperature was at 900ºC and \( n=0.128 \), the kinetic equation of chemical reaction control can be obtained after relevant values substituted into the Eq. (6):

\[
\frac{dY}{dt} = 1.147 - 1.147 \times (100.13 - Y)^{0.128} = kt
\]

The least square method in Origin 9.0 was used to carry out linear fitting of the early roasting experiment results. The results were shown in Table 2, and the linear relation between \( F(Y) \) and \( t \) is shown in Fig. 3.

It can be seen from Table 2 and Fig. 3 that, R² of the curve fitted by \( F(Y) \) and \( t \) had a good linear correlation under different temperatures, indicating that the early roasting stage of sodium carbonate roasting EMR was controlled by chemical reaction.

According to Arrhenius formula, the \( \ln k - 1/T \) diagram (Fig. 4) was drawn. The slope fitted is the apparent activation energy \( E_a \) of chemical reaction controlled and diffusion controlled in the process of roasting.

It can be seen from Fig. 4 that the slope of the chemical reaction controlled stage was -10.557, and the slope of the diffusion controlled stage is -5.452. Substituting the two slopes into Eq. (8), it could be concluded the apparent activation energy of the chemical reaction controlled stage is 87.77 kJ·mol⁻¹ (\( E_{a1} \)), and 45.33 kJ·mol⁻¹ (\( E_{a2} \)) of the diffusion controlled stage. The apparent activation energy of
chemical reaction controlled mode was higher than that of diffusion controlled mode, and the larger the apparent activation energy is the limiting factor of the reaction process [9]. Therefore, chemical reaction controlled is the determining factor of available silicon content in roasting process.

![Graph](image-url)

**Fig. 4.** Relationship between ln\(k\) and 1000/\(T\) during roasting process

### 4. Conclusion

Through the study of reaction kinetics of sodium carbonate roasting EMR, it was found that the roasting experiment was controlled by chemical reaction in the early stage and diffusion in the middle and late stage. From the content of available silicon and the change of control type, the roasting reaction had been basically completed in the initial stage. The apparent activation energy controlled by chemical reaction (\(E_\alpha,1\)) and diffusion is 87.77 kJ\cdot mol^{-1} and 45.33 kJ\cdot mol^{-1} (\(E_\alpha,2\)), respectively. Therefore, chemical reaction controlled mode was the determining factor of silicon-activation in the process of sodium carbonate roasting EMR.

### Acknowledgments

This project was financially supported by the National Natural Science Foundation of China (grant numbers 51804354, 51974279), the National Key Research and Development Program of China [grant numbers 2018YFC18018, 2018YFC18027], KeJunPing [2018] No. 159, the Guangxi Scientific Research and Technology Development Plan [grants number GuikeAB16380287 and GuikeAB17129025], GRINM Science and Development [grants number2020 No 75], which are greatly appreciated.

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