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XPS Investigation of Magnetization Reduction Behavior and Kinetics of Oolitic Hematite in Gas-Based Roasting

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Abstract: Magnetization reduction roasting is an important method for the utilization of oolitic magnetite. In this study, the magnetization reduction behavior and kinetics of oolitic hematite in gas-based roasting were systematically investigated by X-ray photoelectron spectroscopy (XPS). The results revealed that under optimal roasting conditions of 650 °C, a roasting time of 60 min, and a CO concentration of 30%, the magnetization reduction rate of the roasted product reached 44.34%. Furthermore, the weak magnetic separation concentrate presented a TFe of 58.09% and a concentrate iron recovery of 94.3%. The results of the XPS spectrum indicated that the peak area ratio (Fe²⁺/Fe³⁺) gradually increased with an increase in roasting temperature, roasting time, and CO concentration, while over-reduction occurred when the roasting temperature exceeded 750 °C. The investigation of magnetization roasting kinetics for varying particle sizes demonstrated that the magnetization reduction process is controlled by chemical reaction, with a corresponding activation energy range of 42.96 kJ/mol to 63.29 kJ/mol, indicating the particle size has little effect on the magnetization reduction of oolitic hematite.

Keywords: oolitic hematite; gas-based magnetization roasting; magnetic reduction rate; reduction kinetics; XPS



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1. Introduction

Iron ores play a significant role in sustaining the stable development of the steel industry due to their wide applications in manufacturing, technology, and architecture fields. Although China is abundant in iron ore reserves, the majority of these ores cannot be directly used as raw materials for blast furnace ironmaking because of their low iron grade [1]. Therefore, it is necessary to import a large amount of rich iron ore to meet the needs of domestic steel smelting. However, prolonged reliance on imports has adverse implications for the growth of the steel industry and even the national economy [2]. Hence, the utilization of refractory iron ores becomes crucial in enhancing the self-sufficiency rate of domestic iron ores.

Oolitic hematite is a refractory iron ore widely distributed across regions of Hunan, Hubei, and the Yangtze River basins in China, accounting for more than 10% of China's iron ore reserves [3]. The composition of oolitic hematite is intricate, making it widely recognized as the most challenging type of iron ore to recover worldwide. In recent years, various innovative approaches have been attempted to recover oolitic hematite, including gravity separation, high-intensity magnetic separation, reverse flotation, suspension magnetization roasting, and microwave fluidized roasting [4–10]. Among these techniques, magnetization roasting–magnetic separation has demonstrated satisfactory separation

results and is considered a highly efficient method for recovering refractory oxidized iron ore [11–13].

Magnetization reduction roasting can reduce Fe_2O_3 to Fe_3O_4 , which can be used to transform weakly magnetic minerals including hematite, limonite, and siderite into strongly magnetic minerals, enabling these ores obtained by magnetic separation to meet furnace-grade requirements [14,15]. In order to distinguish it from natural magnetite, magnetite obtained by magnetization reduction roasting is called artificial magnetite. Thermodynamic studies indicate that oolitic hematite can be converted into strong magnetic artificial magnetite through magnetization reduction roasting, suggesting its theoretical feasibility [16–21]. However, the dense structure and fine dissemination of oolitic hematite pose challenges during magnetization roasting, leading to high CO diffusion resistance and the occurrence of under-reduction or over-reduction. The new artificial magnetite (Fe_3O_4) is unstable and prone to transforming into iron olivine and spinel. These characteristics result in iron concentrate with TFe (total iron) generally below 60%, high phosphorus and aluminum content, and relatively low effective magnetic susceptibility (FeO exists in the form of $\text{Fe}_2\text{O}_3\cdot\text{FeO}$) during the magnetization roasting and magnetic separation processes. Therefore, it is essential to investigate the thermodynamics and dynamics of the magnetization reduction reaction of cryptocrystalline oolitic hematite. Previous research focused on the reduction kinetics of limonite and hematite, while the reduction kinetics of oolitic hematite were less studied. In this paper, the characteristics of magnetization reduction roasting and reduction kinetics of oolitic hematite were studied by X-ray photoelectron spectroscopy (XPS). The effects of reduction temperature, particle size, atmosphere concentration, and roasting time on reduction roasting were investigated in detail.

2. Materials and Methods

2.1. Materials

Oolitic hematite samples used in this work were collected from Hubei Province, China. The results of the chemical multi-element analysis are shown in Table 1. Notably, the oolitic hematite sample contains 47.65 wt% TFe (the total iron grade of the sample), 5.67 wt% CaO , 10.79 wt% SiO_2 , 1.04 wt% MgO , and 6.74 wt% Al_2O_3 . An XRD pattern was conducted to determine the main compositions of this sample. From Figure 1, it is clear that the main valuable mineral is hematite, and the main gangue minerals are quartz, calcite, chlorite, and apatite.

Table 1. Chemical composition of oolitic hematite.

Compositions	TFe	SiO_2	Al_2O_3	CaO	P_2O_5	MgO	K_2O	Na_2O	MnO
Content (wt%)	47.65	10.79	6.74	5.67	1.98	1.04	0.407	0.2	0.2

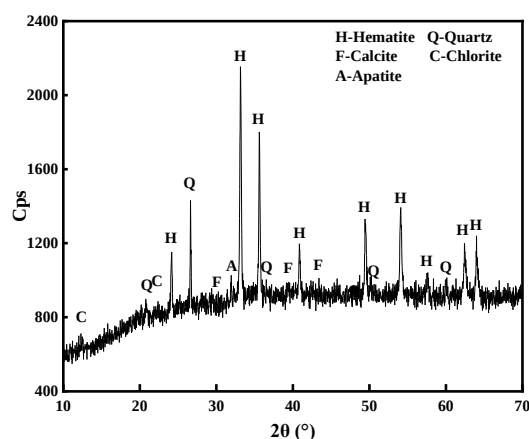


Figure 1. XRD pattern of raw ore.

The XPS spectra of raw ores are shown in Figure 2, where Fe 2p, O 1s, and C 1s are the main components in raw ores (Figure 2a). As shown in Figure 2b, the doublets at 710.8 and 723.9 eV belong to Fe 2p_{3/2} and Fe 2p_{1/2} of Fe³⁺ [22]. Combined with the XRD results of raw ores (as shown in Figure 1), it could be inferred that the primary iron oxide in raw ores is Fe₂O₃.

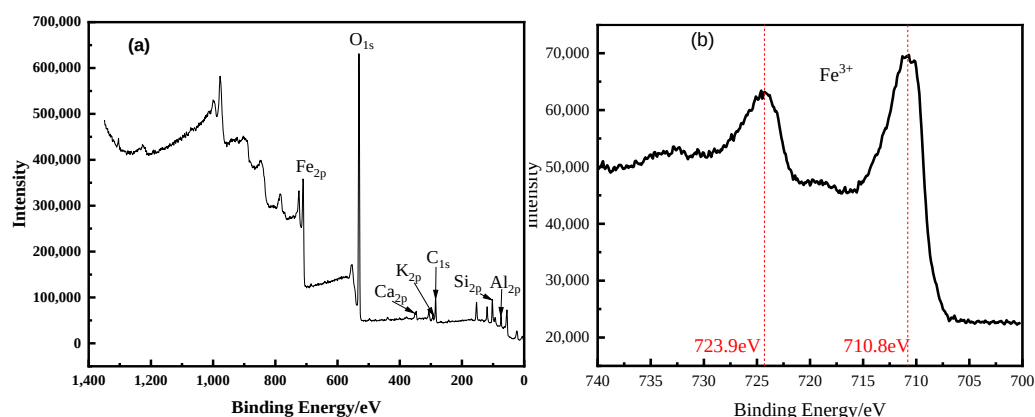


Figure 2. XPS full survey spectrum (a) and high-resolution spectrum of Fe 2p (b).

2.2. Methods

Fifty grams of mineral samples (−2.0 mm) were used in the gas-based magnetization roasting test. The samples were put into a corundum porcelain boat and placed in a tube furnace (Kejing GSL-1400X, Hefei, China). Then nitrogen was inserted into the exhaust air of the tube and heated to the desired temperature at a rate of 10 °C/min. Subsequently, a gaseous mixture of N₂ and CO was passed at a flow rate of 500 mL/min. When the roasting process was complete, the samples were naturally cooled to room temperature in a nitrogen atmosphere. Finally, the roasted samples were mixed with water (1:1) and transferred into a ball mill for grinding. The pulp sample was separated by a magnetic tube to obtain iron concentrates and tailings under a magnetic field intensity of 28.6 kA/m. In this work, the magnetic reduction rate can be calculated as follows:

$$R_{Fe} = \frac{\omega(\text{FeO})}{\omega(\text{TFe})} \times 100\% \quad (1)$$

$$\omega(\text{FeO}) = 1.2857 \times \omega(\text{Fe}^{2+}) \quad (2)$$

where R_{Fe} is the magnetic reduction rate, %; $\omega(\text{FeO})$ is the mass ratio of FeO in the roasted sample, %; $\omega(\text{TFe})$ is the iron grade of the roasted sample, %; and $\omega(\text{Fe}^{2+})$ is the ferrous iron content of the roasted product. Fe₃O₄ can be expressed as FeO·Fe₂O₃; the theoretical optimal value of $\frac{\omega(\text{FeO})}{\omega(\text{TFe})}$ in Fe₃O₄ is about 42.86%.

The iron grade (TFe) of all the solid samples and ferrous iron content of the roasted product were obtained through the Chinese standard organization titrimetric method GB/T 6730.65-2009 and GB/T 34176-2017 [23], respectively, with potassium dichromate as a titrant, while other components of the raw materials were obtained through an X-ray fluorescence spectrometer (PHI 5000 Versaprobe III, Hitachi Tokyo, Japan) by fusion method [23]. The powder pattern X-ray diffraction (XRD, D8 ADVANCE, BRUKER, Saarbrücken Germany) was carried out by using a copper K α X-ray source with a scanning angle in the range from 10° to 70° (2 θ).

Reduction of Fe₂O₃ to Fe₃O₄ is an essential characteristic of magnetization roasting. The theoretical molar ratio of Fe²⁺/Fe³⁺ is approached at 0.50 when Fe₂O₃ in the sample is converted to Fe₃O₄ completely. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) were introduced to determine the iron valency using the Thermo Fischer ESCALAB Xi+ X-ray photoelectron spectrometer (Waltham, MA, USA). An Al K α X-ray source (h ν = 1486.6 eV) was employed, and the anode was operated at 12.5 kV and

16 mA. Analyzer pass energy of 100 eV, narrow spectrum pass energy of 20 eV, and step size of 0.05 eV were fixed. The residence time was 40–50 ms. The vacuum of the analysis chamber was 8×10^{-10} Pa, and all the spectra were recorded in a constant analyzer energy mode. The binding energies were calibrated according to the binding energies of C1s, at 284.8 eV. The collected XPS spectra were analyzed using Aantage Software v5.976. For analysis of the high-resolution Fe 2p spectra, two Shirley backgrounds were used, one each for the 2p_{1/2} and 2p_{3/2} envelopes. The fitting of multiplets, surface structures, and shake-up-related satellites referenced Grosvenor's method [24].

To investigate the constraints of mineral reduction reactions with different particle sizes, various kinetic model equations were employed to fit the magnetization reduction rate R . Among these models, the chemical reaction control model, the internal diffusion control model, and the hybrid control model can be described as Equations (3), (4) and (5), respectively [25–27]. The fitting results obtained from these models were used to determine the appropriate control model:

$$1 - (1 - R)^{\frac{1}{3}} = kt \quad (3)$$

$$1 - \frac{2}{3}R - (1 - R)^{\frac{2}{3}} = kt \quad (4)$$

$$1 + (1 - R)^{\frac{1}{3}} - 2(1 - R)^{\frac{2}{3}} = kt \quad (5)$$

where R is the magnetic reduction rate, %; k is the kinetic parameter; and t is the roasting time, min.

In order to determine the suitable control models for gas-based magnetization reduction, the Arrhenius equation ($k = Ae^{-\frac{E_a}{RT}}$) was employed to calculate the activation energy of the leaching reaction. The Arrhenius equation formula could be derived as follows:

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (6)$$

where k is the reaction rate constant, E_a is the activation energy, kJ/mol; T represents the thermodynamic temperature, K; R is the ideal gas constant, 8.314 J/mol·K; A is the frequency factor; and $\ln A$ denotes an integral constant.

3. Results

3.1. Magnetic Separation

3.1.1. Effect of CO Concentration

The CO concentration plays a significant role in magnetization roasting, which has an effect on the magnetic separation of iron. The magnetization roasting experiments were conducted at a roasting temperature of 650 °C and a roasting time of 60 min. The results are shown in Figure 3a.

The results shown in Figure 3a illustrate that the magnetic reduction rate is significantly enhanced with an increase in CO concentration, consistent with the results of XPS in the following section. The concentrate iron recovery markedly increased from 84.18% to 94.30% and then slightly decreased as CO concentration increased from 10% to 40%. In addition, the total iron grade of iron concentrate (TFe) increases from 56.77% to 59.94% with an increase in CO concentration from 10% to 20%, then decreases significantly to 55.93% at a CO concentration of 40%. However, the values of R increase rapidly with increasing CO concentration, which reveals that the artificial magnetite obtained by magnetization roasting cannot be completely recovered by magnetic separation. Also, it indicates that it is necessary to maintain an appropriate CO concentration in magnetic reduction roasting because a suitable CO concentration is sufficient to reduce hematite to magnetite, while a high CO concentration causes excessive reduction of newly formed Fe₃O₄ into wustite, which cannot be recovered by magnetic separation [28]. Therefore, the CO concentration is maintained at 30% in the following experiments.

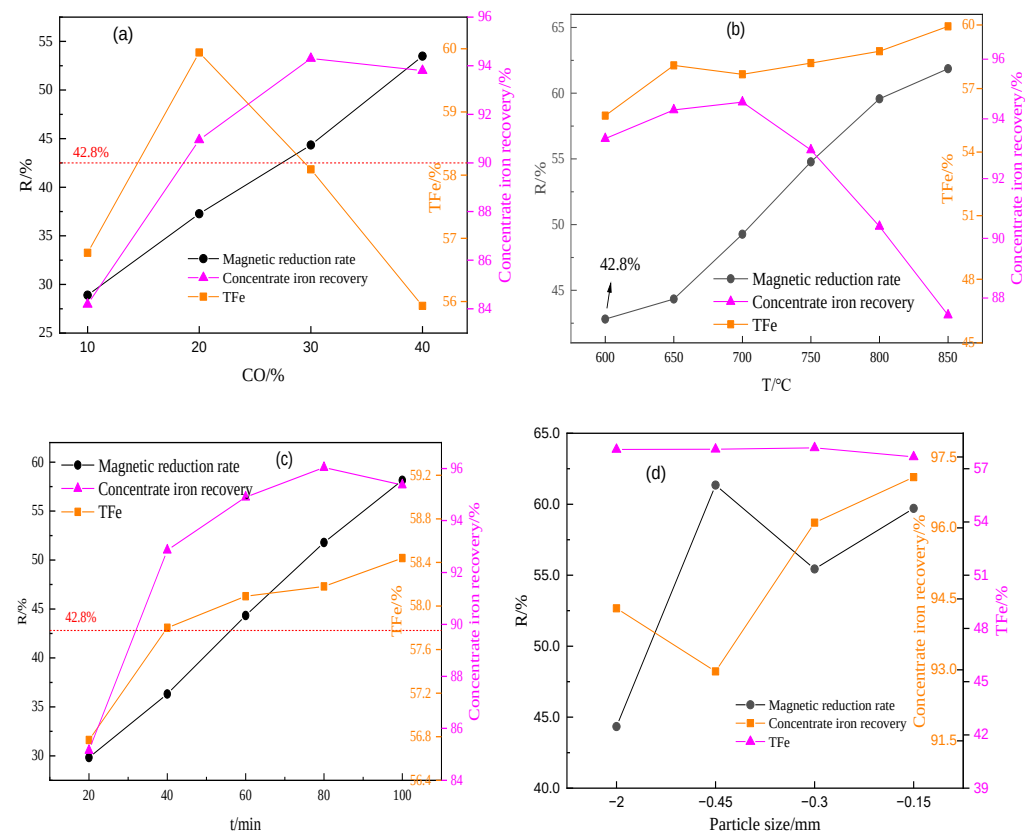


Figure 3. The effects of roasting conditions on magnetic separation: (a) CO concentration, (b) roasting temperature, (c) roasting time, and (d) particle size.

3.1.2. Effect of Roasting Temperature

To investigate the impact of roasting temperature on the magnetization reduction index, the magnetic separation tests were conducted with a CO concentration of 30% and a roasting time of 60 min. The results are displayed in Figure 3b. The magnetic reduction rate (R) drastically improves as the roasting temperature increases, exceeding the theoretical optimal value. At a roasting temperature of 600 °C, the magnetic reduction rate reaches approximately 42.80%, while the TFe is only 55.72%. When the roasting temperature increases to 650 °C, the TFe increases, suggesting that the magnetization of hematite is insufficient at 600 °C. The TFe dramatically increases to approximately 60% at a roasting temperature of 850 °C, while the concentrate iron recovery sharply reduces due to the serious over-reduction. Therefore, the suitable roasting temperature is determined to be 650 °C.

3.1.3. Effect of Roasting Time

Figure 3c displays the results of magnetization separation tests as a function of roasting time. The tests were performed with a CO concentration of 30% and a roasting temperature of 650 °C. It is clear that the magnetic reduction rate increases as roasting time increases and exceeds the theoretical optimal value (42.86%) at a roasting time of 60 min. According to the thermodynamic equilibrium diagram for the reduction of Fe_2O_3 by CO, the roasting product Fe_3O_4 remains stable under the thermodynamic conditions. When the roasting time is more than 60 min, the TFe slightly increases. However, the concentrate iron recovery decreases when the roasting time reaches 100 min. The results might be due to prolonged reduction, resulting in an over-reduction of magnetic minerals into FeO, which enters the tailings. Therefore, the optimal roasting time is determined to be 60 min.

3.1.4. Effect of Particle Size

Particle size is one of the dominant parameters affecting the magnetic separation tests. The tests were performed at a roasting temperature of 650 °C, with a CO concentration of 30% and a roasting time of 60 min. As depicted in Figure 3d, the magnetization reduction rate markedly increases from 44.34% to 61.35% as the particle size decreases from −2.0 mm to −0.45 mm. The particle size is further reduced, and the magnetization reduction rate is reduced to 59.71%. However, TFe of iron concentrate is maintained at about 58% as the particle size increases, and iron recovery decreases first and then increases. Smaller particle sizes can make the diffusion of reductants more efficient, thereby facilitating reduction completely, while also making the over-reduction phenomenon more apparent. Further, smaller particle sizes resulted in decreased permeability of material layers and hindered CO external diffusion, impeding the magnetization reduction of hematite [29]. Therefore, the particle size of oolitic hematite for gas-based roasting should be maintained at −0.45 mm.

3.2. Characteristic of Magnetization Roasting

In order to further reveal the reduction process of iron, the samples roasted under different conditions were analyzed by XPS. Figure 4 shows the XPS high-resolution spectra of Fe 2p under different roasting conditions. The Fe 2p spectra at various CO concentrations are displayed in Figure 4a, where two peaks at 709.60 eV and 710.80~710.90 eV represented Fe²⁺ and Fe³⁺ of Fe 2p_{3/2} without significant shift. In addition, the difference between the binding energies of the two types of Fe-O in Fe 2p_{1/2} and Fe 2p_{3/2} is approximately 13.10~13.20 eV, which also have no apparent movement. The Fe²⁺ area gradually increases with an increase in CO concentration. Meanwhile, the peak area ratio (Fe²⁺/Fe³⁺) increased from 0.24 to 0.36 as the CO concentration increased from 10% to 40% (Table 2), indicating a continuous strengthening of the magnetization reduction process. However, the peak area ratio (Fe²⁺/Fe³⁺) does not reach 0.50, indicating that intensifying the magnetization reduction by increasing the concentration of CO alone is limited.

Table 2. The peak area ratio (Fe³⁺/Fe²⁺) under various roasting conditions.

Conditions		Area Ratio (Fe ³⁺ /Fe ²⁺)
CO concentration (%)	10	0.24
	20	0.28
	30	0.32
	40	0.36
Roasting temperature (°C)	650	0.32
	750	0.45
	850	0.56
Roasting time (min)	20	0.28
	40	0.30
	60	0.32
	80	0.43
	100	0.58
Particle size (mm)	−2.00	0.32
	−0.45	0.39
	−0.30	0.44
	−0.15	0.53

Figure 4b presents the Fe 2p spectra at different roasting temperatures. As noted, Fe²⁺ content and the peak area ratio (Fe²⁺/Fe³⁺) increased as the roasting temperature increased. At a roasting temperature of 650 °C, the binding energies at 709.60 and 710.80~710.85 eV are ascribed to Fe²⁺ and Fe³⁺ of Fe 2p_{3/2}. On the other hand, two peaks at 722.40~722.67 eV and 724.43~724.60 eV belonged to Fe 2p_{1/2} of Fe²⁺ and Fe³⁺, respectively. However, the area ratio (Fe²⁺/Fe³⁺) is 0.32 at 650 °C, which is much lower than 0.50. At a roasting temperature of 750 °C, the peak area ratio (Fe²⁺/Fe³⁺) increased to 0.45, approaching 0.50.

Further increasing the roasting temperature to 850 °C, the peak area ratio ($\text{Fe}^{2+}/\text{Fe}^{3+}$) is higher than 0.50. Referring to previous studies, over-reduction of hematite occurs when the temperature exceeds 750 °C [30,31]. Therefore, the partial peak of Fe^{2+} originated from FeO rather than Fe_3O_4 for the XPS spectrum at 750 °C. What's more, the XPS spectra exhibit strong peaks around the binding energies of 710 and 723 eV regardless of the roasting temperature being 650 °C or 850 °C, and no metal iron peak appears around the binding energies at 706–707 eV. The results reveal that the Fe_3O_4 produced through magnetization reduction is further reduced to FeO without being transformed into metal iron. Hence, the occurrence of over-reduction can be reduced by controlling the roasting temperature.

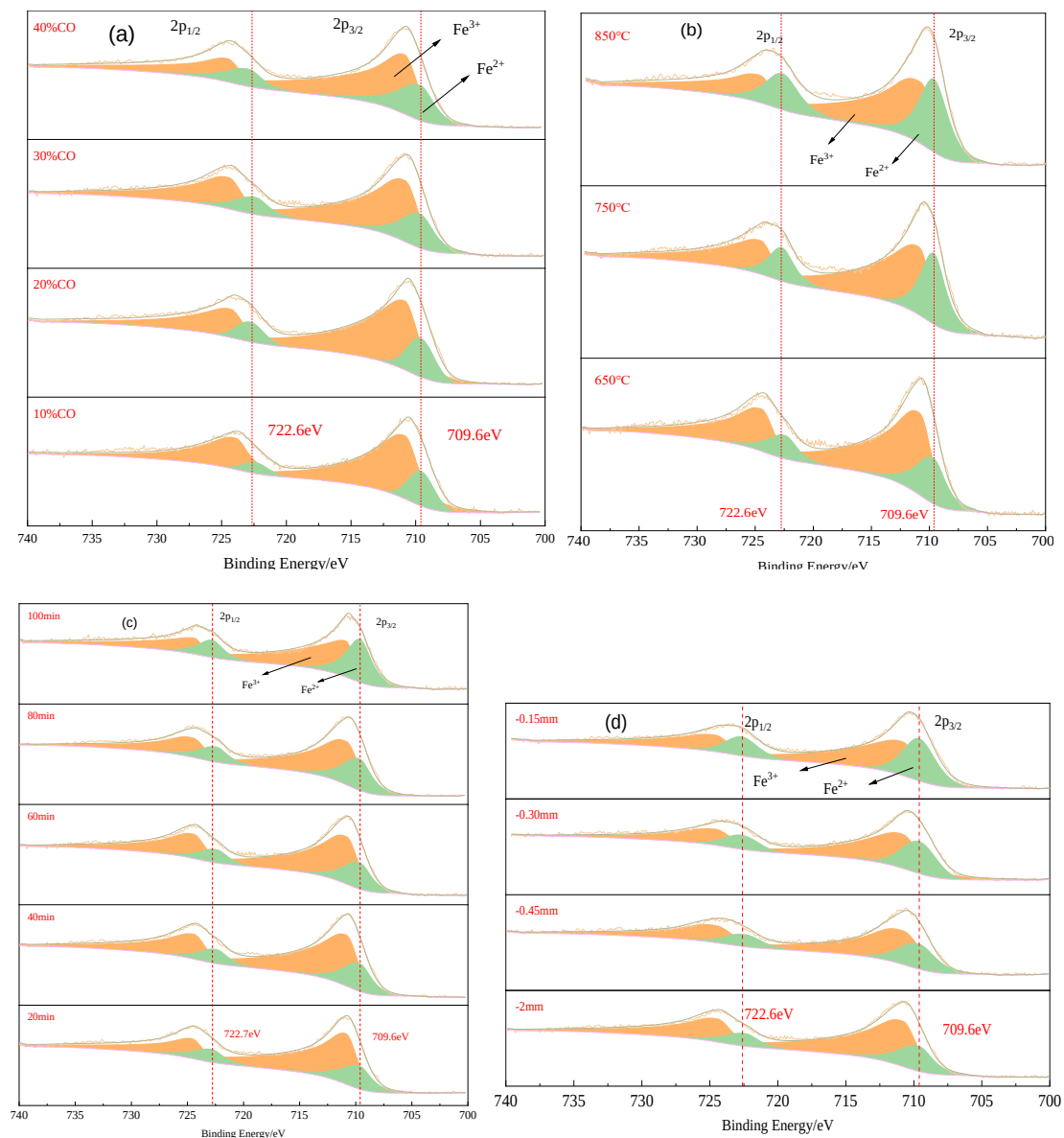


Figure 4. The high-resolution spectrum of Fe 2p under different conditions: (a) CO concentration, (b) roasting temperature, (c) roasting time, and (d) particle size.

In Figure 4c, the binding energy of Fe^{2+} 2p_{3/2} (709.60 eV) increases with an increase in roasting time, indicating the continuous generation of FeO. Conversely, the peak area of Fe^{3+} 2p_{3/2} at 713 eV reduces, revealing the gradual reduction of hematite. In addition, the binding energies of Fe^{2+} 2p_{1/2} (722.70 eV) and Fe^{3+} 2p_{1/2} (725 eV) do not exhibit significant movement. The variation of the peak area ratio corresponding to the two different Fe–O bonds in the 2p_{1/2} orbit is consistent with that in the 2p_{3/2} orbit. The peak area ratio

increased from 0.28 to 0.58 as the roasting time increased from 20 min to 100 min. The result shows that the oolitic hematite was over-reduced after roasting at 650 °C for 100 min. Similarly, the spectra only display two strong peaks at 712 and 725 eV, and no metal iron is detected, suggesting that Fe_3O_4 remains stable at a roasting temperature of 650 °C with an increase in roasting time. The results reveal that extended roasting time can promote the magnetization reduction process. What's more, the over-reduction of oolitic hematite is very weak after a roasting time of more than 100 min.

Oolitic hematite with different particle sizes undergoes varying degrees of reduction at a roasting temperature of 650 °C, a CO concentration of 30%, and a roasting time of 60 min. Figure 4d displays the XPS spectra of various particle sizes. The results show the binding energy does not shift as obviously as the particle sizes. The XPS peak area ratios ($\text{Fe}^{2+}/\text{Fe}^{3+}$) are 0.32, 0.39, 0.44, and 0.53 for roasting ores with particle sizes of −2.00, −0.45, −0.30, and −0.15 mm, respectively. As the particle size decreased, the mass ratio of FeO in roasting ores increased and exceeded the theoretical value, indicating that the fineness of oolitic hematite resulted in a higher susceptibility to over-reduction.

Under optimal conditions, the peak area ratios ($\text{Fe}^{2+}/\text{Fe}^{3+}$) in samples obtained by magnetization reduction are less than 0.50, indicating that hematite has not been completely magnetized. That may be due to the ores being surrounded by other minerals, preventing the contact of iron ores with the reducing atmosphere. What's more, the magnetization reduction process of oolitic hematite particles is a process from the surface to the inside. When the interior oolitic ores were fully magnetized and reduced, over-reduction occurred in the exterior artificial magnetite. In the case of over-reduction, the peak area ratios ($\text{Fe}^{2+}/\text{Fe}^{3+}$) increased while the magnetism of the roasting ore decreased, leading to poor recovery by magnetic separation. Improving the diffusion efficiency of reductant is essential to promoting the magnetization of the interior ores and preventing over-reduction of the exterior ores. Therefore, reasonable magnetic separation results required suitable magnetization reduction conditions.

3.3. Magnetic Roasting Kinetics

The results of magnetization roasting show that the particle size of oolitic hematite has an effect on the magnetization reduction of iron. Therefore, the reduction kinetics of oolitic hematite with different particle sizes were investigated under a roasting temperature of 600 to 850 °C, a CO concentration of 30%, and a time of 0 to 100 min.

Figure 5 shows the fitting results of the reduction kinetics of oolitic hematite with a particle size of −0.15 mm based on the magnetic reduction rate (R). Table 3 lists the squared correlation coefficients (R^2) and the value of parameter k for three different control models. Obviously, the R^2 of the hybrid control model varied between 0.08 and 0.96 under different temperatures, indicating that the magnetization roasting process of oolitic hematite was inconsistent with the hybrid control model. That's to say, the magnetization roasting kinetics of oolitic hematite with a particle size of −0.15 mm were controlled by chemical reaction or internal diffusion.

To further evaluate the leaching kinetics, the $\ln k$ is fitted against $1/T$, as shown in Figure 6. The apparent activation energy calculated from the fitting results is presented in Table 4. It was evident that the values of apparent activation energy were 42.96 kJ/mol and 52.10 kJ/mol for chemical reaction control and internal diffusion control, respectively. The apparent activation energy of chemical reaction control was generally more than 40 kJ/mol, and that of internal diffusion control was generally less than 20 kJ/mol. Hence, the chemical reaction control is suitable for describing the magnetization reduction, and it can be described by the following equation:

$$1 - (1 - R)^{\frac{1}{3}} = e^{-\frac{5167.19}{T} - 0.16t}$$

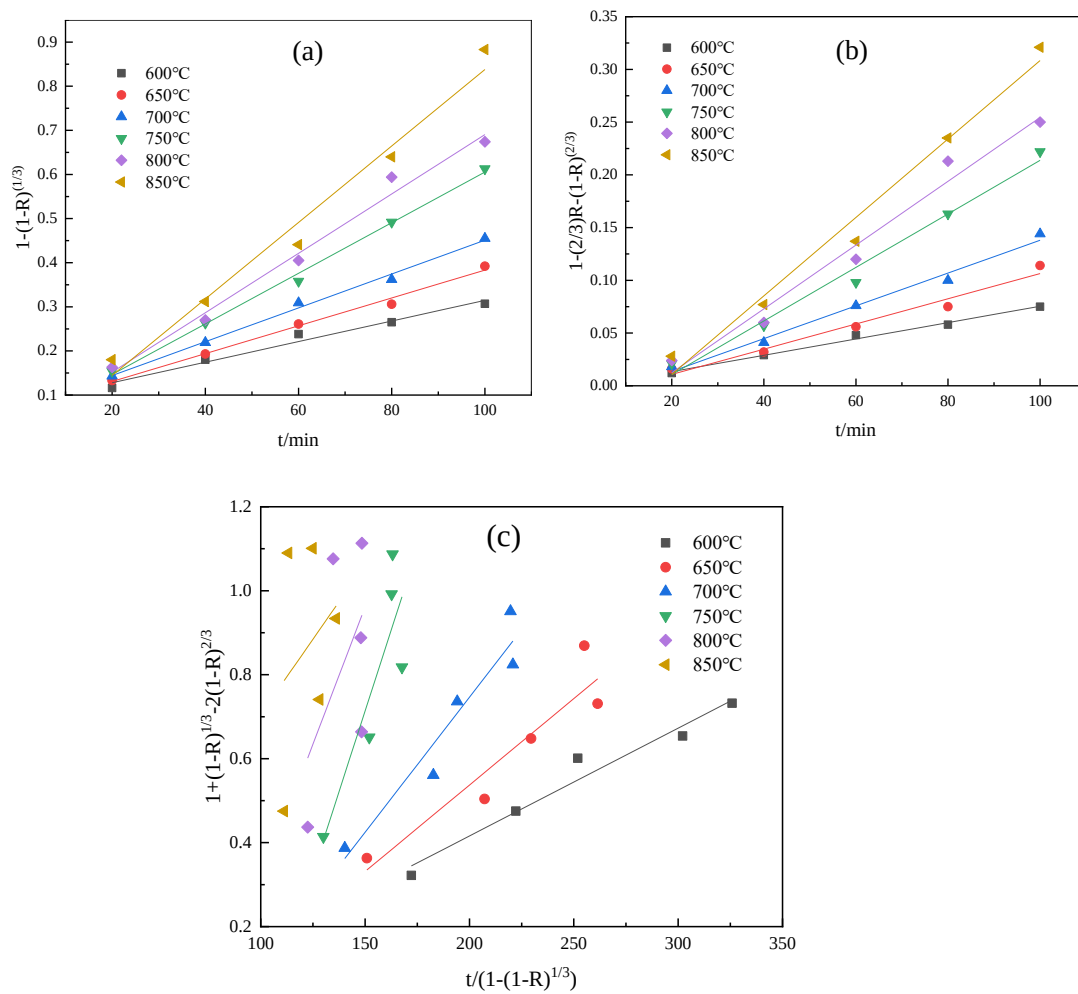


Figure 5. Magnetization reduction kinetics fitting with three control models at a particle size of -0.15 mm: (a) chemical reaction control; (b) internal diffusion control; and (c) hybrid control.

Table 3. Three control models fit the squared correlation coefficient R^2 and rate constant (-0.15 mm).

Temperature/K		873.15	923.15	973.15	1023.15	1073.15	1123.15
Chemical reaction control	R^2	0.98	0.99	0.99	0.99	0.82	0.90
	$k/\times 10^{-4}$	23.40	31.60	38.40	57.40	67.30	86.70
Internal diffusion control	R^2	0.99	0.97	0.99	0.98	0.98	0.98
	$k/\times 10^{-4}$	7.75	12.00	15.60	25.40	30.30	37.20
Hybrid control	R^2	0.96	0.87	0.92	0.75	0.28	0.08
	$k/\times 10^{-4}$	25.70	41.20	64.30	154.00	130.90	71.50

Table 4. Arrhenius model parameter fitting results (-0.15 mm).

Control Model	Slope/ k'	$E_a/\text{kJ}\cdot\text{mol}^{-1}$	R^2
Chemical reaction control	-5167.32	42.96	0.990
Internal diffusion control	-6266.14	52.10	0.989
Hybrid control	-5569.28	46.30	0.613

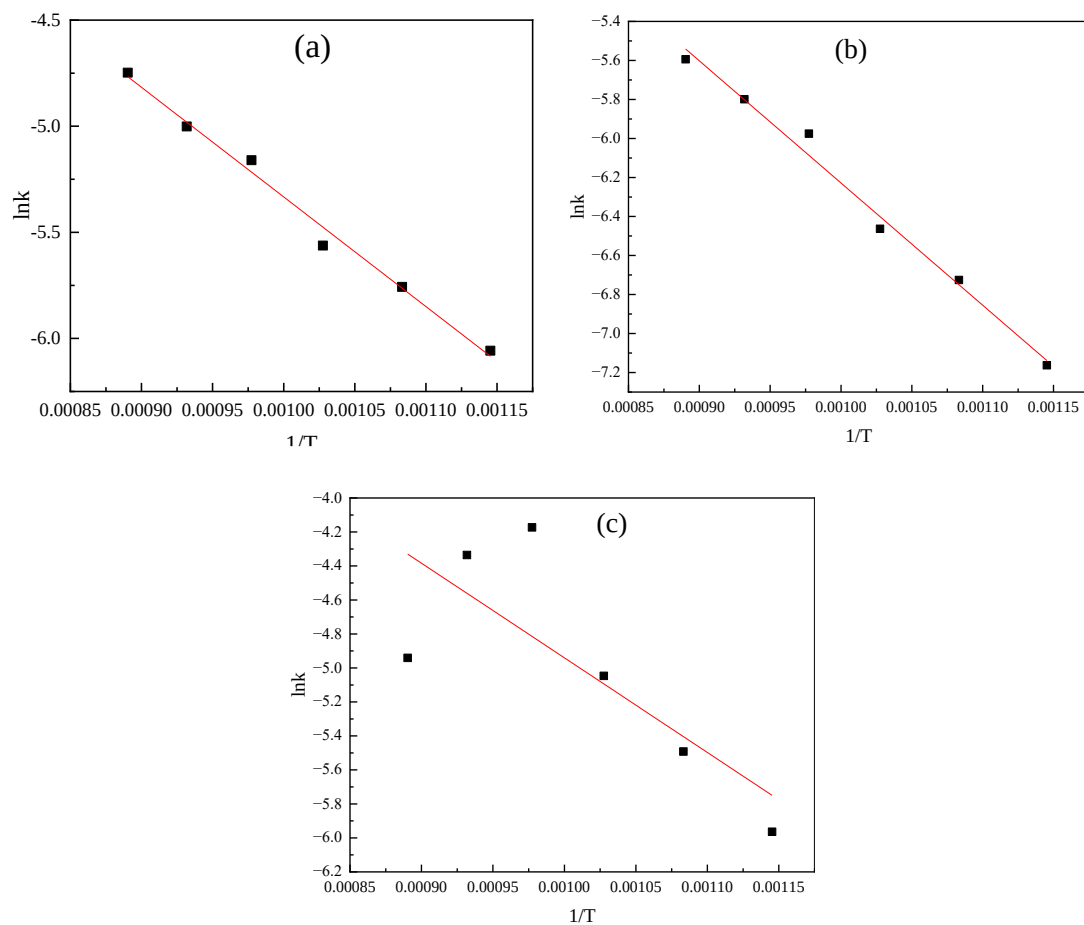


Figure 6. Arrhenius plot of data in different control models at a particle size of -0.15 mm: (a) chemical reaction control; (b) internal diffusion control; and (c) hybrid control.

Similarly, the kinetics of magnetization reduction of oolitic hematite with a particle size of -0.30 mm are fitted according to Equations (3) and (4). The results are presented in Figure 7. In addition, Figure 8 shows the apparent activation energy of two control models obtained by fitting $\ln k$ against $1/T$. The squared correlation coefficients and apparent activation energy calculated from the fitting curves are summarized in Tables 5 and 6, respectively.

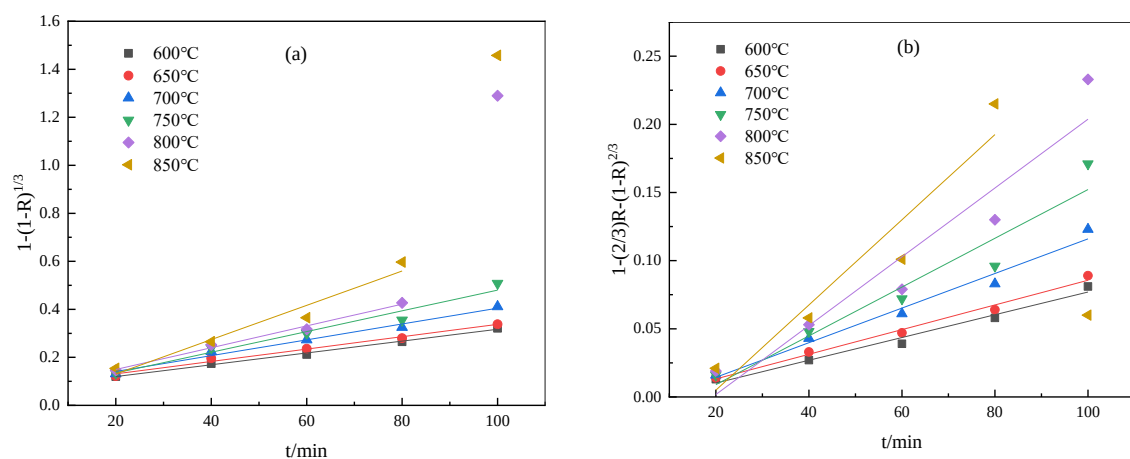


Figure 7. Magnetization reduction kinetics fitting with two control models at particle size of -0.30 mm: (a) chemical reaction control; (b) internal diffusion control.

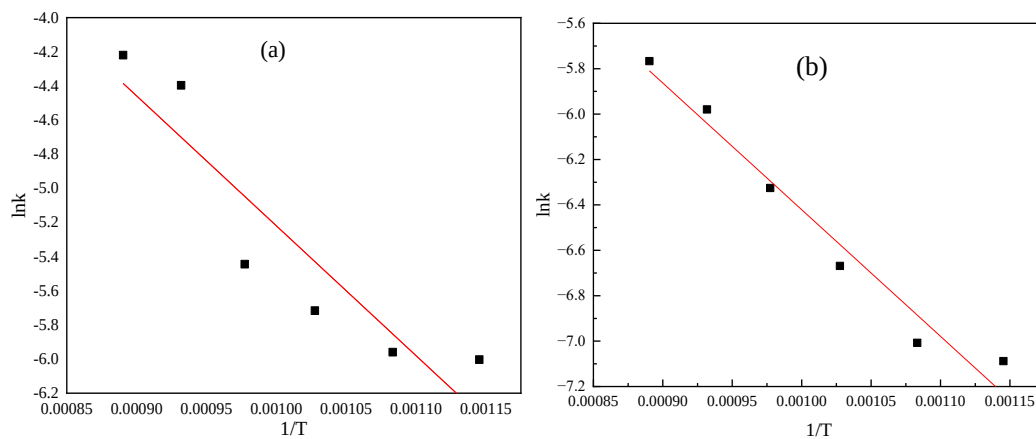


Figure 8. Arrhenius plot of data in different control models at a particle size of -0.30 mm: (a) chemical reaction control; (b) internal diffusion control.

Table 5. Two control models fit the squared correlation coefficient R^2 (-0.30 mm).

T/K	873.15	923.15	973.15	1023.15	1073.15	1123.15
Chemical reaction control	0.996	0.989	0.986	0.965	0.991	0.956
Internal diffusion control	0.982	0.990	0.979	0.934	0.918	0.920

Table 6. Arrhenius model parameter fitting results (-0.30 mm).

Control Model	Slope/ k'	$E_a/kJ \cdot mol^{-1}$	R^2
Chemical reaction control	-7609.53	63.27	0.847
Internal diffusion control	-5580.38	46.40	0.965

According to the results in Tables 5 and 6, it could be inferred that the magnetization reduction kinetics for a particle size of -0.30 mm obeyed the chemical reaction control model with an apparent activation energy of 63.27 kJ/mol. The kinetics model equation was determined as follows:

$$1 - (1 - R)^{\frac{1}{3}} = e^{-\frac{7609.53}{T} + 2.39t}$$

Likewise, the fitting results of control models and apparent activation energy for a particle size of -0.45 mm are shown in Figures 9 and 10. Tables 7 and 8 present the correlation coefficient and activation energies with the respective models.

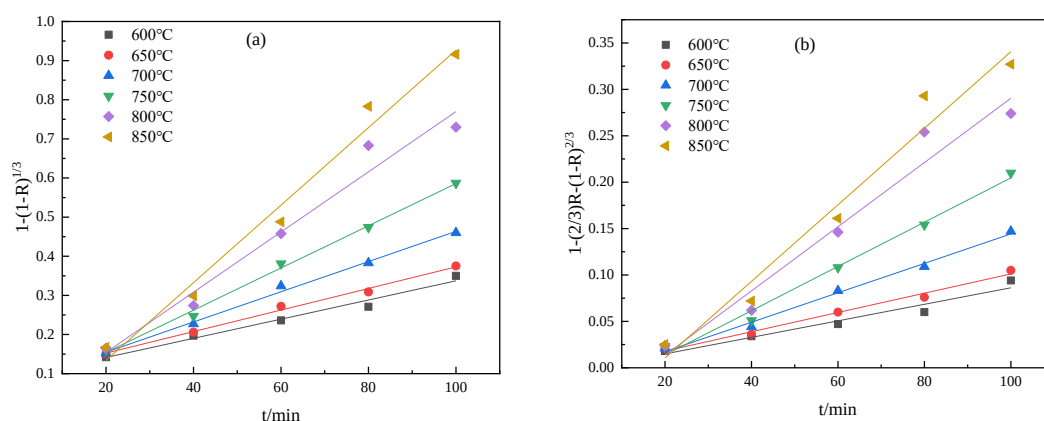


Figure 9. Magnetization reduction kinetics fitting with two control models at a particle size of -0.45 mm: (a) chemical reaction control; (b) internal diffusion control.

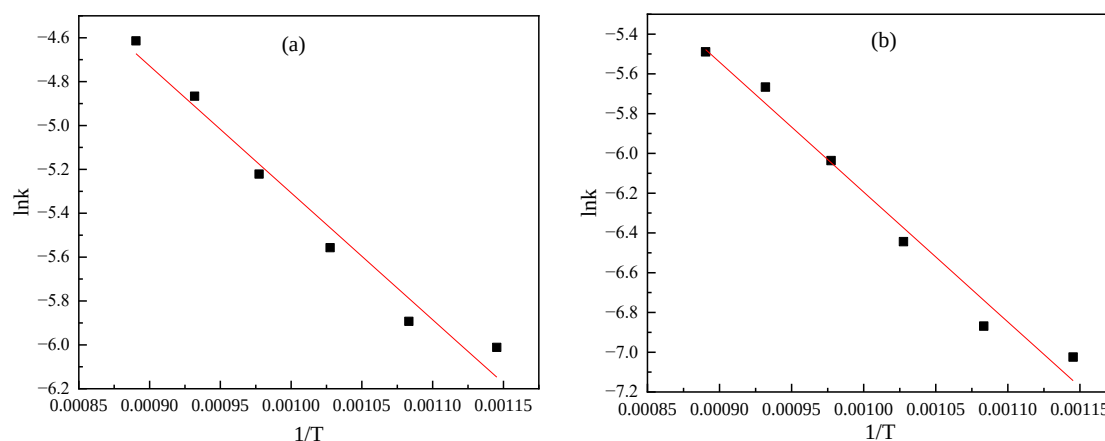


Figure 10. Arrhenius plot of data in different control models at a particle size of -0.45 mm (a) chemical reaction control; (b) internal diffusion control.

Table 7. Two control models fit the squared correlation coefficient R^2 (-0.45 mm).

T/K	873.15	923.15	973.15	1023.15	1073.15	1123.15
Chemical reaction control	0.979	0.994	0.995	0.996	0.970	0.982
Internal diffusion control	0.953	0.988	0.997	0.990	0.961	0.968

Table 8. Arrhenius model parameter fitting results (-0.45 mm).

Control Model	Slope/ k'	$E_a/(kJ \cdot mol^{-1})$	R^2
Chemical reaction control	-5784.22	48.09	0.971
Internal diffusion control	-6534.26	54.33	0.978

Notably, the values of the squared correlation coefficient (R^2) were very close for the two control models. In addition, the magnetization reduction process for a particle size of -0.45 mm mainly conformed to a chemical control model with an activation energy of 48.09 kJ/mol. The kinetic model could be inferred as follows:

$$1 - (1 - R)^{\frac{1}{3}} = e^{-\frac{5784.22}{T} + 0.48t}$$

As can be seen from the results of kinetics, the reduction process of magnetization for different particle sizes is a chemical reaction control process. The apparent activation energy varies between 42.96 kJ/mol and 63.29 kJ/mol, indicating the particle size has little effect on the magnetization reduction of oolitic hematite. Therefore, temperature and reductant concentration are still the most significant factors among all the impacts influencing the magnetization reduction process.

4. Conclusions

The magnetization reduction behavior and kinetics of oolitic hematite in gas-based roasting were systematically investigated. The results indicated that under optimized conditions of a particle size of -2 mm, a roasting temperature of 650 °C, a CO concentration of 30%, and a roasting time of 60 min, iron concentrate with a yield of 87.32%, TFe of 58.09%, and concentrate iron recovery of 94.30% was obtained by low-intensity magnetic separation. Simultaneously, the magnetic reduction rate of the roasting ore was 44.34%.

The results of XPS show that the peak area ratio (Fe^{2+}/Fe^{3+}) ranged from 0.32 to 0.44 under the optimal roasting conditions. When the peak area ratio reached 0.50, an over-reduction occurred during the magnetization roasting process, resulting in the formation of wustite, which cannot be recovered by magnetic separation. The precise control of the reductant diffusion is essential to achieving a complete magnetization reduction. The

reduction process of magnetization for different particle sizes is a chemical reaction control process. The apparent activation energy varies between 42.96 kJ/mol and 63.29 kJ/mol, indicating the particle size has little effect on the magnetization reduction of oolitic hematite.

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