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STUDY ON ZINC REMOVAL BEHAVIOR IN SIMULATED PRE-REDUCTION SINTERING PROCESS

In this study, blast furnace dust and iron concentrate were used as raw materials and graphite as reducing agent for mixed compacts. The briquettes were roasted in a high temperature tube furnace at 1200°C and kept for a certain time to simulate the pre-reduction sintering dezincification process. The reduced briquettes were characterized by X-ray diffraction, scanning electron microscopy, Energy Dispersive Spectroscopy and flame atomic absorption spectrometry. The effects of C/O molar ratio, basicity and pre-reduction time on the zinc removal rate and pre-reduction degree of the pre-reduction sintered products were studied, and the removal mechanism of zinc was further investigated. The results show that the pre-reduction sintering process can effectively achieve the zinc volatility removal while meeting the requirements of subsequent blast furnace production. The zinc removal rate of pre-reduced sintered products increased with the prolongation of pre-reduction time, increased first and then decreased with the increase of C/O molar ratio and basicity. The pre-reduction degree and Zn removal rate showed the same variation pattern. When the briquettes with C/O molar ratio of 1.0 and basicity of 1.9 were reduced for 20 min, the zinc removal rate and pre-reduction degree could reach 90.40% and 87.74%, respectively, indicating that a large amount of zinc was removed and most of the metallic iron had been reduced. The research results can provide some theoretical basis for industrial production.

Keywords: Pre-reduction sinter; blast furnace dust; Zn removal rate; pre-reduction degree; removal mechanism

1. Introduction

The steel industry is a pillar industry in China, which plays an indispensable role in the development of economic construction. In 2021, China's crude steel production reached 1.03 billion tons, accounting for more than 50% of global crude steel output [1]. Metallurgical dust, such as blast furnace dust, is generated from various processes of steel smelting and accounts for 9-12% of the annual crude steel output, which is not only rich in Fe, C elements also contains a large number of Zn and other harmful elements [2-5]. Up to now, a great deal of metallurgical dust has not been effectively utilized every year, resulting in a waste of resources.

According to previous studies, pyrometallurgical technology is an effective method to recover and treat blast furnace dust [6-16], but it has not been widely used because of high investment and operation costs and energy consumption. In order to achieve comprehensive resource utilization and reduce environmental pollution, zinc-rich blast furnace dust is also usually used as a raw material for sintering. However, the conventional sintering

process is less effective in dezincification, and the cyclic enrichment of zinc in the raw material will negatively affect the sintering and subsequent blast furnace ironmaking processes [17-20]. It not only influences the quality and production of sinter, but also damages the furnace lining and leads to consequences such as overhang, tumor formation, and higher energy consumption in the blast furnace [21], which adversely impacts the normal operation of the blast furnace. Therefore, the removal of zinc elements while achieving comprehensive utilization of blast furnace dust in the sintering process has become an urgent issue [22-23].

Pre-reduction sintering is a production process in which partial reduction of iron ore occurs during the sintering process, which can transfer part of the reduction of iron ore to the sintering process and help to reduce the reduction load of the blast furnace and reduce the overall energy consumption [24]. In Japan, JFE developed the pre-reduction sintering technology [25-28], which mainly involves placing part of the iron reduction in the sintering process, saving the use of coke in the blast furnace and thus reducing CO₂ generation, and improving the low-temperature pulverization of the sintered ore and reducing

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the coke ratio and pressure difference in the blast furnace. T. Sharma [29] produced a composite pre-reduced pellet ore as early as 1994 and the sintering and pre-reduction of fine-grained material occurred simultaneously during the roasting process. S. Ueda et al. [30] found that the amount of energy consumed in the sintering process increases as the degree of reduction increases, but the amount of energy consumed in the whole blast furnace decreases, which is conducive to energy saving. The University of Science and Technology Beijing [31] conducted an experimental study of pre-reduction sintering using laboratory sinter cups, and the metallization of the resulting pre-reduction sintered ore reached 45.7% with good metallurgical properties. Bing Hu et al. [32] studied the quality index of sintered minerals and the removal rate of harmful elements by simulating the production conditions of pre-reduction sintering with reasonable ore blending of difficult to treat dust and common sintering raw materials. The results show that the pre-reduction sintering method can achieve the efficient separation and enrichment of hazardous elements in steel mill dust, and the resources can be used rationally while obtaining the ideal pre-reduction sintering ore. In summary, the pre-reduction sintering method can not only reduce energy consumption, but also has a significant effect on the removal of harmful elements such as Zn from blast furnace dust. Although past studies have confirmed the realistic feasibility of this technology, the pre-reduction sintering process is still in the experimental research stage. For the engineering application, some key technologies need further exploration and study.

This study is based on the theory of pre-reduction sintering. Simulated pre-reduction sintering experiments were carried out

in a high-temperature tube furnace using blast furnace dust, iron concentrate as raw materials and graphite as reducing agent. Determination of zinc content in the product by flame atomic absorption spectroscopy (FAAS). The effects of C/O molar ratio, basicity and pre-reduction time on the Zn removal rate and pre-reduction degree of the pre-reduction sintered products were investigated. Then, the phase composition and microstructure of the pre-reduction sintered products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The phase transformation and distribution of Zn and Fe during the pre-reduction process were analyzed, and the mechanism of pre-reduction sintering dezincification was elaborated to provide a theoretical basis for further studies.

2. Experimental

2.1. Raw materials

The raw materials used in this study are blast furnace dust and three kinds of iron ore fines, were collected from a steel plant in China. The chemical compositions of the experimental raw materials were obtained by chemical analysis, and the results are shown in TABLE 1. As shown in the table, iron concentrate B and C with high iron grade and are valuable iron-bearing resources. The low iron grade and high Zn content of blast furnace dust, which limit its ability to be recycled through conventional steel production processes. Fig. 1 shows the XRD spectrograms

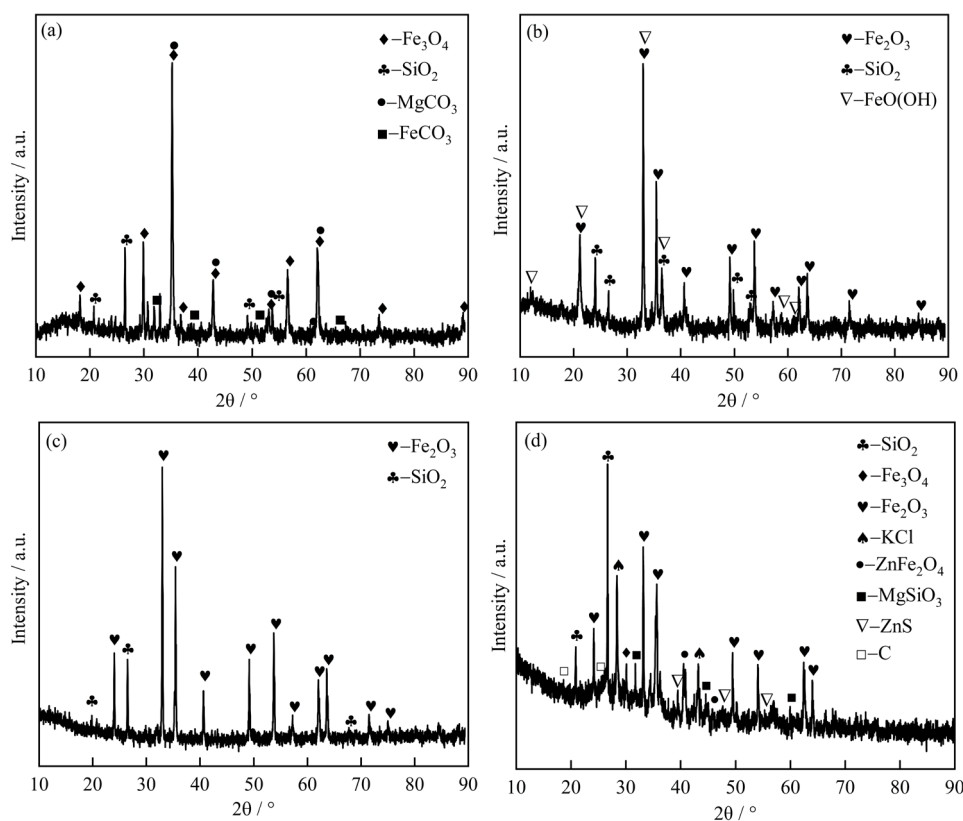


Fig. 1. XRD spectrograms of the raw materials: (a-c) iron concentrate A,B and C, (d) blast furnace dust

Chemical compositions of the raw materials, wt.%

Item		Fe _{total}	CaO	SiO ₂	Al ₂ O ₃	K ₂ O	Na ₂ O	ZnO	MgO	C
Iron concentrate	A	52.90	2.27	8.12	1.18	0.34	0.04	0.05	3.20	—
	B	61.28	0.17	5.27	2.69	0.02	<0.01	0.01	0.26	—
	C	62.16	0.95	6.93	1.02	0.17	—	0.02	1.86	—
Blast furnace dust		28.12	5.47	9.41	3.26	4.18	0.56	7.12	1.77	22.95

of the four raw materials. As shown in Fig. 1(a-c), Fe in iron concentrate A is mainly in the form of magnetite (Fe₃O₄), with a small amount in the form of siderite (FeCO₃); Fe in iron concentrates B and C is mainly in the form of hematite (Fe₂O₃). As shown in Fig. 1(d), the iron containing phase in the blast furnace dust is mainly hematite (Fe₂O₃), and also contains a small amount of magnetite (Fe₃O₄). Zn mainly exists in the form of zinc ferrite (ZnFe₂O₄) and sphalerite (ZnS), while the presence of carbon was detected.

Quicklime and limestone as fluxes. Chemically pure graphite powder is used as the reducing agent, and blast furnace dust can also be used as part of the reductant in the pre-reduction sintering process because it contains a lot of carbon. The above-mentioned raw materials were ground to 200 mesh and mixed in certain proportions, and then placed in an oven for drying at 105°C for 2 h.

2.2. Experimental methods

In this study, when the addition of blast furnace dust was 10 wt.%, different amounts of graphite were added to change the carbon content, and the amount of limestone was changed to change the basicity. Five different C/O molar ratios and five different basicity of briquettes were used to study the effect of

different carbon contents and basicity on the metallization rate and Zn removal rate of the pre-reduction sintered ore. Where, O is the O in FeO_x to be reduced, and the basicity is defined as CaO/SiO₂. When the carbon content changes, the fixed basicity is 1.9, and the fixed C/O molar ratio is 1.0 when the basicity changes. When preparing the sample, add 1% binder to the dried mixture and mix well, put it into a manual hydraulic briquette machine under a certain pressure and pressure holding time for briquetting. Each briquette weighs about 3 g. and measures 25 mm×25 mm×5 mm. Due to the small amount of binder, the effect on reduction is negligible.

The prepared briquettes were dried in an oven at 105°C for 2 h, then loaded into corundum porcelain boat and placed in a high temperature tube furnace for pre-reduction sintering. With Nitrogen (N₂) as the protective gas, the briquettes was heated from room temperature to the set reduction temperature (1200°C) and kept for a certain time (10,15,20,25,30 min). The effects of different pre-reduction time on Zn removal rate and pre-reduction degree of pre-reduction sintering products were studied. Once the reaction reaches a given holding time, the porcelain boat is quickly removed and the briquettes was covered with graphite to stop the reaction, isolate the air and prevent secondary oxidation. The experimental apparatus and the temperature curve of pre-reduction sintering are shown in Fig. 2 and Fig. 3.

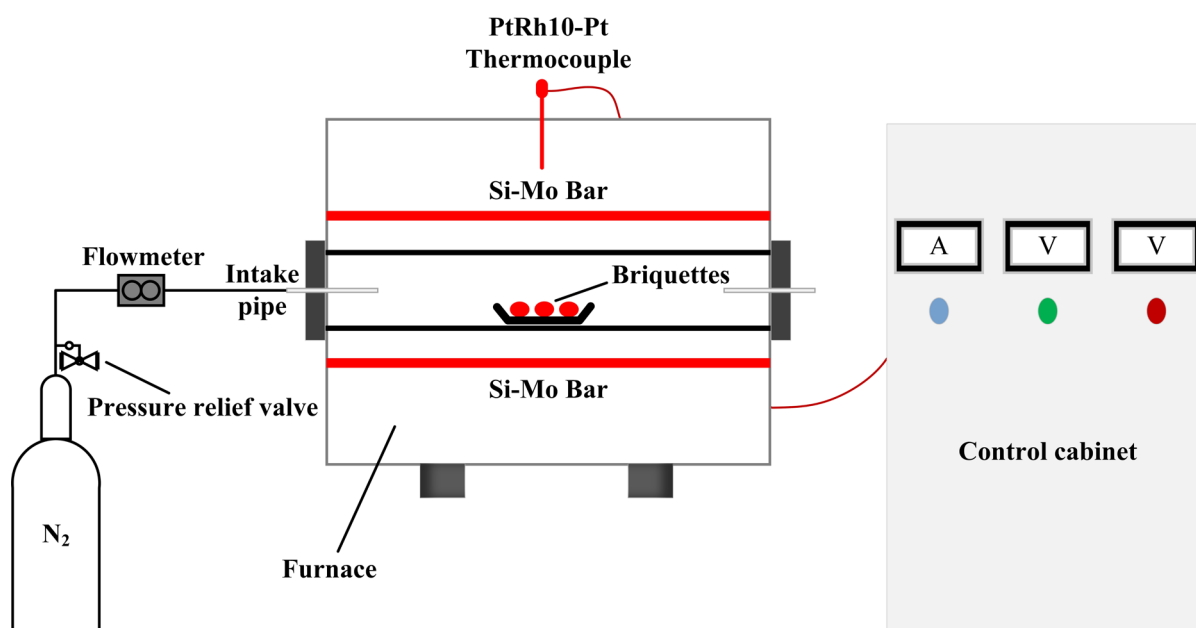


Fig. 2. Schematic diagram of the experimental apparatus for pre-reduction sintering

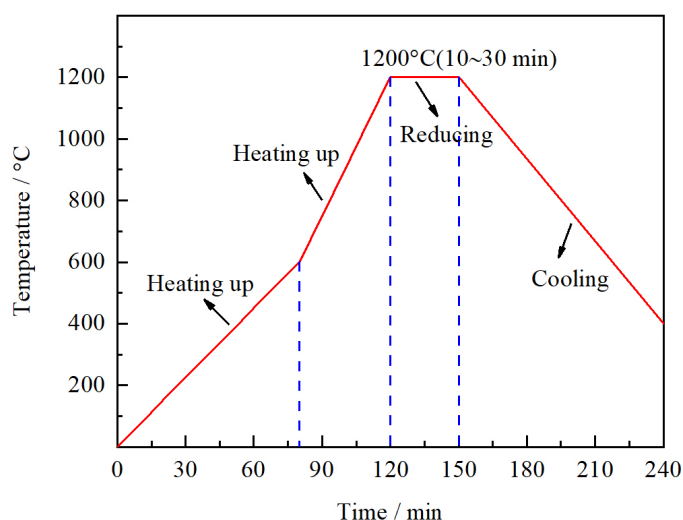


Fig. 3. The temperature curve of pre-reduction sintering

2.3. Characterization methods

After the briquettes were cooled to room temperature, the zinc content was determined by FAAS and the content of total iron and metallic iron was measured by chemical analysis method. Then Zn removal rate and pre-reduction degree of pre-reduction sintering products were calculated.

The Zn removal rate is expressed by R_{Zn} , which is defined as follows:

$$R_{Zn} = \left[1 - \frac{M_P \times \omega(Zn)_P}{M_D \times \omega(Zn)_D} \right] \quad (1)$$

Where, $\omega(Zn)_P$ and $\omega(Zn)_D$ represent the total mass of Zn in the pre-reduction sintering products and initial briquettes, respectively, %. M_P and M_D refer to the weight of the pre-reduction sintering products and initial briquettes, respectively, kg.

The pre-reduction degree is expressed by D , which is calculated as follows [20]:

$$D = 0.679M + 32 \quad (2)$$

Where, M is the metallization rate of pre-reduction sintering products, %.

The metallization rate is expressed by M , which is defined as follows:

$$M = \frac{\omega(M_{Fe})}{\omega(T_{Fe})} \times 100\% \quad (3)$$

Where, $\omega(M_{Fe})$ and $\omega(T_{Fe})$ refer to the mass fraction of metallic iron and total iron, respectively, in the pre-reduced sinter, %.

At the same time, the phase composition and the microstructure of the pre-reduction sintered ore was analyzed by XRD, and SEM-EDS was used to analyze the compositional analysis of minerals in sintered products.

3. Results and discussion

3.1. Influence of carbon content on Zn removal rate and pre-reduction degree of sintered products

The briquettes with different carbon content (C/O molar ratio of 0.4, 0.6, 0.8, 1.0 and 1.2, respectively) and fixed basicity of 1.9 were heated at 1200°C and kept for 20 min. The effect of carbon content on Zn removal rate and pre-reduction degree of pre-reduction sintered products is shown in Fig. 4.

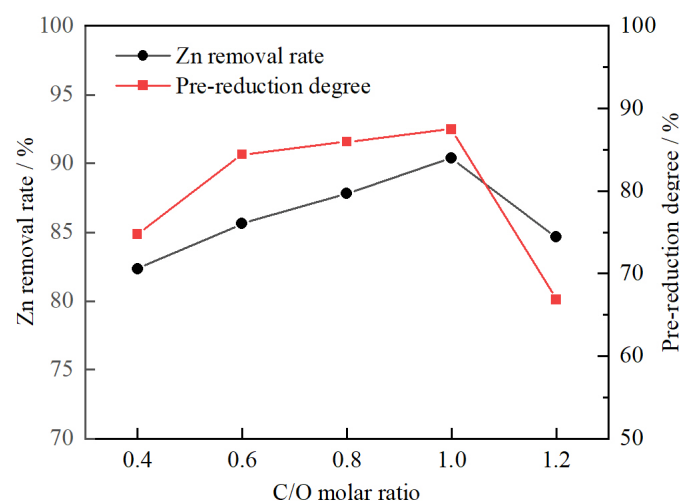


Fig. 4. Effect of carbon content on Zn removal rate and pre-reduction degree of pre-reduction sintered products

It can be seen that the Zn removal rate and the pre-reduction degree first increased and then decreased. When the C/O molar ratio increased from 0.4 to 1.0, the Zn removal rate increased gradually from 82.34% to 90.40%, and the pre-reduction degree increased from 74.77% to 87.74%, both of which reached the maximum value. When the C/O molar ratio was further increased to 1.2, the Zn removal rate and pre-reduction degree decreased to 84.66% and 66.85%, respectively.

With constant basicity and pre-reduction time, both Zn removal rate and pre-reduction degree showed a trend of increasing and then decreasing with the increase of carbon content, but the overall trend was increasing. The pre-reduction was unfavorable when the C/O molar ratio was too high or too low. When the C/O molar ratio is low, the carbon content is low, the reducing atmosphere is insufficient, only a small amount of zinc and iron can be reduced, and the Zn removal rate and pre-reduction degree are low. As the C/O molar ratio increases, the carbon content increases, which makes more reducing agent and will reduce more zinc and iron. The increase of pre-reduction degree because of the increase of metallization rate. The increase of metallization rate due to the increase of metallic iron content, and the zinc becomes zinc vapor at high temperature and escapes to increase the Zn removal rate. However, when the carbon content is too high, the unreacted carbon will easily to block the pores and cracks in the sinter, which deteriorates the mass transfer conditions and hinders the further reduction of zinc oxide and iron

oxide in the mixed ore powder, thus reducing the Zn removal rate and pre-reduction degree.

3.2. Influence of basicity on Zn removal rate and pre-reduction degree of sintered products

The briquettes with fixed carbon content (C/O molar ratio of 1.0) and different basicity of 1.0, 1.3, 1.6, 1.9 and 2.2 were heated at 1200°C and kept for 20 min. The effect of basicity on Zn removal rate and pre-reduction degree of pre-reduction sintered products is shown in Fig. 5.

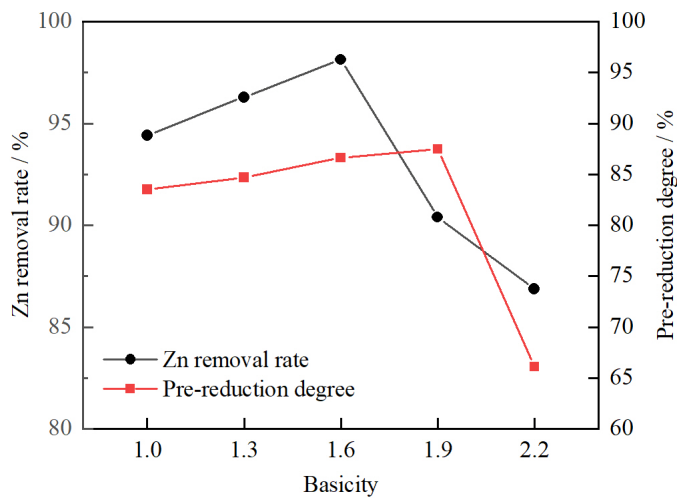


Fig. 5. Effect of basicity on Zn removal rate and pre-reduction degree of pre-reduction sintered products

It can be seen that both Zn removal rate and pre-reduction degree rose gradually when the basicity increased from 1.0 to 1.6. The Zn removal rate reached maximum of 98.13% at basicity of 1.6, while the pre-reduction degree continued to rise and reached maximum of 87.74% at basicity of 1.9. When the basicity continued to increase to 2.2, both Zn removal rate and pre-reduction degree decreased significantly to 90.40% and 66.10%, respectively.

With constant carbon content, pre-reduction time, both Zn removal rate and pre-reduction degree showed a trend of slowly increasing and then rapidly decreasing with increasing basicity. Increasing the basicity in a certain range increases the calcium oxide content. The greater porosity of the pre-reduced iron facilitates the penetration of the reducing gas and increases the contact area between the reducing agent and the zinc-bearing oxide and iron-bearing oxide. Beneficial to its reduction, accelerate its reduction, so that the Zn removal rate and pre-reduction degree is higher. When slag phase is formed in the later period, the increase of calcium oxide content will also increase the porosity of sintered slag phase. It is also conducive to the penetration of reducing gas and the escape of zinc vapor generated by the reduction of zinc containing oxides, which will further increase the Zn removal rate and pre-reduction degree. However, too high basicity will cause an increase in the composition of the

low melting point liquid phase, which will hinder the contact between the reducing agent and iron-containing oxides and zinc-containing oxides and prevent the reduction reaction from proceeding, resulting in a decrease in the Zn removal rate and pre-reduction degree.

3.3. Influence of pre-reduction time on Zn removal rate and pre-reduction degree of sintered products

The briquettes with fixed carbon content (C/O molar ratio of 1.0) and fixed basicity of 1.9 were heated at 1200°C and kept for different time (10,15,20,25,30 min). The effect of pre-reduction time on Zn removal rate and pre-reduction degree of pre-reduction sintered products is shown in Fig. 6.

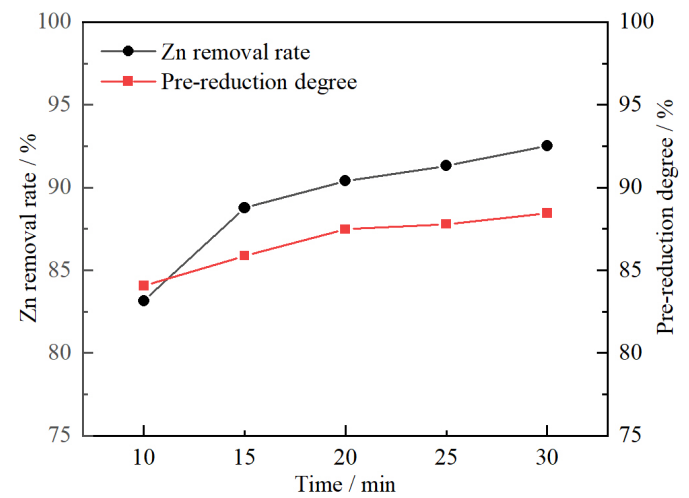


Fig. 6. Effect of pre-reduction time on Zn removal rate and pre-reduction degree of pre-reduction sintered products

It can be seen that both the Zn removal rate and pre-reduction degree increased with the prolong of the pre-reduction time. When the pre-reduction time was extended from 10 min to 20 min, the increase of Zn removal rate and pre-reduction degree were both faster, from 83.16% and 84.06% to 90.40% and 87.74%, respectively. After that, the Zn removal rate and pre-reduction degree rose slowly and reached the maximum of 92.51% and 88.45% at 30 min, respectively.

Under the condition of constant carbon content and basicity, extending the pre-reduction time within a reasonable range can make good contact conditions exist between the reducing agent and the mixed ore powder, so that iron oxide, zinc oxide and reducing agent can fully react. The longer the pre-reduction time, the more adequate the reduction reaction will be, more iron and zinc will be reduced out, the Zn removal rate and pre-reduction degree are elevated, and the pre-reduction degree also shows an increasing trend. However, if the pre-reduction time is further extended, it may have little effect on the Zn removal rate and pre-reduction degree, and may even make it show a decreasing trend. This may be due to the fact that as the pre-reduction time is extended, the carbon is gradually consumed and the reducing

atmosphere in the furnace is weakened, which makes the reduced iron and zinc oxidized again and the secondary oxidation phenomenon occurs.

Fig. 7 shows the SEM images and EDS spectrum of the briquettes reduced at 1200°C for various times (10 min, 20 min, 30 min). It can be seen that only a small amount of zinc is present

in the metal phase and slag phase regardless of the pre-reduction time, indicating that most of the zinc has been reduced and removed by volatilization. Therefore, the Zn removal rate is high. As the pre-reduction time was extended from 10 min to 30 min, the pre-reduction sintered products became denser and more bright white, and clearer boundaries between the metal

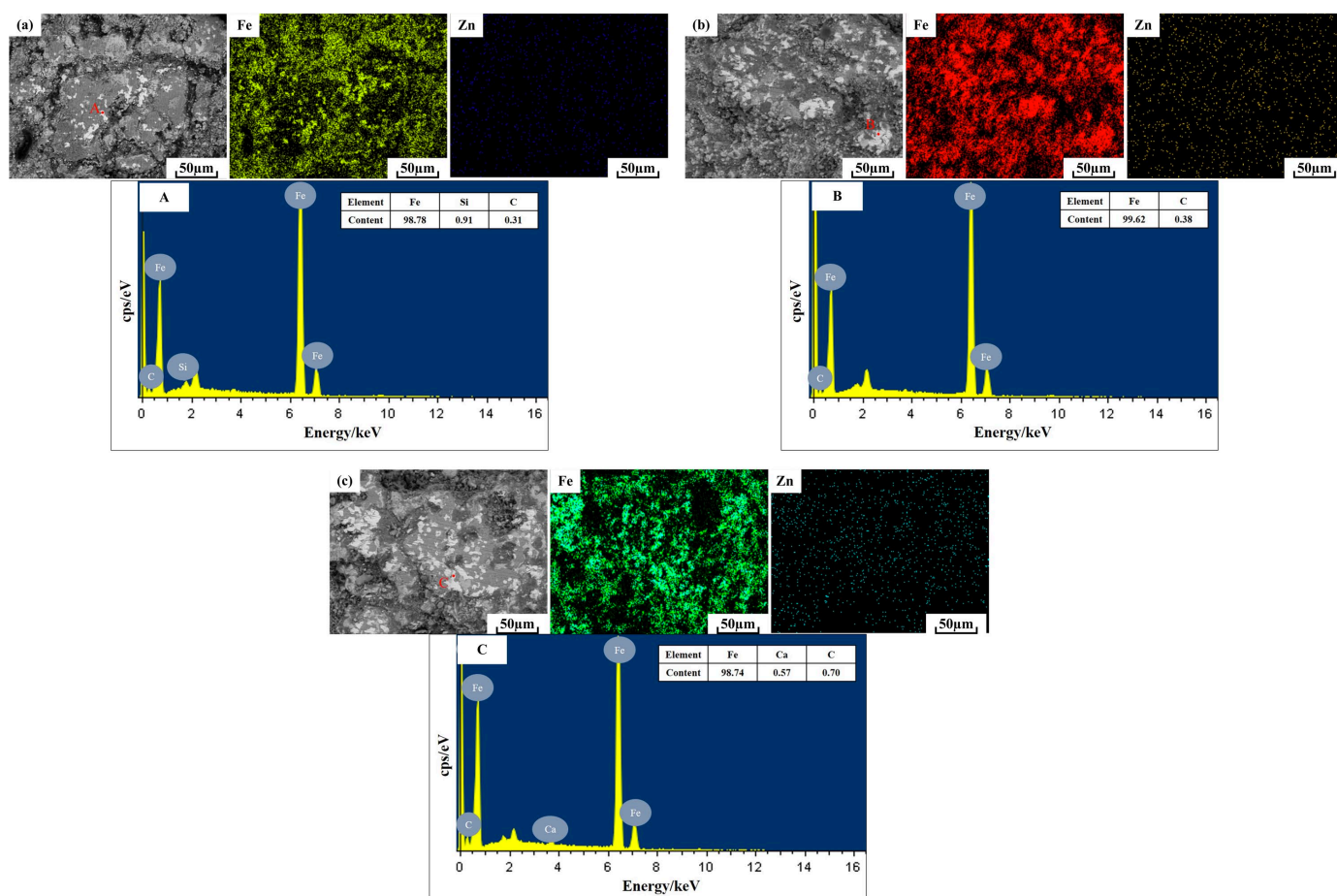


Fig. 7. Representative SEM-EDS analysis of briquettes obtained at 1200°C for various times. (a) 10 min, (b) 20 min, (c) 30 min

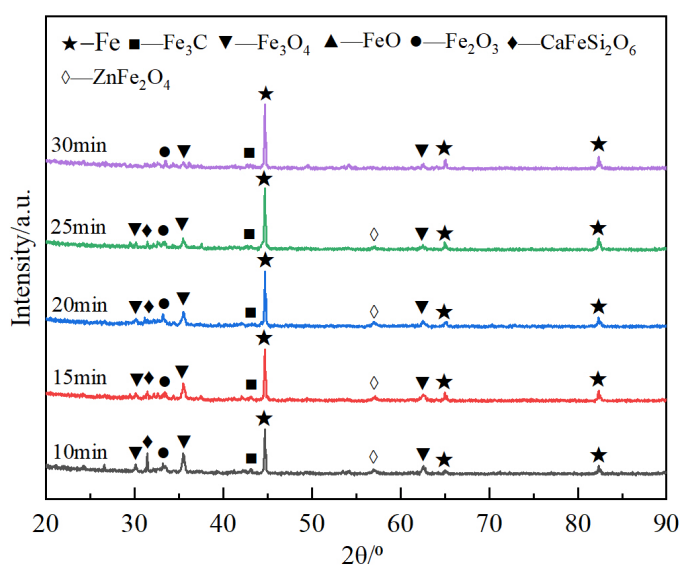


Fig. 8. XRD pattern of pre-reduction sintered products for the various pre-reduction time

particles and slag. This shows that more and more metallic iron was reduced by hematite and magnetite. The metallization rate of the pre-reduction sintered product gradually increased, and the pre-reduction degree also increased. It is consistent with the above analysis.

3.4. Phase transition of pre-reduction sintered products

XRD pattern of pre-reduction sintered products after reduced at 1200°C for the different time are shown in Fig. 8. Zinc ferrite (ZnFe₂O₄) decomposes into zinc oxide (ZnO) and magnetite (Fe₃O₄) at 1200°C. Zinc sulfide (ZnS) reacts with calcium oxide (CaO) at 1100°C to form ZnO. With the pre-reduction time extending from 10 min to 30 min, the diffraction peak intensity of zinc ferrite decreases gradually, indicating that zinc ferrite continuously decomposed into ZnO and Fe₃O₄ with the prolonga-

tion of the pre-reduction time. ZnO has a low boiling point and is easily reduced to metallic zinc (Zn) at a reaction temperature set for experiment. So most of the Zn will be reduced from ZnO and later converted to Zn vapor to escape. Therefore, very little Zn remains in the pre-reduction sintering products, which is the reason why no Zn or ZnO diffraction peaks are observed in the XRD spectrum.

Ferric carbonate (FeCO_3) begins to decompose into ferrous oxide (FeO) and CO_2 at 200°C . At high temperature, FeO reacts with CaO and silicon dioxide (SiO_2) to form calcium ferrite ($\text{CaFeSi}_2\text{O}_6$). It is observed from Fig. 7 that the diffraction peak intensity of $\text{CaFeSi}_2\text{O}_6$, hematite (Fe_2O_3), magnetite (Fe_3O_4) and FeO decrease continuously, and the diffraction peak intensity of metal iron (Fe) increase continuously, indicating that with the pre-reduction sintering process, $\text{CaFeSi}_2\text{O}_6$, hematite (Fe_2O_3), magnetite (Fe_3O_4) and FeO are gradually reduced to metal iron. A part of iron is carbonized to form a cementite (Fe_3C) which has high chemical stability and is not easy to be reoxidized.

XRD results show that more and more zinc and metal iron are reduced with the pre-reduction sintering process. The zinc removal rate and metallization rate of pre-reduction sintering products are higher and higher with the prolongation of pre-reduction time, which is consistent with the previous analysis results.

3.5. Removal mechanism of zinc from pre-reduction sinter

In the process of pre-reduction sintering, the reduction of metal oxides by solid carbonaceous reductant has two forms. One is through the direct reduction of solid carbon (C), the other is through the indirect reduction of carbon monoxide (CO). Direct reduction reaction is solid-solid reaction and indirect reduction reaction is gas-solid reaction. For the more stable metal oxides, the direct reduction reaction is dominant, while for the less stable metal oxides, the indirect reduction reaction is dominant.

The direct and indirect reduction reactions of zinc oxides and iron oxides in the pre-reduction sintering process are as follows:

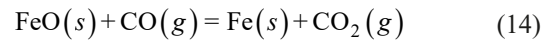
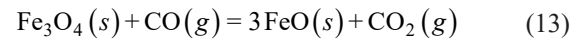
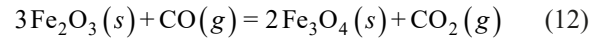
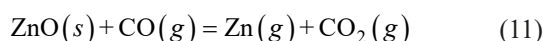
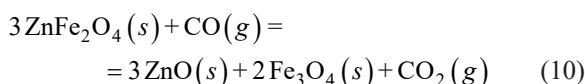
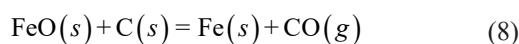
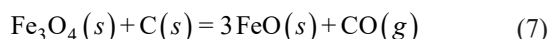
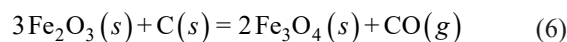
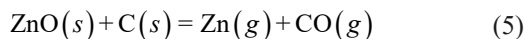
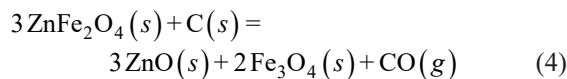


Fig. 9 shows the changes in the standard free energy of these reactions in the temperature range of $0\text{--}1500^\circ\text{C}$. It can be clearly seen that almost all of the listed reactions can occur normally under the experimental conditions. At the beginning of the reduction reaction, no carbon monoxide is formed in the briquettes, so carbon is the main reducing agent, and the reduction reaction is mainly direct reduction, depending on the contact degree between carbon and the raw material particles. The direct reduction reaction Eqs. (4), (5) occurring between metal oxides and solid carbon are more favorable than the indirect reduction reaction Eqs. (10), (11) caused by carbon monoxide. Zinc ferrite is first reduced to zinc oxide and magnetite, and carbon monoxide is produced. As the reduction reaction proceeds, the carbon in the briquettes is gradually consumed and the Boudouard reaction Eq. (9) also generates carbon monoxide. But Eq. (11) is even not ideal in the whole temperature range. Therefore, the reduction of zinc oxide is more dependent on the direct reduction reaction, which is the reason for the higher zinc removal capacity of the pre-reduction sintering process. Throughout the pre-reduction sintering process, the zinc removal can be simply described as $\text{ZnFe}_2\text{O}_4(s) \rightarrow \text{ZnO}(s) \rightarrow \text{Zn}(g)$. Metallic zinc is extremely volatile, so the zinc in the briquettes is eventually converted into zinc vapor, which is then carried away by the continuous airflow to complete the evaporation removal.

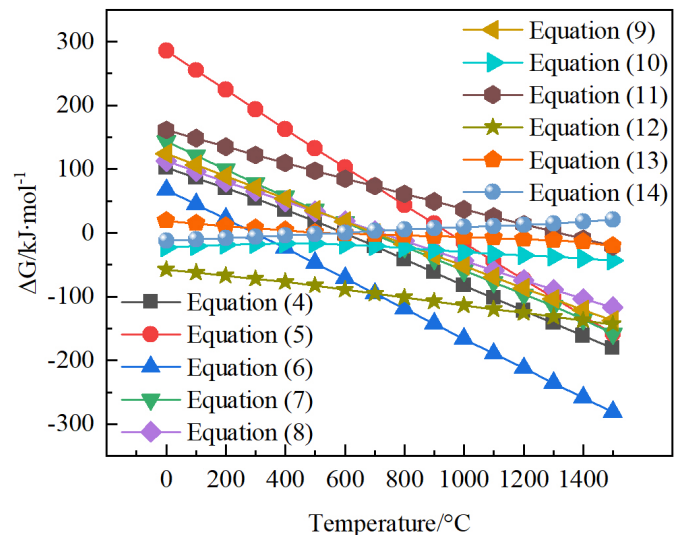


Fig. 9. Standard free energy changes for the Eqs. (4)-(14) in the temperature range of $0\text{--}1500^\circ\text{C}$

Under the conditions of this study, indirect reduction reaction can be used to describe not only the reduction process of zinc oxides, but also the partial reduction process of iron oxides. Observing Eqs. (6)-(8) and Eqs. (12)-(14), it can be seen that the reduction from hematite to magnetite to ferrous oxide may depend on the indirect reduction reaction, while the reduction of FeO to

metallic iron is more dependent on the direct reduction reaction. The reduction of iron oxides can be summarized in the following steps: $\text{ZnFe}_2\text{O}_4(\text{s})/\text{Fe}_2\text{O}_3(\text{s}) \rightarrow \text{Fe}_3\text{O}_4(\text{s}) \rightarrow \text{FeO}(\text{s}) \rightarrow \text{Fe}(\text{s})$. A small amount of iron is reduced by zinc ferrite, which also affects the metallization rate and further affects the pre-reduction degree.

4. Conclusions

- (1) The pre-reduction sintering process can play an obvious Zn removal effect, which is beneficial to blast furnace production. The Zn removal rate of the pre-reduction sintered products rose with the increase of the pre-reduction time, and showed a trend of increasing and then decreasing with the increase of the carbon content and basicity. The Zn removal rate of the pre-reduction sintered products was 90.40% when the briquettes was reduced at 1200°C for 20 min at C/O molar ratio of 1.0 and basicity of 1.9.
- (2) The pre-reduction degree of the pre-reduction sintered products showed a trend of increasing and then decreasing with the increase of carbon content and basicity, and increased with the increase of pre-reduction time. When the briquettes was reduced at 1200°C for 20 min at C/O molar ratio of 1.0 and basicity of 1.9, the pre-reduction degree of the pre-reduction sintered products was 87.47%, which could meet the requirements of the blast furnace.
- (3) In the pre-reduction sintering process, the reduction of zinc oxides and iron oxides is greatly influenced by indirect reduction reaction. The phase transformation of zinc can be described as $\text{ZnFe}_2\text{O}_4(\text{s}) \rightarrow \text{ZnO}(\text{s}) \rightarrow \text{Zn}(\text{g})$, and the phase change of iron can be described as $\text{ZnFe}_2\text{O}_4(\text{s})/\text{Fe}_2\text{O}_3(\text{s}) \rightarrow \text{Fe}_3\text{O}_4(\text{s}) \rightarrow \text{FeO}(\text{s}) \rightarrow \text{Fe}(\text{s})$. The metal zinc in zinc ferrite finally escapes as gas to realize volatilization removal.
- (4) Through the experimental study of simulated pre-reduction sintering, it is confirmed that the pre-reduction sintering process is feasible to realize the zinc removal and iron reduction in the front of blast furnace, which has a beneficial effect on the subsequent blast furnace production.

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