Study on the reduction reaction characteristics of Quasi-east coal and blast furnace dust mixed combustion

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Abstract. Based on Gibbs' minimum free energy principle, the change of iron and zinc reduction and the change of sulfur dioxide during the mixed combustion process of quasi-east coal and blast furnace dust were studied. The results show that the reducing atmosphere of the reaction system is enhanced as Actual oxygen flux and theoretical oxygen demand ratio decreased and the temperature increased, and the reaction characteristic is more favorable for the reduction and precipitation of zinc and iron. When Actual oxygen flux and theoretical oxygen demand ratio is 0.5 and 0.75, the generation rate of elemental zinc and elemental iron increases as the temperature reaches 600 °C-800 °C. At this time, the amount of SO₂ is small as the Actual oxygen flux and theoretical oxygen demand ratio is 1,1.25 and 1.75. When the temperature continues to rise from the 800 °C to 1800 °C, the amount of zinc production is stable at 4.225mol, elemental iron production decreased rapidly, sulfur dioxide content continues to rise.

1. Introduction

The dust produced by blast furnace ironmaking contains a large amount of zinc and iron, which has a high recovery value [1]. China stipulates that blast furnace ironmaking furnace dust is a hazardous waste, and the main treatment method is to be directly buried in designated places [2, 3]. When the zinc-containing blast furnace dust is recycled into the iron making process for recycling [4], a part of the zinc in the dust is volatilized with the flue gas, and a part of the zinc falls back into the bottom of the furnace. The zinc in the furnace is easily on the throat and the body of the furnace. When the tumor root is formed and the degree of nodulation is serious, it will affect the effective volume of the blast furnace, resulting in the blast furnace not working properly [5].

The use of carbon in the blast furnace slag to reduce the iron in the blast furnace dust can reduce the iron oxide in the blast furnace dust at 1500 °C. After the iron beads are reduced, it is easy to separate and has little influence on the slag composition [6]. El-Hussiny NA [7] studied the use of blast furnace dust instead of coke to sinter iron ore. During the sintering process, 7% molasses and 15% water were added as organic binders. It was found that the bond strength increased with the increase of blast furnace dust. The weight loss caused by the reduction of iron ore in the sintering process is reduced, but the production efficiency of the sintering machine is lowered. Hesham I Saleh [8] and other studies used ammonium sulfate to extract zinc from blast furnace dust. The results show that the zinc oxide in the blast furnace dust reacts with ammonium sulfate at a molar ratio of 1:8 at 350 °C after calcination, and the recovery of zinc can reach 95%. Chairaksa-Fujimoto, Romchat [9] used NaOH solution to remove
zinc from blast furnace dust, and the treated dust can be recycled as steelmaking raw materials. The results show that 2mol/L sodium hydroxide is disposed at 70 °C and the solution has a solid-liquid ratio of 1:300 for 2 hours, which can achieve the best dezincification effect. Yang Xueming [10] and other studies found that blast furnace dust can be used to remove SO2 from flue gas from coal combustion. The temperature is in the range of 523-823K, and the desulfurization rate is 87%-93%, the desulfurization effect increases with the increase of temperature.

At present, there are many researches on the recycling and utilization methods of blast furnace dust. Most of these studies focus on the direct recycling of dust, some of which use blast furnace dust to other processes to reduce the cost of recycling, but the method is difficult to promote. This study utilizes the method of mixed combustion of blast furnace dust and Zhundong coal in order to provide reference for the recovery of zinc and iron elements in blast furnace dust and the reduction of SO2 emitted by Zhundong coal. In this study, the inductively coupled plasma spectrometer (ICP emission spectrometer) was used to measure the content of each element in blast furnace dust and Zhundong coal of a steelmaking plant. The Gibbs minimum free energy principle was used to study the combustion of Zhundong coal to reduce Zn and Fe in blast furnace dust. The variation of Zn and Fe elements under different working conditions and the formation of sulfur dioxide in this process were analyzed.

2. Thermodynamic analysis of iron-zinc reduction

The thermodynamic study of the reduction reaction of iron and zinc found that the zinc-iron reduction process is theoretically composed of several continuous gas-solid reactions [11]:

\[
\begin{align*}
\text{ZnO} + \text{CO} &\rightarrow \text{Zn} + \text{CO}_2 & \lg K_{R(1)} = -\frac{9740}{T} + 6.12 \\
\text{CO}_2 + \text{C} &\rightarrow 2\text{CO} & \lg K_{R(2)} = -\frac{8916}{T} + 9.113 \\
\end{align*}
\]

Combined reactions (1) and (2):

\[
\begin{align*}
\text{ZnO} + \text{CO} &\rightarrow \text{Zn} + \text{CO}_2 & \lg K_{R(3)} = -\frac{18656}{T} + 15.233 \\
\end{align*}
\]

It can be seen from the reaction (3) that the critical temperature at which zinc oxide is reduced is 947.15°C, and the temperature during combustion is generally greater than 800 ° C. Therefore, the reaction equilibrium constants of reactions (1) and (2) are greater than 10^5, which is considered to be irreversible reaction. The reactions (1) and (2) are both endothermic reversible reactions, so the reaction can proceed in the forward direction only when the temperature is high and the reducing atmosphere of the reaction environment is strong, and the reduction of zinc can be relatively thorough.

The reduction reaction of iron oxide is carried out in steps, and the reaction steps are as follows:

\[
\begin{align*}
\text{3Fe}_2\text{O}_3 + \text{C} &\rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2 & \Delta G = -51221 - 41.0T \\
\text{Fe}_3\text{O}_4 + \text{CO} &\rightarrow 3\text{FeO} + \text{CO}_2 & \Delta G = -35380 - 40.16T \\
\text{FeO} + \text{CO} &\rightarrow \text{Fe} + \text{CO}_2 & \Delta G = -22800 + 24.26T \\
\end{align*}
\]

The reactions (4) to (6) are exothermic reactions. During the actual heating process, the Gibbs free energy of the reaction (4) and the reaction (6) are both less than zero, and the reaction can proceed spontaneously when the temperature reaches 800 °C. The Gibbs free energy of the reaction (6) is greater than zero, and the reaction cannot proceed spontaneously. With continuous heating, the positive energy
of the Gibbs is increasing, and the reaction tends to proceed in a reverse direction. The reversibility of the reactions (4) to (6) is low, and a small amount of CO can be carried out in the reaction. In order to make the reduction of iron more thorough, the environment has a high demand for a reducing atmosphere (CO content). In the process of blast furnace dust reduction of iron and zinc, there are two ways of direct reduction and indirect reduction, among which indirect reduction is the main driving force of the reduction process [12]. From the above thermodynamic analysis, the ratio between CO and CO2 in the reaction environment is important. The P(CO)/P(CO2) value can be used to reflect the extent of the reducing atmosphere of the reaction environment. The higher the ratio, the higher the degree of reduction atmosphere, and the more favorable the reduction reaction. The zinc and iron in the dust exist in the oxidation state. The positive divalent zinc and the positive trivalent iron are the main states. In the formulas (1) to (6), the P(CO)/P(CO2) values are positive. It is a factor of the reaction quotient of these reduction reactions. It is known from the principle of equilibrium reaction that the larger the ratio, the more favorable the reaction proceeds.

3. Reduction reaction conditions and calculation methods

3.1. Reduction reaction conditions
The blast furnace dust samples of this experiment were provided by the enterprise. The contents of each element in the coal and blast furnace dust measured by ICP test are shown in Table 1 and Table 2. It can be seen from Table 2 that the dust in this experiment contains a large amount of iron, and the fixed carbon content in coal and blast furnace dust is relatively high, which provides favorable conditions for the reduction of iron and zinc. The working conditions of actual oxygen demand and theoretical oxygen demand ratios of 0.5, 0.75, 1, 1.25 and 1.5 were selected to investigate the effect of mixed combustion of Zhundong coal and blast furnace dust on zinc-iron reduction. The calculated temperature range was 600 °C. Between 2000 °C. With 10kg sample, the ratio of coal to blast furnace dust is 7:3. According to the principle of minimum Gibbs free energy, the final content of each reaction substance in equilibrium state is obtained. The reaction is assumed to be carried out under normal pressure, and the influence law of reducing zinc and iron in dust under different working conditions is obtained. In the process, the change in the amount of sulfur dioxide produced is analyzed.

| Tab.1 The content of each element in coal |
|-------------------------------------|
| C        | H        | O        | N        | S        | A        | M        |
| 46.55    | 3.06     | 6.11     | 0.86     | 1.94     | 32.48    | 9        |
| Ca       | Na       | K        | Mg       | Al       | Fe       | Cl       |
| 0.91     | 0.28     | 0.007    | 0.246    | 0.27     | 0.221    | 0.304    |

| Tab.2 The content of various elements and compounds in blast furnace dust |
|-------------------------------------|
| FeO       | SiO2     | Al2O3    | Fe2O3    | CaO      | MgO      | ZnO      | Cl       | C        |
| 7.9       | 9.68     | 5.85     | 24.16    | 5.39     | 1.85     | 4.17     | 4.41     | 22.02    |

3.2. Calculation method
Assume that there is an ideal gas phase and a pure solid phase in this research system, and no solution phase exists. The following is the Gibbs minimum free energy formula:

\[ G = \sum_{ideal \ gas} n_i \left( g_i^o + RT \ln p_i \right) + \sum_{pure \ condensed \ phases} n_i g_i^o \]

The calculation process of this study is shown in Figure 1:
4. Results and analysis

4.1. Change law of CO and CO$_2$ content under different working conditions

Figure 2 shows the variation of P(CO)/P(CO$_2$) value with temperature under different actual oxygen demand and theoretical oxygen demand ratio. With the increase of temperature, the ratio increases, and the actual oxygen flux and the theoretical oxygen demand ratio is 0.5, the P(CO)/P(CO$_2$) value increases obviously. From formula (1) to formula (6), the thermodynamic reaction of iron-zinc reduction is at least when the ratio is at least 1. In theory, it can be spontaneously carried out. When the ratio of actual oxygen demand to theoretical oxygen demand is 0.5 and 0.75, on the one hand, due to incomplete combustion of carbon, the CO content increases. On the other hand, the Budor reaction begins [13], resulting in an increase in the rate of CO production and an increase in the P(CO)/P(CO$_2$) value. When the ratio of actual oxygen demand to theoretical oxygen demand is greater than 1, the complete combustion of carbon dominates and the P(CO)/P(CO$_2$) value decreases. The temperature rises between 500°C and 800°C. Faster as the oxygen supply increases, the ratio tends to zero, which is not conducive to the above-mentioned reversible reduction reaction.

![Figure 2](image-url)
4.2. Reduction of Zn and Fe under different working conditions

When the combustion of blast furnace dust and Zhun-dong coal is carried out from 600 °C to 2000 °C, the change in the quality of elemental iron and zinc can reflect the overall reduction of iron and zinc compounds in the blast furnace dust, according to the two elements, the change law gives the optimal working condition of the mixed combustion of blast furnace dust and coal.

It can be seen from Fig.3 that when the ratio of actual oxygen demand to theoretical oxygen demand is 0.5 and 0.75, and the temperature is around 800 °C, the rate of formation of elemental zinc is faster, when the ratio of actual oxygen demand to theoretical oxygen demand is 1. When the temperature is about 1000 °C, the formation rate of elemental zinc increases. When the ratio of actual oxygen demand to theoretical oxygen demand is 1.25 and 1.5, the temperature should reach 1600 °C, and the formation rate of elemental zinc can be significantly accelerated. The temperature at which the formation rate of elemental zinc and elemental iron is accelerated is a significant reduction point. When the temperature increases, the ratio of the actual oxygen demand to the theoretical oxygen demand increases, and the apparent reduction point moves to the right, indicating that the zinc element needs to be reduced. The lower the ratio of the actual oxygen demand to the theoretical oxygen demand, the easier the zinc element is reduced and the faster the reaction rate. There is a competitive relationship between the reaction of oxygen and carbon in the complete combustion of CO2 and the reduction reaction of zinc (1.1) to (1.3) [12]. The actual oxygen ratio and the theoretical oxygen demand ratio are directly related to the zinc reduction reaction. The degree of reactant participation and temperature conditions are directly related to the thermodynamic reaction conditions of zinc reduction reaction, which reflects the joint influence of the two working conditions on the reduction reaction of zinc and iron, and the best working conditions are obtained. Figure 4 is a fitting diagram of Zn under different temperatures and different actual oxygen ratios and theoretical oxygen demand ratios. When the temperature is 1600 °C, the ratio of the actual oxygen demand to the theoretical oxygen demand is 0.5, the amount of elemental zinc is 1.536 mol. At this time, the best conditions under the conditions of the study.

![Fig.3 Changes of elemental Zinc formation in different oxygen conditions with temperature.](image-url)
Fig. 4 Effect of different excess oxygen coefficient at different temperatures on elemental zinc generation.

It can be seen from Fig. 5 that when the ratio of actual oxygen demand to theoretical oxygen demand is 0.5 and 0.75, and the temperature is from 600 °C to 750 °C, the amount of elemental iron is increased, and the amount of elemental iron is continuously reduced after 750 °C. When the ratio of quantity to theoretical oxygen demand is 1, 1.25 and 1.5, the amount of elemental iron is small, and the change with temperature is not large. The reduction of iron element is significantly affected by the ratio of actual oxygen demand to theoretical oxygen demand. When the ratio of theoretical to theoretical oxygen demand is 0.5 and 0.75, the temperature of the elemental iron can only continuously rise and reach the maximum when the temperature is lower than 750 °C. When the temperature continues to rise until 1800 °C, the amount of elemental iron continues to decrease. Under the influence of temperature, the thermodynamic reaction between elemental iron and other substances causes the amount of elemental iron to be reduced throughout the system. When the temperature continues to rise from 1800 °C, the amount of elemental iron starts to rise. This is because when the actual oxygen demand and the theoretical oxygen demand ratio are 0.5 and 0.75, and the temperature is lower than 750 °C, the reaction mainly occurs (1.6), and when the temperature continues to rise until about 1800 °C, the reaction (1.6) of Gibbs The free energy is greater than 0, and the reverse reaction is a spontaneous trend. When the temperature continues to rise, the P(CO)/P(CO₂) value of the actual oxygen demand and the theoretical oxygen demand ratio of 1, 1.25, and 1.5 increases. The reducing atmosphere of the reaction environment is enhanced, resulting in an increase in the amount of elemental iron produced at this time.

Fig. 5 Changes of elemental iron production in different excess oxygen coefficient with temperature.
Figure 6 is the result of fitting the variation of elemental iron production under different actual oxygen demand and theoretical oxygen demand ratio and different temperature conditions. It can be seen from the figure that when the temperature is 750 °C, the ratio of the actual oxygen demand to the theoretical oxygen demand is 0.5, the amount of elemental iron is 9.907 mol, which is the best condition under the conditions of this study.

Fig.6 Effects of Different Oxygen Permeability and Different Temperature on Formation of Elemental Iron.

4.3. Changes of SO$_2$

Figure 7 shows the change of sulfur dioxide production with temperature under different oxygen-passing conditions. When the ratio of actual oxygen demand to theoretical oxygen demand is 1, 1.25 and 1.5, when the temperature is 800 °C, the rate of SO$_2$ formation increases, 800 °C is the obvious generation point of SO$_2$, and the apparent generation point of SO$_2$ moves to the right as the ratio of actual oxygen demand to theoretical oxygen demand increases. The apparent production point of SO$_2$ moves to the right as the ratio of actual oxygen demand to theoretical oxygen demand increases, and finally reaches the equilibrium concentration of 4.25 mol. When the actual oxygen demand and theoretical oxygen demand ratio are 0.5 and At 0.75, the amount of SO$_2$ produced was lower than the equilibrium concentration of 4.25 mol. The amount of SO$_2$ produced in this study system increases with increasing temperature, and the decrease in the ratio of actual oxygen demand to theoretical oxygen demand can inhibit the formation of SO$_2$. Figure 8 is a plot of the variation trend of SO$_2$ production with different temperatures and different actual oxygen fluxes and theoretical oxygen demand ratios. As can be seen from Fig.8, when the temperature is 1800 °C and the ratio of the actual oxygen demand to the theoretical oxygen demand is 1.25, the amount of SO$_2$ produced has reached a maximum of 4.225 mol. Before the temperature reaches 800 °C, the amount of SO$_2$ generated is less than 0.15 mol, which is less affected by the ratio of actual oxygen demand to theoretical oxygen demand. When the actual oxygen demand and theoretical oxygen demand ratio are lower than 0.5 and 0.75, the elemental mass is low. The formation rate of zinc and iron is higher, in which elemental iron reaches a maximum at 750 °C, and the amount of SO$_2$ is small. When the ratio of actual oxygen to theoretical oxygen demand is 1, 1.5 and 1.75, P(CO)/P (CO$_2$) The value of is less than 1, and the content of CO$_2$ in the reaction environment is relatively high. It has a negative effect on the sulfur-fixing reaction in the reaction system at a temperature ranging from 600 °C to 750 °C [14].
5. Conclusion

(1) The thermodynamic conditions of iron-zinc reduction were analyzed. Under the conditions of this study, when the ratio of actual oxygen demand to theoretical oxygen demand is 0.5 and 0.7, the $P(\text{CO})/P(\text{CO}_2)$ value is greater than 1, and with the increase of temperature, the ratio is continuously increased. When the ratio of the actual oxygen demand to the theoretical oxygen demand is 0.5, the temperature is greater than 700 °C, the ratio of the actual oxygen demand to the theoretical oxygen demand is 0.75, and the temperature is greater than 1250 °C. The use of Zhundong coal to reduce the zinc in the blast furnace iron is theoretically feasible.

(2) The variation law of zinc iron and sulfur dioxide in the process of temperature rise of different actual oxygen demand and theoretical oxygen demand is analyzed. When the ratio of actual oxygen demand to theoretical oxygen demand is 0.5 and 0.75, the temperature is about 600-800 °C. The rate of formation of Fe is the highest, and the amount of SO$_2$ generated is low. When the ratio of actual oxygen demand to theoretical oxygen demand is 1, 1.25 and 1.5, and the temperature rises to 1800 °C, the amount of Zn is stable to reach 1.535 mol. When the ratio of actual oxygen demand to theoretical oxygen demand is 0.5, and the temperature rises from 750 °C to 1800 °C, the amount of Fe is continuously decreased. When the temperature continues to rise, the value of $P(\text{CO})/P(\text{CO}_2)$ increases. This leads to an increase in the amount of Fe generated.

(3) The variation law of SO$_2$ generation in the mixed combustion of Zhundong coal and blast furnace dust in different actual oxygen demand and theoretical oxygen demand temperature is analyzed. When the temperature is lower than 800 °C, the SO$_2$ production is less than 0.15 mol. When the ratio of oxygen demand to theoretical oxygen demand is 0.5 and 0.75, the temperature is greater than 1200 °C, and the rate of SO$_2$ formation increases. When the ratio of actual oxygen demand to theoretical oxygen demand
is 1, 1.25 and 1.5, P(CO)/P(CO$_2$) decreases, and the increase in CO$_2$ suppresses the sulfur fixation reaction of the reaction system, resulting in an increase in the amount of SO$_2$ produced.

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