Degradation Behavior of Coke Reacting with H₂O and CO₂ at High Temperature

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The degradation behaviors of coke which reacts with CO₂ and H₂O were explored in self-made gas-solid reacting apparatus. It was observed that the temperature loss of coke with H₂O in initial and violent solution were about 37°C and 125°C lower than that with CO₂ respectively. The gasification rate of coke with H₂O was about 1.27–3.16 times faster than that with CO₂. But the difference of gasification rate will reduce with the lower temperature. The coke strength after reaction (CSR) with H₂O was lower than with CO₂ at 950°C–1 100°C, but higher at 1 200°C. The coke’s apparent porosity and changing rate after reacting were both smaller with H₂O than with CO₂. It is mainly due to the reaction that occurred closer to the coke particle surface with H₂O than with CO₂.

KEY WORDS: coke; CO₂; H₂O; gasification reaction; degradation.

1. Introduction

Currently, reducing greenhouse gas CO₂ emission from fossil fuel combustion focuses on energy conservation and emission reduction in the blast furnace (BF)1,2) of ironmaking process. In order to reduce energy consumption and pollution emission, many researchers have tried many studies around fuel structure of BF and new technologies of iron-making. H₂ can replace carbonaceous fuel as heating agent and reducing agent of BF under certain conditions.3) Furthermore, Japan and other countries have been developing the new BF technology with pure oxygen and injecting hydrogen fuel.4,5) This technology has not only achieved zero CO₂ emissions but also reduced atmospheric haze caused by coal-fired. However, the reaction between a large amount of H₂O in BF created by hydrogen fuel injection and coke has a significant impact on the properties of coke.6,7) In this respect, many researchers have done a lot of studies. Takahata8) considered that the solution loss of coke with H₂O is more severe and the reaction rate is about 3–4 times as fast as that with CO₂. Kashihara et al.9) compared coke strength after reaction (CSR) reacting with CO₂ and H₂O at the same solution loss rate (30%), and found that CSR of coke reacting with H₂O was higher than that with CO₂ at the temperature of 950°C–1 500°C. Wang et al.10) studied the effect of temperature on apparent porosity using spherical coke, and found that apparent porosity decreased with the temperature. Pusz et al.11) studied the pore structure and matrix structure of coke before and after reacting with CO₂, and found that pore structure had a larger influence on the strength and reactivity of coke. Iwanaga et al.12) considered that the reaction region with H₂O was closer to the coke surface than that with CO₂ at 1 150°C, but at 1 700°C the both reactions occurred at the surface.

However, researches on the degradation behavior of coke are mainly on the effects of CO₂ and few studies on the influence of H₂O on coke degradation and on the difference between the two had been reported. Thus this work reported on the gasification reaction, CSR and apparent porosity of coke reacting with H₂O and CO₂ respectively. Furthermore, the changes of bulk density distribution and microstructure of coke before and after reaction were also studied.

2. Experimental

2.1. Materials

Coke specimens used in this experiment were obtained from Ma’anshan Steel Company in China. Their proximate analysis and strength are listed in Table 1. The purity of N₂ and CO₂ were 99.999% and 99.99% respectively. Water

<table>
<thead>
<tr>
<th>Fc (%)</th>
<th>Ad (%)</th>
<th>Vd (%)</th>
<th>S (%)</th>
<th>M₄₀ (%)</th>
<th>M₁₀ (%)</th>
<th>Apparent porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>84.92</td>
<td>12.82</td>
<td>2.26</td>
<td>0.71</td>
<td>88.25</td>
<td>5.35</td>
<td>42.25</td>
</tr>
</tbody>
</table>

Fc, Ad, S and Vd stand for the mass percent of fixed carbon, ash, volatile matter and sulphur in the coke, respectively. M₄₀ and M₁₀ stand for the mass percent of the coke whose diameter > 40 mm and 10 mm, respectively.

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vapor used in this study was made by distilled water.

2.2. Apparatus and Methods

2.2.1. Determination of Gasification Reaction Temperature of Coke with CO₂ and H₂O

The experiments were carried out in accordance with the Chinese national standard (GB/T 4000-2008). The test of solution loss reaction temperature was conducted in the device shown in Fig. 1. A Si–Mo resistance furnace with a maximum working temperature of 1 550±30°C was used for heating. A 1 500±1 g sample with the grain size of 23–25 mm was placed into the furnace. The samples were then heated up at a rate of 15°C/min before 500°C and at a rate of 6°C/min after 500°C. The inlet gas was 100% CO₂ (or 100%H₂O) when the coke reacting with CO₂ (or H₂O) and its velocity was set as 5 L/min. The Reynold’s number of solution loss reaction temperature was conducted in the Chinese national standard (GB/T 4000-2008). The test was carried out in a continuous measurement. A Si–Mo resistance furnace with a maximum working temperature of 1 550±30°C was used for heating. A 200±0.5 g sample with the grain size of 23–25 mm was placed into the furnace. The measurement range and precision of balance were 5–100 g and 0.1 g. The N₂ gas was introduced to protect the coke at the rate of 0.8 L/min until the experimental temperatures (950°C, 1 000°C, 1 100°C and 1 200°C). Pure CO₂ or H₂O reacted with the samples respectively at the experimental temperature. The flow of CO₂ or H₂O was set as 5 L/min and the time of reaction was 2 h. After reacting, cut off the experimental gas and gave the N₂ to cool the sample to 100°C below at the rate of 2 L/min.

Gasification rate of coke was calculated by

\[ X = \left( m_0 - m_1 \right) \times 100\% / \left( m_0 \times m_2 \right) \] ........................ (1)

\[ SLR = \left( m_0 - m_1 \right) \times 100\% / m_0 \] ........................ (2)

Where \( X \) is gasification rate (%), \( m_0 \) is initial weight of coke (g), \( m_1 \) is fixed carbon content (%) and \( m_2 \) is the weight of balance (g). Solution loss rate (SLR) is the gasification rate at the end of reaction.

2.2.2. Measurement of Coke Gasification Rate

The test of coke gasification rate was carried out in a gas-solid reaction apparatus with continuous measuring of coke weight, as shown in Fig. 2. A Si–C resistance furnace with a maximum working temperature of 1 250±30°C was used for heating. A 200±0.5 g sample with the grain size of 23–25 mm was placed into the furnace. The measurement range and precision of balance were 5–100 g and 0.1 g. The N₂ gas was introduced to protect the coke at the rate of 0.8 L/min until the experimental temperatures (950°C, 1 000°C, 1 100°C and 1 200°C). Pure CO₂ or H₂O reacted with the samples respectively at the experimental temperature. The flow of CO₂ or H₂O was 5 L/min and the time of reaction was 2 h. After reacting, cut off the experimental gas and gave the N₂ to cool the sample to 100°C below at the rate of 2 L/min.

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2.2.3. Measurement of Coke Strength and Apparent Porosity after Reaction

The coke after the reaction in Section 2.2.2 was put into I-type rotating drum (Ø130 mm×700 mm), and measured for 30 min at the speed of 20 r/min. Next, the samples were sieved by two sieves of 5 mm and 10 mm apertures size. Then the samples were divided into three parts, every part of samples was weighed. Finally, Coke strength after reaction (CSR) was given by

\[ CSR = m_2 / m_1 \times 100\% \] ........................ (3)

Where \( m_1 \) is the weight of coke after reaction (g) and \( m_2 \) is the weight of sample with a particle size more than10 mm (g).

Apparent porosity of coke after reaction was measured by apparent porosity-bulk density analyzer (XQK-02). First, the dry weight \( m_1 \) of coke was measured, and then the sample was place into the vacuum hood of the bulk density analyzer for vacuum pumping and injection operation. After that the sample was taken out and the suspended weight \( m_4 \) and saturate weight \( m_5 \) were measured in the water. At last, the apparent porosity \( \pi \) was calculated by

\[ \pi(\%) = \left( m_5 - m_4 \right) \times 100\% / \left( m_5 - m_6 \right) \] ........................ (4)

2.2.4. Measurement of the Bulk Density Distribution of Coke after Reaction

For a more accurate analysis of bulk density distribution of coke after reaction, some more experiments of coke reacting with CO₂ and H₂O were carried out at 950°C, 1 000°C, 1 100°C, and 1 200°C, respectively. In this test, a single coke sample was also carried out in a gas-solid reaction apparatus with continuous measuring of coke weight, but as shown in Fig. 3. The measurement range and precision of balance were 0.02–210 g and 0.001 g. A single coke sample was processed to a cylindrical shape with the size of Ø25 mm×25 mm before the test. In this test, the gas method and
cooling method were the same as the test shown in Fig. 2, only changing the test ending time from 2 h to when weight loss reaching 30%.

After experiments, bulk density of coke sample was measured for many times also by apparent porosity-bulk density analyzer (XQK-02). The method of bulk density is the same as that of apparent porosity, the bulk density was calculated by

\[ \rho = \frac{m_1 \times \rho_w}{(m_5 - m_2)} \]

where \( \rho_w \) is the density of water (g/cm\(^3\)). Before each measurement coke sample was grinded off 0–1.5 mm thickness around the sample surface. For the first measurement, bulk density was marked as \( \rho_i \) and the following time marked as \( \rho_i \), \( \rho_{i}^{\cdots} \) and \( \rho_{i}^{\cdots} \), respectively. In order to reduce the influence of grinding on pore, the sample was cleaned roundly with alcohol after each grinding.

3. Results and Discussions

3.1. Solution Loss Reaction Temperature of Coke

The initial and violent solution loss temperatures of coke were significantly effected on the fuel consumption and energy utilization of blast furnace. Generally, the reactivity of coke will be high but CSR will be low if the initial and violent solution loss temperatures are low.

The equations of coke reacting with \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) are shown as (6) and (7). In theory, \(^{13}\) the initial solution loss temperatures of the two reactions are 701.0°C and 672.4°C respectively. As can be seen the difference of the two rates increases with the increase of temperature, and this conclusion agrees with the literature. \(^{14}\)

\[ \text{CO}_2 + \text{C} = 2\text{CO} \quad \Delta G^o = 166.550 - 171.07T \] \(^{(6)}\)

\[ \text{H}_2\text{O(g)} + \text{C} = \text{CO} + \text{H}_2 \quad \Delta G^o = 133.300 - 141.07T \] \(^{(7)}\)

The initial and violent solution loss temperatures of coke can be measured by the composition of off gas at the apparatus shown in Fig. 1. The solution loss test was carried out at 400°C–1 300°C and other experimental conditions are shown in Section 2.2.1. The relationship between the composition of off gas and temperature is illustrated in Fig. 4. The curve marked with \( \text{H}_2 \) shows the reaction of coke with \( \text{H}_2\text{O} \) and marked with \( \text{CO} \) shows the reaction of coke with \( \text{CO}_2 \). For the reaction of coke with \( \text{CO}_2 \), the initial and violent solution loss temperatures are 826°C and 1 289°C respectively. Whereas for the reaction of coke with \( \text{H}_2\text{O} \), the two temperatures are 789°C and 1 164°C respectively. Evidently, irrespective of the initial or violent temperatures, the temperature with \( \text{H}_2\text{O} \) is lower than that with \( \text{CO}_2 \), 37°C lower for initial temperature and 125°C lower for violent temperature.

3.2. Effect of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) on the Gasification Rate

A 200±0.5 g sample with the grain size of 23–25 mm was placed into the furnace shown in Fig. 2. \( \text{N}_2 \) gas was then introduced into the furnace with a flowing rate of 0.8 L/min before 400°C. When the reaction temperature reached, \( \text{CO}_2 \) or \( \text{H}_2\text{O} \) was used instead with a flowing rate of 5 L/min. The reaction temperatures were set as 950°C, 1 000°C, 1 100°C and 1 200°C. After 2 hrs, \( \text{N}_2 \) was used again at a flowing rate of 2 L/min for cooling the sample until 100°C.

From Fig. 5, it can be seen that gasification rate of coke increases with the temperature. The gasification of coke with \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) is endothermic reaction, so temperature increase has benefited on the gasification. In addition at the zone of 950°C–1 200°C, gasification rate of coke reacting is higher with \( \text{H}_2\text{O} \) than with \( \text{CO}_2 \) at the same temperature. At 950°C, 1 000°C, 1 100°C and 1 200°C, the rates are 3.16, 1.94, 1.90 and 1.27 times faster with \( \text{H}_2\text{O} \) than with \( \text{CO}_2 \) respectively. As can be seen the difference of the two rates decreases with the increase of temperature, and this conclusion agrees with the literature.\(^{14}\)

In the reaction of coke with \( \text{CO}_2 \) and \( \text{H}_2\text{O} \), no solid product layer but the porous ash layer forms on the surface of unreacted core, and the unreacted core shrinks as the reaction proceeds. So The solution loss process is in line with the unreacted shrinking core model.\(^{13}\) Assuming the reaction occurring at one interface, the main reaction process includes the following: (1) \( \text{CO}_2 \) or \( \text{H}_2\text{O} \) diffuses through the gas phase boundary layer of coke; (2) \( \text{CO}_2 \) or \( \text{H}_2\text{O} \) diffuses into the surface of the unreacted coke through ash and stomata; (3) \( \text{CO}_2 \) or \( \text{H}_2\text{O} \) reacts with the coke; (4) \( \text{CO} \) or \( \text{H}_2 \) desorbs and diffuse away, as shown in Fig. 6.

If coke gasification process is controlled by the interfacial chemical reactions, the gasification reaction rate can be expressed by the equation:\(^{15}\)

\[ 1 - (1 - x)^{1/3} = kt \] \(^{(8)}\)
where \( k \) is the rate constant of the reduction reaction. If the gasification is controlled by the diffusion, the gasification reaction rate can be expressed by

\[
1 - (1 - x)^{2/3} + 2(1 - x) = kt. 
\]

According to the Eqs. (8) and (9), the experimental results are analyzed and the correlation coefficient \( R^2 \) are shown in Tables 2 and 3. From the two Tables, it can be found \( 1 - (1 - x)^{2/3} \) has a better linear relationship than \( 1 - (1 - x)^{3/3} + 2(1 - x) \). So the interfacial chemical reaction is the rate determining step, showing that the diffusion play a weak role in the experiment temperature range. Owning to the porous structure of coke outer layer, the diffusion resistance is very small and CO\(_2\) and H\(_2\)O can easily diffuse into the center of coke. Actually, the Reynold’s numbers (1 000–3 000) of the gas across the burden in the blast furnace is much larger than the Reynold’s numbers (2.64–13.96) of the gas across the samples in this experiments, showing the gas across the burden in the blast furnace much faster than that in this experiments. Thus, the gas diffusion is easier in the blast furnace than that in the experiments and play a weaker role in the gasification in the blast furnace.

### 3.3. Effects of CO\(_2\) and H\(_2\)O on CSR

After the reaction, the coke samples were put on I-type (CSR) drum. The grain diameter distribution of coke was measured after drum treatment, shown in Fig. 7. The diameter distribution was different for the different temperatures. The proportion of coke with a particle size > 10 mm (CSR) decreases with the temperature increasing, irrespective of reacting with CO\(_2\) or reacting with H\(_2\)O. However, the proportion of coke with particle sizes with 5 mm–10 mm and
−5 mm increases with the temperature. Compared with CO₂, CSR of coke reacting with H₂O is lower at 950°C, 1 000°C and 1 100°C, but higher at 1 200°C.

The relationship between CSR and SLR is shown in Fig. 8. Where there is a strong negative correlation between CSR and SLR, the specific relationship of them is shown in Eqs. (10) and (11). It is calculated that when SLR increases 1%, CSR reduces 1.200% reacting with CO₂, but reduces 0.786% reacting with H₂O, indicating at the same SLR the destruction of the coke by CO₂ is more intense than by H₂O.

\[
CSR_{\text{CO}_2} = 96.12047 - 1.200 \text{SLR} \% \quad (10)
\]

\[
CSR_{\text{H}_2\text{O}} = 90.12943 - 0.786 \text{SLR} \% \quad (11)
\]

3.4. Apparent Porosity of Coke after Reaction

The vacuum drainage method was used in the experiment to determine apparent porosity of coke. Figure 9 shows the relationships between the apparent porosity of coke and its change rate with the temperature, where its change rate is the differential value of apparent porosity to temperature. In both cases when coke reacts with H₂O and CO₂, the apparent porosity and its change rate both increase with the temperature. Due to that increasing temperature leads to much more solution loss of coke, forming new pores and unifying old holes by breaking their wall. Moreover, the apparent porosity and its change rate of coke are higher with CO₂ than with H₂O at the same temperature. It indicates that CO₂ can spread into a deeper depth of coke and form much more new pores than H₂O does.

3.5. Analysis of Interior Reaction of Coke

After the reaction, the coke sample was taken out from the reactor for the particle diameter measurement without drum treatment. For each sample, ten positions in axial direction were taken for diameter measurement, and the average of ten diameter value was defined as the particle diameter of coke sample. The particle diameter change of cokes after reacting with CO₂ and H₂O is shown in Fig. 10. The particle diameter of cokes decreases with temperature increasing, in particular when the temperature more than 1 200°C reduces obviously. In addition, the particle diameter of cokes after reacting with H₂O is less than that with CO₂ at the same temperature. Actually, when the reaction of gas-solid occurs with only gas product produced, the limited step of the reaction is interior diffusion. So the total reaction tends to be an interfacial reaction particularly when it at a fast reaction velocity, in other words, the interior reaction is very weak. The total reaction appears as core shrinking, or pores increasing of superficial particles, or both of them. However, the appearance is different for coke reacting with H₂O and CO₂, as shown in Fig. 10, the coke shrinks more after reacting with H₂O than that with CO₂.

Figure 11 shows the results of interior reaction of coke after the reaction carried on at the apparatus shown in Fig. 3. \(p_0\) is the bulk density of coke before reaction, \(d_0\) is the diameter of coke before polishing. In order to better show-
The relationship between \( \rho/\rho_0 \) and \( d/d_0 \) fitting curves are drawn using points. \( \rho/\rho_0 \) increases with the decrease of \( d/d_0 \), meaning that the amount of solution loss reduces from outside to inside. At the high temperature (1 100°C, 1 200°C and 1 250°C), \( \rho/\rho_0 \) of the sample after reacting with H\(_2\)O is larger than that with CO\(_2\), indicating the destruction of coke by H\(_2\)O is weaker than that by CO\(_2\). However at the low temperature (950°C and 1 000°C), \( \rho/\rho_0 \) of the sample after reacting with H\(_2\)O is smaller than that with CO\(_2\) in the coke outside but larger than that with CO\(_2\) in the coke inside, indicating the destruction of coke by H\(_2\)O is stronger than that by CO\(_2\) in the coke outside but weaker than that by CO\(_2\) in the coke inside.

4. Conclusions

The degradation behavior of coke reacting with CO\(_2\) and H\(_2\)O was studied in laboratory conditions. The following conclusions were obtained:

1. The initial solution loss temperatures of coke reacting with CO\(_2\) and H\(_2\)O are about 826°C and 789°C. The violent solution loss temperatures are about 1 289°C and 1 164°C respectively. The initial and violent solution loss temperatures of coke reacting are 37°C and 125°C lower with H\(_2\)O than with CO\(_2\).

2. The gasification rate of coke reacting is faster with H\(_2\)O than with CO\(_2\). The former is about 1.27–3.16 times of the latter but the difference of the two decreases with the increase of temperature.

3. CSR of coke reacting is lower with H\(_2\)O than with CO\(_2\) at 950°C–1 100°C but higher at 1 200°C. CSR reduces 1.200% with 1% increase of SLR reacting with CO\(_2\), but reduces only 0.786% for reacting with H\(_2\)O with the same SLR increase.

4. The coke’s apparent porosity and changing rate after reacting were both smaller with H\(_2\)O than with CO\(_2\). It is mainly due to the reaction that occurred closer to the coke particle surface with H\(_2\)O than with CO\(_2\). At the high temperature (1 100°C, 1 200°C and 1 250°C), the destruction of coke by H\(_2\)O is weaker than that by CO\(_2\). However, at the low temperature (950°C, and 1 000°C), the destruction of coke by H\(_2\)O is stronger than that by CO\(_2\) in the coke outside but weaker than that by CO\(_2\) in the coke inside.

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