Effect of Lignite Addition on Gasification Properties and Coke Strength after Reaction

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In order to clarify the effect of lignite addition on the CO_2 gasification properties and strength after reaction of coke, the carbon structure, micro morphology, specific surface area of coke were studied by X-ray diffraction (XRD), scanning electron microscope (SEM) and BET. The results show that the lignite can decrease the coke strength after reaction, especially for the lignite content in coke more than 8%. The results of X-ray diffraction profiles show that the change of the carbon structure has no connection with the addition content of lignite, and is not responsible for the decrease of the coke strength after reaction. However, because of the consume of isotropic and fine mosaic textures enhanced by lignite addition during gasification, the generation, enlargement and coalescence of coke pores were promoted, leading to the increase of specific surface area. With the addition content of lignite increasing, the homogeneous reaction, which is transition from surface reaction to, enhanced the permeation of CO_2 gas further into coke. The external reaction of lignite-enriched coke accelerated the rupture of bonds between coke particles, which results in the decrease of coke strength after reaction.

KEY WORDS: lignite; coke; gasification; strength after reaction; influence mechanism.

1. Introduction

Metallurgical coke, as a porous carbon material with high strength and low reactivity, acts as the skeleton of stock column. Therefore, it is irreplaceable and plays a decisive role in the permeability of the blast furnace. Coking coal produces certain amount of colloid in the process of carbonization, from the production and solidification of which coke was generated. The coke strength after reaction (CSR) and reactivity (CRI) are two important parameters to evaluate determining the quality of coke. A direct relationship between colloid formation and values of CSR and CRI and namely the behavior of metallurgical coke in blast furnace during production was noticed.

Due to the shortage and progressively rising price of coking coal, a series of exploratory studies has been carried out to explore cheaper carbon materials for partly replacing the application of coking coal in coke production. Lignite, an abundant and cheap resource, characterized as high reactivity and cohesionless, usually referred as a char. Attempts were made by Mollah et al. to produce blast furnace coke from the lignite, whereas the products from lignite was too fragile and reactive to be utilized as the blast furnace coke. Besides, other researchers also tried to control coking procedures in order to obtain a strong coke suitable for industrial application, but strength of these cokes could hardly meet the demand of metallurgical coke. Finally, Kanai et al. found that the strength of coke containing low-quality coals was mainly controlled by the rate of non-adhesion grain boundaries rather than the specific surface area or porosity of coke.

However, the degradation mechanism on strength of coke containing lignite after reaction was rarely reported until date. Based on the results of our previous studies, investigations on the effect of lignite addition on the pore structure and the carbon structure of coke after gasification reaction were carried out to clarify the mechanism in order to explore an accessible method to produce blast furnace coke from the lignite.

2. Experimental Materials and Methods

2.1. Preparation of Samples

The coking coal (labeled as PC) was sampled from a coking plant. The lignite (labeled as HC) was obtained from a coal mine with an abundant production near the coking plant. The coals were crushed and sieved to be less than 1 mm as the samples for coking treatment. In order to eliminate the effect of moisture on the quality of coke, samples were dried at 105°C for 3 h in a drying oven. Basic properties of coking coal and lignite were listed in Table 1.
0/100, 2/100, ......10/100, which was labeled as RC, HC-2, ......HC-10. The blend samples were mixed together for 20 min and approximately 5±0.1 g of blend was loaded into a graphite crucible. An iron rod was inserted into the graphite crucible to provide 6 kPa pressure on mixed sample to simulate the effect of coal stock column during coking process. The schematic diagram of mentioned was shown in Fig. 1. The graphite crucible was placed into a muffle furnace and heated from ambient temperature to 500 °C at the rate of 5 °C/min and then to 950 °C at the rate of 10 °C/min in N2 gas atmosphere. After carbonizing at 950 °C for 1 h, the sample was cooled to ambient temperature in N2 atmosphere. The above carbonization method has been reported in our previous study.15)

2.3. CO2 Gasification and Coke Strength Test

About 2±0.1 g of the prepared coke was charged into a temperature control furnace to be heated in N2 atmosphere. When the furnace temperature reached to 1200°C, the neutral atmosphere was switched to CO2 with a flow rate of 4 L/min and hold for 30 min. The weight loss of the samples was measured by an electric balance and recorded by a computer. The samples were cooled in N2 atmosphere after gasification and was labeled as GRC, GHC-2, ......GHC-10. The schematic diagram of temperature control furnace was shown in Fig. 2. The coke strength after reaction was determined by using an I-type drum (φ130 mm, L700 mm) at a rotation speed of 20 r/min for 30 min. The samples were took out from the drum every 5 min and the coke lump size of more than 1 mm was weighed. The coke strength after reaction was calculated by the following Eq. (1):

\[ T1_{1+} = W_{1+}/W * 100 \] ...........................(1)

Where W is the initial mass of coke before reaction, and \( W_{1+} \) is the mass of the coke lump size of more than 1 mm.7)

3. Results and Discussion

3.1. Effect of Lignite Addition on the Drum Strength after Reaction of Coke

The weight loss curves of coke with the increase of lignite content are exhibited in Fig. 3. It is shown in the comparison among coke samples that the weightless rate of coke gradually increased with the increasing of lignite addition. When the addition of lignite addition reached 10%, the weight loss rate soared up to 50% within 30 min gasification. This increment was probably related to the catalytic effect of lignite on the CO2 gasification reaction. The index of \( T1_{1+} \) was introduced to determine the strength of coke before and after CO2 gasification reaction in order to study the effect of lignite addition on the strength of coke, the value of which are shown in Fig. 4. The strength of coke after gasification decreases dramatically at the first 5 min, especially for coke with the addition content of lignite over 8% and then tends to be steady as shown in Fig. 4(a), which is totally different from that of the unreacted coke as presented in Fig. 4(b). The obtained result indicates that lignite can degrade the strength of coke, and the degradation degree is proportional to the addition content of lignite.15)

It is well known that the gasification reaction of coke is relevant to many factors, such as chemical reaction activity and structure feature.16,17) Therefore, in order to determine the effect mechanism of lignite addition on the gasification reaction, micrograph morphology, carbon structure, pore structure of coke have been in-depth investigated in follow.

3.2. Effect of Lignite Addition on the Carbon Structure of Reacted Coke

X-ray diffraction profiles of the coke before and after
the main mineral in these samples is quartz at around 26°, observed along with carbon based peaks. The characteristic peak (002) band at ~25° can been seen clearly in the X-ray diffraction profile, which is related to the stacking space of the aromatic layers. Another characteristic peak (100) band at ~42° is shown, whereas the diffraction peak (101) of the three-dimensional structure of the crystal is not observed probably due to the superimposition of the two characteristic peaks of (100) and (101) during the gasification reaction.

From the results as shown in Fig. 5(a), the crystallite height of (002) band for unreacted coke is much higher. However, with the increasing of lignite content, the crystallite height of (002) band becomes lower gradually, indicating that the amount of layered graphite-like structures becomes less. Compared with the X-ray diffraction profiles of the unreacted coke, the X-ray diffraction profiles of reacted lignite-enriched coke increases gradually and almost overlaps each other, as shown in Fig. 5(b).

The values of Lc for unreacted cokes firstly increase from 17.80 Å to 19.08 Å and then decreases to 15.05 Å, whereas the values of Lc for reacted cokes slightly decrease to 17–18 Å as showed in Figs. 6(a) and 6(b). Meanwhile, it can be observed that no matter what the content of lignite addition is, the values of d002 for reacted lignite-enriched coke are found decreasing from ~3.60 Å to ~3.50 Å slightly, as listed in Table 2. Through calculating the $N_{ave}$ (Average number of layers in crystalline stacks: $N_{ave} = Lc/d_{002} + 1$) as presented in Fig. 6(c), it is found that the $N_{ave}$ of the reacted coke is unchanged and virtually independent on the content of lignite addition. It should be pointed out that the reason why the $N_{ave}$ of reacted lignite-enriched coke still increases at the content of lignite addition more than 8% is that the temperature rising is more responsible for the growth of the carbon structure than the gasification reaction. Thus, the carbon structure of coke matrix changes into more ordered. However, the value of $L_a$ regarding the crystalline diameter decreases to 45–50 Å after the gasification, not connected with the addition content of lignite, indicating that CO2 gas reacted preferentially with the carbon on the edge of crystallite. The reaction rate is faster in the plane perpendicular to (002) plane than in the (002) plane. The schematic diagram of the effect of CO2 on the carbon structure is shown in Fig. 7. It is consistent with the study reported by Kashiwaya and Ishii. These results testify that changes in the carbon structure are the not main cause of the strength decrease of the reacted lignite-enriched coke, i.e. $L_c$, $d_{002}$, and $L_a$. There may be another dominant factor.

3.3. Effect of Lignite Addition on the Pore Structure of Coke

3.3.1. Evolution of Macroscopic Pores

The difference of the pore structure of original coke and lignite-enriched coke after and before gasification are well...
visible in Fig. 8. As we can see in Figs. 8(a) and 8(c), the surface of original coke and enriched-coke is flat and smooth with uneven pore distribution. However, compared with the round dashed line described in Figs. 8(a) and 8(b), the visible pore changes from approximately circular in the original coke to irregular in the reacted coke. This result indicates that macroscopic pores provide a good dynamic condition for CO\textsubscript{2} gasification reaction, which is very different from the previous study.\textsuperscript{21) Additionally, compared with the surface image binarized using image analyzing software as shown in the bottom right image of Figs. 8(c) and 8(d), the surface of the coke matrix also changed very substantially, which varied approximately flat to obviously rough. The highly porous structure appears mainly due to the consume of isotropic and fine mosaic textures during the gasification.\textsuperscript{17) From the Figs. 8(e) and 8(f), with the lignite addition ratio of 6%, some layered structures were observed in the coke matrix,\textsuperscript{22) which resulted in the degradation of coke strength and absorption of some alkalis into the coke matrix. The recycle of alkalis in blast furnace has the negative effect of alkalis on the coke properties.\textsuperscript{23,24) The potassium or sodium vapor would penetrate into the coke matrix through pores and absorb on the pore, resulting in enhancing the solution loss reaction of coke. The more detailed study is

Table 2. Carbon structure parameter (d\textsubscript{002}) of coke before and after CO\textsubscript{2} gasification at 1 200°C.

| Ratio, % | 0 | 2 | 4 | 6 | 8 | 10 |
|----------|---|---|---|---|---|----|
| Before gasification reaction, Å | 3.59 | 3.61 | 3.61 | 3.61 | 3.60 | 3.63 |
| After gasification reaction, Å | 3.53 | 3.53 | 3.54 | 3.55 | 3.54 | 3.53 |

Fig. 7. Schematic diagram of the effect of CO\textsubscript{2} on the carbon structure.

Fig. 8. SEM images of coke before and after gasification, (a, b): RC and GRC, (c, d): HC-2 and GHC-2, (e, f): GHC-6.
required on the degradation mechanism of lignite-enriched coke strength by alkalis.

3.3.2. Evolution of the Specific Surface Area

It is well known that coke is porous solid, the gasification reaction with CO₂ occurs not only at the outer surface of the coke particle, but also at the inner surface. Also, the micropore accounts for 90% surface area of coke, which is main reaction area of the gasification reaction.25) As listed in Table 3, the specific surface area of coke before gasification increases gradually with the increase of lignite content, varying from 1.25 to 3.83 m³/g. However, the specific surface area of reacted lignite-enriched coke increases rapidly (from 18.21 to 66.68 m³/g), basically related to the generation and enlargement of pores.26) Then, the surface area decreases to 35.25 m³/g due to the mergence between pores.27) The results indicate that the lignite would not significantly affect the surface area for the unreacted coke, probably attributed to the formation of the plastic state during carbonization.27) Nevertheless, the higher reactive lignite in the coke would increase the amount of available carbon reactive sites and accelerate the generation, enlargement and coalescence of pores of reacted lignite-enriched coke during the gasification process.28) It can be also found that compared with the pores of reacted lignite-enriched coke during the gasification reaction, the effect of lignite addition provide a favorable condition for the penetration of CO₂ along the macrospores into the microspores.29) It indicates that the coalescence or collapse of the pores results in the transition from microspores to macropores, and finally exceeds the measurement range of instrument.

The generation and expansion of pores caused by the lignite addition provide a favorable condition for the permeation of CO₂ along the macropores into the micropores during gasification reaction. It should be pointed out that although the macropores mainly act as the transportation corridor during gasification reaction, the effect of lignite addition on the distribution of macropores and the degree of the transformation from microspores to macropores need further study.

### Table 3. BET surface area and pore volume of coke before and after CO₂ gasification.

| Ratio, % | Before gasification | After gasification |
|---------|---------------------|--------------------|
|         | BET surface area, m³/g | Pore volume, 10⁻³ mm³/g | BET surface area, m³/g | Pore volume, 10⁻³ mm³/g |
| 0       | 1.25               | 1.27              | 18.21               | 31.83               |
| 2       | 2.11               | 2.25              | 54.46               | 58.22               |
| 6       | 3.62               | 5.47              | 66.68               | 80.25               |
| 10      | 3.83               | 8.18              | 35.25               | 45.06               |

### Table 4. Pore volume of coke before and after gasification.

| Ratio, % | Pore volume, 10⁻³ mm³/g | Conversion rate | Absolute pore volume of mass loss | Volume of pores generated | η |
|---------|-------------------------|-----------------|----------------------------------|---------------------------|---|
| 0       | 1.27                    | 24.22           | 0.2497                           | 0.0148                    | 16.87 |
| 2       | 2.25                    | 58.22           | 0.3089                           | 0.0335                    | 9.21 |
| 6       | 5.47                    | 80.25           | 0.3545                           | 0.0514                    | 6.89 |
| 10      | 8.18                    | 45.06           | 0.5087                           | 0.0364                    | 13.97 |

### 3.4. The Influence Mechanism of Lignite Addition on the Strength after Gasification of Coke

Considering that the micropore play an important role during gasification, the pore volume of micropores increases as well with the lignite content as the above observation. However, as listed in Table 4, it can be found that the absolute pore volume of mass loss of the carbon material is greatly larger in comparison with the volume of pores generated during gasification and increases with the lignite content increasing. The η (η = absolute pore volume of mass loss/ volume of pores generated) is from 6.89 to 16.87. In other words, the gasification reaction of coke particles mainly occurs on their external surface rather than pores inside coke particles.29)

According to the schematic representation of the coke lump consumed at a high conversion as shown in Fig. 9, the gasification reaction changes from step (a) to step (b), the pores existing in the coke matrix will enlarge and merge. Then, the coke particle will shrink due to the external reaction. Our previous study reports that under the degradation effect of lignite, the bonding between coke particles becomes weaker.11) And inevitably, the rupture of bonds under the influence of the external reaction results in the connection between coke particles becoming looser as shown in Fig. 8(d). The reactant gas would easily penetrate into the coke through the void between coke particles, leading to a more intense gasification reaction. Thus, both the thinner coke wall and the looser bonds may be the major reasons for the decrease of the strength of the reacted lignite-enriched coke.

In addition, according to Rouzaud30) and Stanislav,31) graphite crystals can concentrate on the surface of the grains or pores and probably decrease the reactivity of coke. Hence, as the gasification progresses, the bonds between coke particles are broken and lower reactive graphite structure will cover on the surface of the coke particle, as shown in Fig. 9. Since graphite has high lubricity and can act as lubricant to facilitate the graphene layers easily sliding...
along each other.\textsuperscript{31,32} On macro level, the reacted lignite-enriched coke, especially for the lignite content of more than 4%, is broken up quickly in the drum experiment.

As we all know that most of isotherms reaction are fitting to a double exponential model,\textsuperscript{33} which is defined by Eq. (2):

\[ y = A \exp(-kt_{1}) + B \exp(-kt_{2}) + C \]  \hspace{1cm} (2)

Where \( y \) represents the weight percentage of coke, \( t \) is the time, \( k_{1} \) and \( k_{2} \) are the exponential constants for the reaction of carbon with CO\(_{2}\) controlled by C–CO\(_{2}\) reaction and the reaction of carbon with CO\(_{2}\) controlled by CO\(_{2}\) and CO diffusion, respectively. The pre-exponential factors A and B imply the intervals at different controlling process and the C is the y-intercept.

The exponential constant value of coke gasification at 1200\(^{\circ}\)C is listed in Table 5. As we can see, \( k_{1} \) values are almost along each other.\textsuperscript{31,32} On macro level, the reacted lignite-enriched coke, especially for the lignite content of more than 4%, is broken up quickly in the drum experiment.

### Table 5. Kinetic Parameters Obtained at 1200\(^{\circ}\)C for 30 min.

| Ratio, % | \( k_{1} \times 10^{-2} \) (sec\(^{-1}\)) | \( k_{2} \times 10^{-2} \) (sec\(^{-1}\)) | A          | B          | C          | \( R^{2} \) |
|---------|-----------------|-----------------|-----------|-----------|-----------|-----------|
| 0       | 6.69            | 0.36            | −0.95     | −315.56   | 58.71     | 0.9990    |
| 2       | 10.01           | 0.33            | −1.67     | −305.89   | 307.73    | 0.9998    |
| 4       | 12.26           | 0.51            | −3.09     | −351.43   | 134.24    | 0.9998    |
| 6       | 1.33            | 1.33            | −52.03    | −52.03    | 104.84    | 0.9998    |
| 8       | 1.98            | 1.98            | −46.34    | −46.34    | 92.67     | 0.9998    |
| 10      | 2.14            | 2.14            | −50.98    | −50.98    | 103.88    | 0.9996    |

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