Influence of anthracite, char, coke and graphite microstructures on reactivity

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Abstract – In order to study the influence of anthracite, char, coke and graphite microstructures on reactivity, a thermogravimetry experiment was carried out for these carbons at 1200 °C. As a comparison, some experiments were conducted at 1600 °C. The microstructure of anthracite, char, coke and graphite after treatment was depicted by SEM. The results showed that reaction of char 1, CA 3 and coke 5 in CO₂ gas at 1600 °C led to a large, smooth pore structure, in contrast to the carbons’ reaction at 1200 °C. The porosity of all carbons increased with reaction time and the porosity of graphite was far less than the other carbons. Besides, the variation of porosity determined the value of the reactivity. An appropriate carbon type can be chosen based upon reactivity for pulverized coal injection in a blast furnace.

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Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>D</td>
<td>Diffusion coefficient (m²·s⁻¹)</td>
</tr>
<tr>
<td>Jₙ</td>
<td>Diffusion flux (g·m⁻²·s⁻¹)</td>
</tr>
<tr>
<td>kₚ</td>
<td>Mass transfer coefficient (m·s⁻¹)</td>
</tr>
<tr>
<td>L</td>
<td>Characteristic length (m)</td>
</tr>
<tr>
<td>R</td>
<td>Gas constant (J·mol⁻¹·K⁻¹)</td>
</tr>
<tr>
<td>Re</td>
<td>Reynolds number</td>
</tr>
<tr>
<td>Sc</td>
<td>Schmidt number</td>
</tr>
<tr>
<td>W₀(A,B)</td>
<td>Collision integral of A and B</td>
</tr>
<tr>
<td>Sh</td>
<td>Sherwood number</td>
</tr>
<tr>
<td>T</td>
<td>Temperature (K)</td>
</tr>
<tr>
<td>u</td>
<td>Flow velocity (m·s⁻¹)</td>
</tr>
<tr>
<td>v</td>
<td>Kinematic viscosity (m²·s⁻¹)</td>
</tr>
<tr>
<td>ρ</td>
<td>Density (kg·m⁻³)</td>
</tr>
<tr>
<td>η</td>
<td>Dynamic viscosity (N·s·m⁻²)</td>
</tr>
</tbody>
</table>

Reactivity is defined as the rate at which the char reacts in an oxidizing/reducing atmosphere, and subsequently its devolatilization, describing the case with which the char reacts with the gasification agent, CO₂ [1–3]. The stronger the reactivity of the coal, the more coke will be conserved in the blast furnace. The reactivity of coals strongly depends on the coal properties and the operating conditions. Coke is essential and the most expensive raw material for iron-making in a blast furnace. Due to growing costs and increasing environmental concerns, efficient utilization of coke has become one of the top priorities of iron producers. Coke performs many roles in a blast furnace. In recent years, there has been growing interest in examining the role of the inorganic matter of coals on the reactivity and hence on coke strength in high-temperature zones of a blast furnace [4]. The effect of coal organic matter such as the rank and maceral types on coke strength and reactivity has been extensively studied by some authors [5, 6].

Although reactivity may be efficiently determined by thermogravimetry, no standard testing method has been established as yet in regard to pulverized coal injection performance [7]. In this context, CO and CO₂ were used to treat anthracite, char, coke and graphite; also, thermogravimetry was used to describe the reactivity. CO was chosen for the removal of volatiles in the carbons and CO₂ was used to react with the carbons. The microstructure of anthracite, char, coke and graphite after treatment was depicted by SEM.
1 Experimental

Five carbons (as-received) were used in the present study as reductants, including char 1, CA 3 (calcined anthracite), coke 5, coke 7 and pure graphite. The major differences among the various types are in the content of fixed carbon (FC), volatile matter (VM), sulfur content and ash composition. The graphite is spectroscopically pure and contains no ash. These properties are listed in Table 1. The reactivity of these carbons was determined by weight loss of the carbon in 500 ml min\(^{-1}\) CO\(_2\) gas flow at 1200 °C. Also, treatments with 500 ml min\(^{-1}\) CO\(_2\) at 1600 °C and 1500 ml min\(^{-1}\) CO at 1200 °C were used for microstructure and weight loss analysis. About 2-g carbon samples (8–10 mm diameter) were used for all tests. The experiments were carried out in a 32-mm inner diameter (ID) alumina reaction tube.

2 Results and discussion

2.1 Carbon treated in CO\(_2\) and CO

The results of carbons treated in 500 ml min\(^{-1}\) CO\(_2\) and 1500 ml min\(^{-1}\) CO at 1200 °C for 40 min are shown in Table 2.

It can be seen from Table 2 that after the treatment in CO\(_2\) gas the weight loss of the carbons is in the range of 20–84%. Char 1 has the highest reactivity in CO\(_2\) and graphite has the lowest reactivity in CO\(_2\). After the treatment in CO gas the weight loss of cokes and graphite is nearly zero, and char 1 and CA 3 have approximately 10% weight loss. As-received and CO\(_2\)-treated carbons were sent to the Particle and Surface Sciences Applications Laboratory, Sydney, for mercury porosimetry analysis. The results are summarized in Table 3.

It can be seen from Table 3 that after treatment in CO\(_2\) at 1200 °C for 40 min:

1. The pore volume (ml g\(^{-1}\)) was increased for all carbons.
2. The total pore area increased for CA 3 and coke 7 and decreased for char 1, coke 5 and graphite.
3. The average pore size significantly increased for char 1 and coke 5, and slightly increased for CA 3 and graphite, but decreased for coke 7.

4. Porosity increased for all carbons.

Porosimetry analysis was also used for treated carbons with CO gas (1500 ml min\(^{-1}\) at 1200 °C for 40 min). It was found that, generally, treatment in CO gas did not significantly affect the microstructures of all carbons.

Figures 1–5 show the microstructures of all carbons treated in CO\(_2\) in the experiment.

From these Figures, it can be seen that oxidation of char 1, CA 3 and coke 5 in CO\(_2\) gas at 1600 °C leads to a large, smooth pore structure, in contrast to the materials oxidized at 1200 °C. Also, the porosity of all carbons increases with time at 1200 °C. In Figure 1, the porosities of char treated with CO\(_2\) for 40 min and 90 min at 1200 °C were similar and they were larger than that of as-received char. The char treated with CO\(_2\) for 10 min at 1600 °C has the largest porosity of all the chars. The other carbons show the similar behavior, except graphite. The CA 3
shows distinctly anisotropic behavior, with the formation of layered pores (Fig. 2) on heating. On the surface of the CA 3 at 1600 °C were large acicular mullite (3Al₂O₃·2SiO₂) crystals derived from the coal ash. This indicated high local ash content and wetting of the carbon surface by the slag phase. In contrast, in the other carbons studied the ash concentrations were low and the slags were generally non-wetting on the carbons. From Figure 5, the porosity of graphite was relatively less than the other carbons after reaction for 40 min with CO₂ at 1200 °C; also, the graphite treated with CO₂ for 10 min at 1600 °C did not show obviously larger porosity than that treated with CO₂ for 40 min and 90 min at 1200 °C.

2.2 Calculation of the ideal reaction rate of carbon reactivity in CO₂

\[ k_m = Sh' D / L \]  
\[ Sh = 0.664S_c^{0.343} Re^{1/2} \]  
\[ Sc = v / D = \eta / (\rho D) \]  
\[ Re = uL / \nu = uL \rho / \eta. \]
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Reaction rate: $3.57 \times 10^{-5} \times 3.77 = 1.35 \times 10^{-4}$ g s$^{-1}$.

The reaction rate was used to calculate the reactivity of pure carbon at different times. The calculated and experimentally determined reactivity of the carbons in CO$_2$ are presented in Figure 6.

It can be seen from Figure 6 that the calculated reaction rate of pure carbon with CO$_2$ was higher than graphite but lower than the other carbons. It is also shown in Figure 6 that char1 had the highest reactivity and graphite had the lowest reactivity. It has been pointed out that the reaction rate of gasification of carbon is mainly affected by particle size, temperature, CO$_2$ gas pressure and flow rate, and the pore surface area of the carbon [8]. In the present study the particle size, temperature, CO$_2$ gas pressure and flow rate were all fixed. Therefore, reactivity was closely related to the porosity of the carbons for the current work. From Table 3, after the carbons were treated in 500 ml min$^{-1}$ CO$_2$ at 1200 °C for 40 min, the increase in porosity for char 1, CA 3, coke 5, coke 7 and graphite was 52.53%, 21.01%, 33.17%, 7.91% and 0.96%, respectively. Compared with Figure 6, the reactivity of char 1, coke 5, CA 3, coke 7 and graphite decreased gradually. It can be concluded that the variation of porosity determined the value of the reactivity.

Furthermore, it would give a good guide for choosing an appropriate carbon type as fuel for a blast furnace.

### 3 Conclusions

Based on the present investigations of reactivity carried out on the carbons char 1, CA 3, coke 5, coke 7 and graphite, the conclusions are as follows. The reaction of char1, CA 3 and coke 5 in CO$_2$ gas at 1600 °C led to a large, smooth pore structure, in contrast to carbons’ reaction at 1200 °C. Meanwhile, the porosity of all carbons increased with time and the porosity of graphite was far less than the other carbons after reaction for 40 min with CO$_2$ at 1200 °C. The variation of porosity determined the value of the reactivity. Therefore, an appropriate carbon type can be chosen based upon reactivity for pulverized coal injection in a blast furnace.

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