Effect of Hydrogen Addition on Reduction Behavior of Ore Layer Mixed with Coke

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Low RAR (reducing agent rate) operation of the blast furnace is one of effective techniques for reducing CO₂ emissions. Coke mixed charging is a well-known and available measure to achieve low RAR operation by improving permeability and reducibility. Utilization of hydrogenous reducing agents is also an efficient measure. A reduction test under load was performed to investigate the effect of coke mixing with hydrogen addition on reduction behavior of the ore. Simultaneous use of coke mixing and hydrogen addition accelerated the reduction rate through the carbon gasification rate, and it was also decreased pressure drop. The effect of coke mixing and hydrogen addition on blast furnace operation was examined using a two-dimensional mathematical simulation model. In case of the ore layer mixed with coke, hydrogen addition in the reduction gas increased the hydrogen reduction ratio and decreased the direct reduction ratio. As a result, RAR decreased and permeability improved.

KEY WORDS: blast furnace; CO₂ emission; low RAR operation; coke mixed charging; hydrogen; reducibility; carbon gasification.

1. Introduction

Reduction of CO₂ emissions is a very important issue in the steel industry. Especially, CO₂ exhausted from iron-making plants accounts for about 70% of total steel works CO₂ emissions. Therefore, low RAR operation of blast furnace is effective for reducing CO₂ emissions,1) and iron-making research and development oriented toward low RAR operation of blast furnace is expected. As a past measure to achieve low RAR operation, development of burden distribution control²,³) was mainly carried out with the aim of increasing gas utilization and decreasing heat loss. The main content of research and development was radial distribution control of Lo/Lc³,⁴) or particle size.⁵,⁶) Coke mixed charging was also developed recently to improve reducibility and permeability.⁷,⁸) and is now applied to actual operation.

As an other measure for reduction of CO₂ emissions, high expectations are placed on injection of hydrogenous reducing agents into the blast furnace.⁹) Because this technique utilizes hydrogen instead of carbon as a reducing agent, it is considered an innovative technique for reducing CO₂ emissions. In past research, natural gas was mainly utilized as the hydrogenous reducing agent, and was injected from the tuyere either singly or with pulverized coal. Reformed COG injection technology was also investigated by COURSE50 project in Japan as an innovative technology for reducing CO₂ emissions.¹⁰,¹¹)

In past studies, reduction behavior in the ore layer mixed with coke was investigated, and reduction behavior by hydrogen gas¹²–¹⁵) was also investigated. In both cases, the reduction rate of the ore increased. However, no previous research has considered both reduction behavior of ore in the ore layer mixed with coke and reduction behavior of ore by hydrogen gas. In recent blast furnace operation, coke mixed charging is applied to most actual blast furnaces, although the mixed coke ratio is different. For innovative reduction of CO₂ emissions, clarification of the effect of hydrogen addition on the reduction behavior of the ore layer mixed with coke is important, envisioning future use of hydrogen reducing agents. The changes in blast furnace operation due to use of coke mixing and hydrogen addition are also an important subject to be investigated.

In this study, a reduction test under load was performed to investigate the reduction behavior of the ore layer mixed with coke, and the effects of hydrogen addition on the reduction rate of ore and carbon gasification rate of coke in the ore layer mixed with coke were estimated. Next, a mathematical analysis using a two-dimensional blast furnace operation simulator was performed for the case of utilizing a hydrogen reducing agent with the ore layer mixed with coke, and the change in reduction ratio and temperature and reduction degree distributions in the blast furnace were examined.

2. Experimental Procedure

The effects of hydrogen addition on the reduction behav-
ior of the ore layer mixed with coke were investigated using a under-load-reduction test system. A schematic illustration of the experimental apparatus is shown in Fig. 1. Sinter and coke were used in this test. The amount of sinter was 900 g, and the sinter particle size was 10–15 mm. As coke mixing conditions, 25 g or 68 g of coke was mixed uniformly in the sinter (900 g). The coke particle size was 10–15 mm. The sinter and coke mixture was set into a carbon crucible (100 mm), and sandwiched between coke bed. Because the thickness of the ore layer mixed with coke increased when amount of mixed coke increased, corresponding to the amount of mixed coke, the total height of the sample in the crucible was held constant by adjusting the amount of coke above and below the ore layer mixed with coke. The chemical compositions of the sinter and coke are shown in Table 1.

The crucible was set in an electric furnace, and a reduction was performed under conditions simulating gas composition and temperature in a blast furnace. In this experiment, the gas composition and heating pattern were decided referring to measurements by the vertical probe at Chiba No. 1 and 2 blast furnaces. The gas flow rate was 1.8 Nm³/h. The gas composition is shown in Fig. 2, and the heating pattern and load are shown in Fig. 3. Hydrogen gas (H₂) was added by replacement with CO so that CO+H₂ was constant. Outlet gas collected from the furnace top was analyzed by gas chromatography. The reduction rate of sinter and the carbon gasification rate of coke were calculated by the oxygen balance and carbon balance in the inlet and the outlet gases, respectively. The total reduction degree was calculated by the ratio of amount of reduced oxygen relative to the amount of oxygen for reduction in sinter before the test.

3. Experimental Results and Discussion

3.1. Effect of Mixed Coke and Hydrogen Gas on Reduction Degree and Maximum Pressure Drop

The effect of the mixed coke and hydrogen gas on the reduction degree at 1100°C is shown in Fig. 4. The reduction degree increased as the mixed coke ratio increased, and also increased as the hydrogen gas concentration increased at all mixed coke ratios. Especially, the reduction degree in

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Table 1. Chemical compositions of sinter and coke (Unit : mass%).

<table>
<thead>
<tr>
<th></th>
<th>T–Fe</th>
<th>FeO</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>MnO</th>
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<tr>
<td>Sinter</td>
<td>57.6</td>
<td>9.87</td>
<td>9.68</td>
<td>5.00</td>
<td>1.93</td>
<td>1.26</td>
<td>0.36</td>
</tr>
<tr>
<td>Ash</td>
<td>11.5</td>
<td>0.9</td>
<td>87.6</td>
<td>0.47</td>
<td>0.25</td>
<td>6.35</td>
<td>3.04</td>
</tr>
</tbody>
</table>

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Fig. 1. Schematic illustration of experimental apparatus.

Fig. 2. Experimental condition (gas composition).

Fig. 3. Experimental conditions (heating pattern and load).

Fig. 4. Effect of mixed coke ratio and hydrogen gas concentration on reduction degree.
the case of the ore layer mixed with coke was increased by hydrogen addition more than increase of reduction degree in the case of the ore layer. It was presumed that the increase in the reduction rate by hydrogen addition in the ore layer mixed with coke was greater than the sum of the increase in the reduction rate by hydrogen addition and the increase in the reduction rate by coke mixing.

The effect of the mixed coke and hydrogen gas on maximum pressure drop is shown in Fig. 5. The maximum pressure drop decreased as the mixed coke ratio increased, and the maximum pressure drop decreased further by hydrogen addition. This is estimated to be due to improvement of the high temperature properties of the ore layer such as decrease in shrinkage by the increase of reduction degree due to hydrogen addition in the reduction gas.

3.2. Effect of Mixed Coke and Hydrogen Gas on Carbon Gasification

In case of mixing coke in the ore layer, CO₂ was formed by reduction reaction between the ore in the ore layer mixed with coke and CO, and CO was regenerated by carbon gasification reaction between the coke in the ore layer mixed with coke and CO₂ formed by reduction. After that, regenerated CO was reacted with the ore in the same layer as reducing agent. As a result of these continuous reactions, reduction rate of the ore was accelerated. Therefore, carbon gasification reaction (Eq. (1)) is one of the important reactions for investigation of reduction behavior of the ore in the ore layer mixed with coke.

\[
C + CO₂ = 2CO \quad \text{(1)}
\]

When the reduction gas contains H₂, Eq. (2) should be considered as additional carbon gasification reactions.

\[
C + H₂O = CO + H₂ \quad \text{(2)}
\]

Equation (1) is called a solution-loss reaction, and Eq. (2) is called a water-gas reaction. Thus, in case of a reduction gas with hydrogen addition, it is important to clarify the effect of both reactions (Eqs. (1) and (2)) on accelerating reduction. Therefore, the effect of hydrogen addition in the reduction gas on the gasification rate of the mixed coke in the ore layer was investigated.

The effect of the hydrogen addition on the carbon gasification in case of the ore layer (mixed coke ratio: 0%) and the ore layer mixed with coke (mixed coke ratio: 7.6%) is shown in Figs. 6 and 7, respectively. The value of the x-axis was converted to temperature from time by Fig. 3. The carbon gasification rate is the sum of the reaction rates of Eqs. (1), (2) and (3). Equation (3) is called a direct smelting reduction reaction.

\[
FeO + C = Fe + CO \quad \text{(3)}
\]

In case of the ore layer shown in Fig. 6, the starting temperature of the carbon gasification reaction decreased by hydrogen addition. In case of the ore layer mixed with coke shown in Fig. 7, the starting temperature of the carbon gasification reaction decreased by hydrogen addition, in the same manner as with the ore layer without mixed coke, and furthermore, carbon gasification rate increased totally. And in case of hydrogen addition, the carbon gasification rate decreased in the high temperature zone around 1 500°C, independent of the mixed coke ratio.

The decrease in the starting temperature of the carbon gasification reaction was due to the lower starting temperature of the water-gas reaction (Eq. (2)) than the starting temperature of solution-loss reaction (Eq. (1)). And the reduction rate by H₂ was larger than the reduction rate by CO as reported by Ono et al. In other words, the rate of H₂O formed by H₂ reduction is larger than the rate of CO₂ formed by CO reduction. Therefore, it is estimated that the H₂O reacted with coke in the ore layer mixed with coke was greater than the CO₂ reacted with coke in the ore layer.

![Fig. 5. Effect of mixed coke ratio and hydrogen gas concentration on maximum pressure drop.](image)

![Fig. 6. Change in carbon gasification rate with temperature in case of ore layer.](image)

![Fig. 7. Change in carbon gasification rate with temperature in case of coke mixed ore layer.](image)
mixed with coke, and consequently, the water-gas reaction (Eq. (2)) was accelerated. The decrease in the carbon gasification rate in the high temperature zone was due to decrease in direct smelting reduction reaction (Eq. (3)), because reduction rate in the low temperature zone was accelerated and reduction degree reached in the high temperature zone increased.

3.3. Acceleration of Carbon Gasification by Hydrogen Addition

The acceleration effect of the carbon gasification of coke in the ore layer mixed with coke by reduction gas with hydrogen addition was examined. In this study, the increase in the carbon gasification rate by hydrogen addition was expressed as $\Delta RC$ (Eq. (4)).

$$\Delta RC = \Delta RC_1 - \Delta RC_2$$

$$= (RC_{ij} - RC_{0,j}) - (RC_{i,j} - RC_{0,0})$$

$RC_{ij}$ is the carbon gasification rate in case of mixing coke in the ore layer and hydrogen addition, $RC_{0,0}$ is the carbon gasification rate in case of the ore layer, and $RC_{0,j}$ is the carbon gasification rate in case of the ore layer and hydrogen addition, $i$ is the mixed coke ratio (%), $j$ is the hydrogen gas concentration (%). Thus, $\Delta RC_1$ is the increase in the carbon gasification rate by coke mixing and hydrogen addition, $\Delta RC_2$ is the increase in the carbon gasification rate by coke mixing. In case of the ore layer and the ore layer mixed with coke, it was examined about the increase in carbon gasification rate by hydrogen addition in the reduction gas.

Figure 8 shows the effect of hydrogen addition in the reduction gas on $\Delta RC$ in case of mixed coke ratio 0% and 7.6%. Hydrogen gas concentration was increased from 0% to 4%. $\Delta RC$ by hydrogen addition for the mixed coke ratio of 7.6% was larger than that for the mixed coke ratio of 0%. The carbon gasification rate was accelerated in the temperature zone after the carbon gasification reaction started. Therefore, it is thought that the reaction (Eq. (2)) from H$_2$O to H$_2$ in case of the ore layer mixed with coke was accelerated by hydrogen addition more than that in case of the ore layer. Figure 9 shows schematic illustrations of the presumed reaction behavior by H$_2$ in the ore layer and the ore layer mixed with coke. In case of the ore layer shown in Fig. 9(a), the ore was reduced but a carbon gasification reaction does not occur in the ore layer. However, in case of the ore layer mixed with coke shown in Fig. 9(b), the ore was reduced, and carbon gasification reaction is also occurred by reaction between mixed coke and H$_2$O generated in the ore layer mixed with coke. As a result of these reactions, the reduction rate in the ore layer mixed with coke was accelerated more than the reduction rate in the ore layer, because H$_2$ formed by carbon gasification reaction with H$_2$O was utilized for reduction in the same layer.

4. Numerical Analysis of Hydrogen Addition on Blast Furnace Operation

The laboratory tests in this study showed that a carbon gasification reaction was accelerated by hydrogen addition in a ore layer mixed with coke. To examine the effect of these phenomena on blast furnace operation as RAR and permeability, a two-dimensional mathematical simulation model$^{17}$ was used. In this simulation, inner volume of blast furnace is 5153 m$^3$. The calculation conditions and results are shown in Table 2. In this study, to estimate the change in operation by hydrogen addition, the operation with coke mixing in the ore layer (120 kg/t mixture)$^9$ is the base condition. Case 1 is a condition in which input H was increased by natural gas injection$^{11}$. Productivity and amount of mixed coke was the same under these conditions. Oxygen enrichment was adjusted so as to maintain a constant theoretical flame temperature (TFT) in the raceway. The burden radial distribution of Lo/(Lo+Lc) shown in Fig. 10 was used for both conditions. Lo and Lc are the thickness of the ore layer and the coke layer, respectively.

Figure 11 shows the calculation results of the detail of the reduction pass (Base, Case 1). Direct reduction is sum of two types of reduction reactions. One is a direct smelting reduction reaction, and the other is a reduction reaction by sum of carbon gasification reaction and indirect reduction reaction. When input H was increased, the indirect reduction ratio by CO decreased and the indirect reduction ratio by H$_2$ increased. And the direct reduction ratio decreased because of the increase of the sum of the indirect reduction ratios.
(CO+H₂ reduction ratio). Figure 12 shows the relationship between input H and the indirect reduction ratio under condition with coke mixing in the ore layer (120 kg/t mixture) at an actual blast furnace (Chiba No. 6 blast furnace). The calculation results shown in Fig. 11 are the same tendency of the operating results of the actual blast furnace.

Figure 13 shows the calculation results for the temperature distribution in the blast furnace (Base, Case 1). The temperature in the upper part of the blast furnace was decreased as isothermal line of 800°C descended, for example, by the increase in input H. It was due to decrease in CO reduction (exothermic reaction) and increase in H₂ reduction (endothermic reaction) as shown in Fig. 14 as calculation results for the overall reaction rate. 18

Figure 15 shows the calculation results for the reduction degree distribution in the blast furnace (Base, Case 1). The reduction degree in the lower part of the blast furnace increased because line of equal reduction degree of 90%, for example, in the lower part of blast furnace shifted upward.

Table 2. Calculation conditions and results.

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<tr>
<th>Calculation conditions</th>
<th>Base</th>
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<tbody>
<tr>
<td>Blast volume Nm³/min</td>
<td>8825</td>
<td>8128</td>
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<tr>
<td>Blast temperature °C</td>
<td>1100</td>
<td>1100</td>
</tr>
<tr>
<td>Blast moisture g/(Nm³/min)</td>
<td>32</td>
<td>32</td>
</tr>
<tr>
<td>Oxygen enrichment %</td>
<td>2.39</td>
<td>4.12</td>
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<tr>
<td>PCR t/h</td>
<td>55.0</td>
<td>46.0</td>
</tr>
<tr>
<td>NGR t/h</td>
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<td>9.0</td>
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<tr>
<td>O/C</td>
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<td>4.18</td>
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<tr>
<td>Input H kg/t</td>
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<td>12.7</td>
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<table>
<thead>
<tr>
<th>Calculation results</th>
<th>Base</th>
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<tr>
<td>Production t/d</td>
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<td>12137</td>
</tr>
<tr>
<td>Hot Metal temp. °C</td>
<td>1508</td>
<td>1515</td>
</tr>
<tr>
<td>RAR kg/t</td>
<td>497</td>
<td>493</td>
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</table>

Fig. 10. Burden distribution used for simulation.

Fig. 11. Calculation results of reduction ratio.

Fig. 12. Relationship between input H and indirect reduction ratio under condition with coke mixing in the ore layer at actual blast furnace.

Fig. 13. Calculation results of temperature distribution.

Fig. 14. Calculation results of overall reduction rate.

18
It was due to acceleration of reduction rate by increased H₂ reduction in the upper part of the blast furnace as shown in Fig. 15. Therefore, direct reduction (endothermic reaction) in the lower part of the blast furnace decreased. As a result, the hot metal temperature increased as shown in Table 2.

From these calculation results, in case of an increase in input H with a ore layer mixed with coke, the temperature in the upper part of the blast furnace decreased because of the increase in the endothermic reaction resulting from increased H₂ reduction. However, reduction rate increased by acceleration of the carbon gasification reaction. As a result, improvement of the heat balance as decrease in RAR in the lower part of the blast furnace was expected because of the decrease in the endothermic reaction due to the decrease in direct reduction.

Permeability is also improved by an increased H₂ concentration in the reduction gas, as shown in Fig. 5. This was examined by using the mathematical simulation model to estimate that operation, which was calculated as a condition (Case 2) in which increase in ratio of ore to coke (O/C) from 4.18 to 4.20, was applied and the pressure drop was equal to that in the Base condition. Figure 17 shows the calculation results. The coke rate could be decreased by 2.1 kg/t from Case 1. Based on those calculation results, a decrease in the coke rate can be expected by increase in O/C, utilizing the increment of permeability improvement resulting from increased input H.

5. Conclusions

The effect of hydrogen addition on the reduction behavior of the ore layer mixed with coke in the blast furnace was studied in a reduction test under load. Numerical analysis of blast furnace operation in case of increased input H with a ore layer mixed with coke was carried out using a two-dimensional mathematical simulation model. The following conclusions were obtained.

(1) In the case of a ore layer mixed with coke, the reduction degree was improved by hydrogen addition at all mixed coke ratios. Especially, the reduction degree of the ore layer mixed with coke with a high mixed coke ratio was improved by hydrogen addition more than the reduction degree in the ore layer. Permeability was also improved by the increase in the reduction rate.

(2) In the case of hydrogen addition in a ore layer mixed with coke, the carbon gasification rate was accelerated more than the carbon gasification rate with hydrogen addition in the ore layer. This is due to an increase in H₂O formed by H₂ reduction and the carbon gasification reaction of the mixed coke in the ore layer. The reduction rate was also accelerated by the reduction reaction of H₂ formed by the carbon gasification reaction.

(3) In the case of increased input H with a ore layer mixed with coke, the indirect reduction ratio increased and the direct reduction ratio decreased. A simulation using the mathematical model showed that the temperature in the upper part of the blast furnace was decreased by the increase in H₂ reduction. However, in the lower part of the blast furnace, the hot metal temperature increased as a result of the decrease in direct reduction. A further decrease of the coke rate was expected by increase in O/C utilizing permeability improved by increase in input H.
REFERENCES