Carbon Requirement for Ironmaking under Carbon and Hydrogen Co-existing Atmosphere

Hiroshi NOGAMI*

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai, 980-8577 Japan.

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The minimum carbon requirement for ironmaking under carbon and hydrogen co-existing condition was discussed. The reaction system consisted of the reductions of iron oxides by carbon monoxide, hydrogen and solid carbon, the partial combustion of solid carbon, and melting of metallic iron and slag. The analysis took into account the equilibrium constrains for the reductions of the iron oxides and thermal requirement to produce hot metal and molten slag. The carbon requirement was plotted against the contributions of solid carbon, carbon monoxide and hydrogen to the FeO reduction. A valley (minimum route) of carbon requirement appeared from the C–CO reduction to the CO–H₂ reduction condition on the ternary diagram, and the requirement got smaller with increase in H₂ contribution. The carbon requirement decreased with lowering the temperature of FeO reduction. The effect of the water gas shift reaction was also analyzed. The water gas shift reaction (direction to generate CO₂ and H₂) decreased the carbon requirement due to its exothermic reaction heat.

KEY WORDS: ironmaking; carbon requirement; hydrogen; water gas shift reaction.

1. Introduction

In recent years the world crude steel production exceeds 1.5 billion tons, and the steelmaking industries emits huge amount of carbon dioxide to the atmosphere. To decrease this CO₂ emission is one of the most important issues to the industries. About 70% of energy usage in the integrated steelworks is supplied to the ironmaking process, and the coals are used as major reducing agents. Thus it is considered that the improvement of the ironmaking processes is a key measure. Various approaches to decrease the carbon usage in the blast furnace, which is the principal process of ironmaking, have been developed, such as the control of reactivity of coke and arrangement of carbonaceous material and iron oxide, the utilization of hydrogen containing reducing agents, the increasing the hydrogen reduction, the coke mixed charging. Although each approach needs breakthroughs in individual aspects, the target of the all process is the theoretical minimum of the carbon consumption. Nakatani et al. reported a method to estimate the minimum coke rate of blast furnace process based on the combined theory of mass balance, equilibrium constrain and heat balance. They showed the minimum coke rate under the blast furnace operating condition in those days. Akiyama and Yagi reported the minimum carbon requirement to generate hot metal independent of processes, and it would be a target for the optimization of the process efficiency. These analyses, however, considered only the carbon and the carbon monoxide as the reducing agent. In other words, the analysis was made under no hydrogen condition. In the actual operation, the hydrogen participates in the reduction of iron oxides in the processes, and some projects aim to increase the contribution of hydrogen to decrease the CO₂ emission. Calderon developed a method to estimate the carbon consumption in blast furnace process. His model also considered the mass balance, the equilibrium constrains and the heat balance. This model took into account temperature dependencies of thermophysical properties, heat loss and reductions of impurity oxides, and hydrogen and steam were included as gaseous materials. He searched the minimum carbon consumption of the blast furnace process on a direct reduction degree-top gas composition diagram. Although this analysis gave important information, the model included an unknown parameter and the contribution of the hydrogen on the carbon consumption was not discussed. With such background, this study discusses the minimum carbon requirement for ironmaking under carbon and hydrogen co-existing condition.

2. Method of Analysis

This analysis derives the minimum carbon requirement for ironmaking process, namely the hot metal production from the iron ore. Figure 1 shows the overall material flowchart of the ironmaking process. To simplify the problem, the following assumptions are applied. The iron ore consists of Fe₂O₃ and the gangue material which has the same composition of slag (specified as Slag (s) in Fig. 1), and its temperature is 25°C. The products are the hot metal...
(molten iron) and the molten slag of which temperatures are 1510°C. The hot metal consists of Fe and C, and the carbon contents in the molten iron is specified. The reducing agents are originally supplied as the solid carbon and the gaseous hydrogen at 25°C. As the results of the reduction of the iron oxide, the mixture gas of carbon monoxide, carbon dioxide, hydrogen and water vapor at 25°C flows out from the ironmaking process. As explained later, the enthalpy balance between inflow and outflow materials is taken, and the temperatures of gaseous inflow and outflow are the same. Additionally, nitrogen participates in no reaction. Thus, the nitrogen is excluded from the enthalpy balance, and only oxygen is listed as a blast gas in the flowchart.

The minimum carbon requirement is calculated by taking into account the constrains of the chemical equilibrium and the thermal requirement by the following procedure. Figure 2 shows the process flowchart of the ironmaking system. This flowchart is drawn with the basis of 6 moles of iron. First of all, the indirect reduction ratio of wustite (Fe$_{\alpha}$O) $\alpha$ [-] and the ratio of hydrogen reduction in the indirect reduction of wustite $\beta$ [-] are specified. In the first step, the carbon consumption that satisfies the mass balance and the equilibrium constrain is calculated. In the second step, the enthalpy balance on this carbon consumption is checked, and the supplies of the solid carbon and the oxygen are adjusted if necessary. Finally, the minimum carbon requirement for the given $\alpha$ and $\beta$ is obtained. The following part explains the actual procedures.

Under the given indirect reduction ratio $\alpha$, the solid carbon consumption for the direct reduction is given as 6(1 - $\alpha$)w [mol]. To this reduction step, 6$\xi_r$ [mol] of CO which is generated by the partial combustion of carbon although no supplied CO reacts in this step. To the wustite indirect reduction step, 6x [mol] of CO and 6$\zeta$ [mol] of H$_2$ are supplied. The amount of CO, 6x, is summation of CO supplied to the direct reduction step and the CO generated in the direct reduction step.

$$x = (1 - \alpha)w + \xi_r$$ ..........................(1)

With the equilibrium constrains, the amounts of CO and H$_2$ supplied to the indirect reduction step must satisfy the following relations.

$$\xi_r \geq \alpha(1 - \beta)w \left(1 + \frac{1}{K_{CO}}\right) - (1 - \alpha)w ...............(2)$$

$$\zeta \geq \alpha\beta w \left(1 + \frac{1}{K_{H2}}\right) .........................(3)$$

After the wustite reduction step, 6$r$ [mol] of CO, 6$t$ [mol] of CO$_2$, 6$u$ [mol] of H$_2$ and 6$v$ [mol] of H$_2$O are supplied to the Fe$_3$O$_4$ reduction step. These values are given by the following equations.

$$r = x - \alpha(1 - \beta)w .........................(4)$$

$$t = \alpha(1 - \beta)w .........................(5)$$

Fig. 1. Material flowchart of ironmaking system.

Fig. 2. Process flowchart of ironmaking.
\[ u = \zeta - \alpha \beta w \] …………………………………… (6)
\[ v = \alpha \beta w \] …………………………………… (7)

The ratios of the hydrogen reduction in the FeO and Fe₂O₃ reduction step, \( \gamma \) [\( - \)] and \( \delta \) [\( - \)] are specified by the molar ratios of H₂ to CO supplied to each step, namely
\[ \gamma = u (r + u) \] …………………………………… (8)
\[ \delta = j (f + j) \] …………………………………… (9)

Similar to the wustite indirect reduction step, the equilibrium constrains are checked for both steps. If the equilibrium constrains are unsatisfied, the values of \( \xi \) and/or \( \zeta \) are adjusted till the constrains are satisfied. The top gas composition, namely the values of \( a, b, d \) and \( e \) [mol] are given under the condition that the mass balance and the equilibrium constrains are satisfied.

\[ f = r - (1 - \gamma) \frac{(8 - 6w)}{6}, \quad a = f - (1 - \delta) \] …………… (10)
\[ g = t + (1 - \gamma) \frac{(8 - 6w)}{6}, \quad b = g + (1 - \delta) \] …………… (11)
\[ j = u - \gamma \frac{(8 - 6w)}{6}, \quad d = j - \delta \] …………… (12)
\[ m = v + \gamma \frac{(8 - 6w)}{6}, \quad e = m + \delta \] …………… (13)

At the same time, the carbon consumption is given as
\[ \xi_{\text{req}} = \xi_{t} + (1 - \alpha)w + \xi_{r} \] …………… (14)
where, \( \xi_{t} \) is the amount of carbon dissolved in the hot metal corresponding to the 1 mole of Fe [mol]. Note that all values are tentative ones because it is possibility to be revised depending on the following procedure.

As mentioned above, the heat balance regarding this tentative state is checked. The enthalpy difference between outflow and inflow is given by the following equation.
\[ \Delta H_{\text{tot}} = a \Delta H_{\text{CO}} + b \Delta H_{\text{CO}} + c \Delta H_{\text{H₂O}} + \Delta H_{\text{MFHM}} + \Delta H_{\text{slag}} + 0.5 \Delta H_{\text{FeO}} \] …………… (15)

where \( \Delta H_{t} \) is the heat of formation [kJ mol⁻¹], \( \Delta H_{e} \) is the heat of production corresponding to 1 mole of Fe [kJ mol⁻¹], and the subscript HM stands for the hot metal. When the enthalpy difference \( \Delta H_{\text{tot}} \) has negative value, the heat supply is sufficient and the current value of \( \xi_{t} \) is employed as final value. Contrarily, when the enthalpy difference has positive value, the heat supply is insufficient for the hot metal production. In this case, the amount of carbon for partial combustion \( \xi_{r} \) is increased till the enthalpy difference reaches down to zero. Finally, the minimum carbon requirement for the given ratios of the hydrogen reduction and direct reduction is obtained.
\[ w_{\text{req}} = \frac{M_{c}}{M_{\text{Fe}}} \xi_{\text{req}} \times 1000 (1 - f_{\text{HM}}) \] [kg C/thm] …………… (16)

where, \( M \) is molecular weight [kg kmol⁻¹], \( f_{\text{HM}} \) is carbon content (mass fraction) in the hot metal.

3. Results

3.1. Conditions and Validation

For the analysis of the carbon requirement, the following conditions and the parameters are employed. The temperatures of the inflow materials (C, \( \text{H}_2 \), \( \text{O}_2 \), \text{FeO} \( \text{w} \) and \( \text{Fe}_2\text{O}_3 \) and slag(s)) and the product gas (\( \text{CO} \), \( \text{CO}_2 \), \( \text{H}_2 \) and \( \text{H}_2\text{O} \)) are 25°C. The hot metal and the slag temperatures are 1510°C. The heats of formation and the equilibrium constants for the reaction (2) are summarized in Tables 1 and 2. The composition of \( \text{FeO}_\text{w} \) is assumed as 4.8 wt-%. By following the reference, the slag composition, heats to generate hot metal and molten slag are, 43CaO-35SiO₂-15Al₂O₃-7MgO, 1109 GJ/thm and 1.59 s [GJ/thm], respectively. The variable \( s \) in the heat of slag formation is the slag rate [kg/thm] and is assumed as 250 kg/thm.

In prior to the analysis under the carbon and the hydrogen co-existing condition, the analysis under no hydrogen condition is performed. The variations of the carbon requirement and the gas utilization degree with the indirect reduction ratio are shown in Fig. 3. The wustite reduction temperature (herein after, it is called “thermal reserve zone temperature”

|            | CO          | CO₂         | H₂O         | Fe₂O₃       |
|------------|-------------|-------------|-------------|-------------|
| CO         | -110.7      | -393.5      | -241.8      | -412.8      |

|            | CO         | H₂         |
|------------|------------|------------|
| FeO₂→FeO₄  | \( \exp(\frac{7.255}{T} - 3.720) \) | \( \exp(\frac{10.32}{T} - 3.620) \) |
| Fe₂O₃→FeO₄  | \( \exp(\frac{5.289}{T} - 4.711) \) | \( \exp(\frac{8.980}{T} - 8.580) \) |
| FeOₓ→Fe     | \( \exp(-3.127 + \frac{2.879}{T}) \) | \( \exp(1.300 - \frac{2.070}{T}) \) |

![Fig. 3. Carbon requirement under no hydrogen condition (\( T_{\text{req}}=710°C \).)](https://example.com/fig3.png)
3.2. Carbon Requirement under Carbon-hydrogen Co-existing Condition

Figure 4 shows the carbon requirement for the hot metal production under the carbon and the hydrogen co-existing condition. The thermal reserve zone temperature is set at 1 000°C. In this figure, the carbon requirement is plotted against the contributions of carbon monoxide, solid carbon and hydrogen to the reduction of wustite. The side between “CO” and “C” correspond to the no-hydrogen condition. Similar to Fig. 3, the carbon requirement shows the minimum value of 443.0 kg-C/thm at the CO indirect reduction ratio of 54.0%. Under the hydrogen existing condition, the carbon requirement shows the minimum value under the constant H2 reduction ratio condition. Consequently, the valley of the carbon requirement is formed from the CO–H2 side. This valley deepens with increase in the H2 reduction ratio, and the smallest value, 266.7 kg-C/thm under the same temperature as the theoretical minimum carbon requirement, and the corresponding gas utilization degree was 69%. The differences between two analyses are less than 0.29%, it is considered that the good agreement between the previous and this analyses are obtained.

3.3. Effect of Thermal Reserve Zone Temperature

The effect of the thermal reserve zone temperature on the carbon requirement is shown in Fig. 8. In this figure, the carbon requirements under T_{TRZ} of 950, 900 and 800°C are compared. With lowering of T_{TRZ}, the valley of the carbon requirement shifts toward the corner of CO indirect reduction, and the carbon requirement generally decreases while the value around the H2 indirect reduction corner slightly increases.

3.4. Effect of Water Gas Shift Reaction

The authors carried out a numerical experiments on the intensive hydrogen injection into blast furnace tuyere. The results showed that the contribution of hydrogen indirect reduction increased with the injection rate of hydrogen. Contrarily, the hydrogen utilization decreased and the CO utilization increased with increase in the hydrogen injection rate. The analysis of simulation data revealed that the water gas shift reaction (hereinafter WGSR)

\[ \text{CO} + \text{H}_2 \text{O} = \text{CO}_2 + \text{H}_2 \]

regenerated hydrogen in the indirect reduction zone. From the heat balance of the reaction system (Eq. (15)), the carbon requirement depends on the composition of the top gas. Thus the effect of the WGSR is examined. In this analysis, the reducing gas after Fe₂O₃ reduction turns into the equilibrium composition of the WGSR although the WGSR and indirect reduction occur at the same time in the actual blast furnace. The equilibrated gas composition is subjected to the heat balance. The variation of the equilibrium constant of the WGSR with temperature, which is calculated based on the thermodynamic data, is shown in Fig. 9. With decrease in the temperature, the equilibrium constant increases and the equilibrium composition shifts to the CO₂+H₂ side. In this analysis, the two equilibrium constants at 400 and 1 200 K are employed.

Figure 10 shows the effect of the equilibrium temperature of the WGSR on the carbon requirement. T_{TRZ} is set at 1 000°C. For the 1 200 K case, the distribution pattern shows only a little change compared to the case without the WGSR. The carbon requirement at H₂ indirect reduction corner decreases 13.2 kg/thm and the minimum value increases 2.7 kg/thm. Contrarily, the 400 K case shows fairly large differences. In this case, the carbon requirement at the H₂ corner and the minimum values decrease by 54.5 and 31.7 kg/thm, respectively.

Figures 11 and 12 show the utilization degrees of CO and H₂. The maximum point of CO utilization degree stays on the CO–C side in the 1 200 K case while it locates on the CO–H₂ side. In the range with lower contribution of CO indirect reduction degree, both cases show similar tendency, namely the direct reduction (C) corner shows the minimum \( \eta_{CO} \) and it gradually increases away from the C corner. In the higher CO contribution region, the contour lines of \( \eta_{CO} \) are almost parallel to the CO–H₂ side in 1 200 K case.
Fig. 4. Distribution of carbon requirement under $T_{TRZ}=1\,000^\circ\text{C}$.

Fig. 5. Distribution of CO utilization degree under $T_{TRZ}=1\,000^\circ\text{C}$.

Fig. 6. Distribution of H$_2$ utilization degree under $T_{TRZ}=1\,000^\circ\text{C}$.

Fig. 7. The amount of carbon to compensate heat requirement.

Fig. 8. Effect of thermal reserve zone temperature on carbon requirement.

Fig. 10. Effect of equilibrium temperature of water gas shift reaction on carbon requirement.

Fig. 11. Effect of equilibrium temperature of water gas shift reaction on CO utilization degree.

Fig. 12. Effect of equilibrium temperature of water gas shift reaction on H$_2$ utilization degree.
while they are almost perpendicular to the CO–H₂ side of the ternary diagram. The distribution patterns of η_{H₂} show the similar trends to η_{CO}. The reason for this difference is considered due to the difference between the equilibrated top gas composition and one without WGSR. In the 1 200 K case the difference between these two compositions are fairly small. Contrarily the difference in the 400 K case is large. Under the equilibrium temperature of 400 K, the equilibrium composition of the WGSR tends to shift toward the right side of Eq. (17), namely H₂O formed by the reduction reactions is regenerated to H₂ and CO is converted to CO₂. In addition, the amount of H₂ in the reducing gas increases with increase in the contribution of H₂ indirect reduction. As a result, the η_{CO} increases with the increase in the H₂ contribution. With further increase in the H₂ contribution, the amount of H₂O in the reducing gas becomes larger than the amount of CO that can participate in the WGSR. Therefore, the increase in the η_{CO} slows and the η_{H₂} starts to increase. The WGSR (toward right side of Eq. (17)) is exothermic reaction, and it occurs largely under the 400 K case. This heat generation compensates a part of heat requirement and decreases the carbon requirement. Although this analysis uses somewhat extreme condition, namely 400 K as the equilibrium temperature of the WGSR and the separate treatment of the WGSR and the reduction reactions, this analysis shows the importance of the control of the WGSR in the lower temperature range because the WGSR affects the thermal balance of the ironmaking under the hydrogen co-existing condition.

4. Conclusions
This study discussed the minimum carbon requirement for ironmaking under carbon and hydrogen co-existing condition. The analysis took into account the equilibrium constrains for the reductions of the iron oxides and thermal requirement to produce hot metal. The carbon requirement was plotted against the contributions of solid carbon, carbon monoxide and hydrogen to the FeO reduction. A valley of carbon requirement appeared from the C–CO reduction to the CO–H₂ reduction condition, and the requirement got smaller with increase in H₂ contribution. The analysis also showed that the carbon requirement varied depending on the temperature of FeO reduction and the water gas shift reaction.

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