Reduction Behavior of Packed Bed of Sinter Reduced by CO–CO₂–H₂–H₂O–N₂ Gas

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To mitigate CO₂ emission from a blast furnace, the use of H₂ as a reducing agent is considered to be a prominent method. Reduction of iron ore was reported to be improved by H₂ addition. In the present research, reduction in a sinter-packed bed by CO and H₂ was carried out under various oxygen partial pressures, and the influence of reduction atmosphere on the reaction behavior was investigated. It was confirmed that the reduction rates were higher when using H₂/H₂O and CO/CO₂/H₂/H₂O mixtures than when using a CO/CO₂ gas mixture. The reaction rate constant for iron ore reduction was determined from the experimental result using a numerical model. The influence of the water-gas shift reaction on the reduction rate was analyzed by comparing the results obtained using the numerical model and those in the experiments. Moreover, the longitudinal distribution of the reaction rate in the packed bed was analyzed to examine the influence of the water-gas shift reaction.

KEY WORDS: reduction; sinter ore; hydrogen; blast furnace.

1. Introduction

In order to mitigate CO₂ emission from the steelmaking industry, the use of natural gas and coke oven gas in the blast furnace is proposed.¹) Pulverized coal is injected from tuyeres in conventional blast furnace operation, but nowadays, the injection of a gaseous reducing agent including hydrogen is being considered. The reducing agent injected into the blast furnace can be partially replaced by hydrogen from carbon, thereby decreasing CO₂ emission from the ironmaking process. Therefore, the use of alternative materials including hydrogen can be positively evaluated.

If hydrogen is substituted for the reduction material from a carbon system, the reaction behavior of the burden, such as the reduction of iron ore, would change. Hence, reduction of the sinter by both CO and H₂ should be controlled. CO reduction of the sinter has been well investigated, and the individual rate constants for the each reduction step of hematite, magnetite, and wustite have been reported.²–⁷) However, the chemical and physical properties of the sinter may change with the location of the natural resource and the sintering process, and therefore, it is difficult to design a specific reaction model and generalize the reaction rate constant. The rate constant for iron ore reduction depends on the properties of the material, such as the chemical constitution of the sinter, porosity, and specific surface area; therefore, it is necessary to measure the reduction rate of the target sample.

The rate constants for hematite, magnetite, and wustite reduction by H₂ gas have also been reported.²,6–13) However, there has been no detailed investigation of the individual reduction of Fe₂O₃, Fe₃O₄, and FeO; rather, the total reduction until iron generation was investigated, and then, the reaction rate constants were derived by parameter fitting. Moreover, there has been no study on the reduction degree in a sinter packed bed. The reported rate constants for the reduction of the sinter by H₂ or CO indicate that the reaction rate increases with the usage of a reducing agent including H₂.

When using a H₂-containing reducing agent, metallic iron may be generated at an early stage and catalyze the water-gas shift reaction in the gas phase. The reaction rate might increase locally, thus making the degree of reduction in the sinter layer non-uniform. During simultaneous reduction of a sinter-packed bed by H₂ and CO, the reaction behavior changes with the water-gas shift reaction in the gas phase; hence, the effect of reduction by H₂ cannot be accurately investigated.

In the present research, the reduction behavior in a sinter bed when using a H₂-rich CO/H₂ mixture as the reductant was investigated, and the reaction rate constants were obtained by using a reaction model of the sinter packed bed developed in the present study. Comparison of the model and experimental results indicated an enhancement of the reduction rate by the synergistic effect of mixing CO and H₂. Furthermore, the influence of the water-gas shift reaction on the synergistic effect was discussed and included in the model.
2. Experimental Method

2.1. Specimen

In this research, sinter with a diameter of 2.8–3.4 mm, which is a blast furnace burden material was used as the iron ore sample. The chemical composition of the sinter is shown in Table 1.

2.2. Experimental Apparatus

A schematic of the experimental apparatus is shown in Fig. 1. The PID controller was connected to the electric resistance furnace, whose temperature was arbitrarily controlled. A mullite tube with an inner diameter of 30 mm was used as the experimental tube. Another mullite tube with an outer diameter of 25 mm was placed in the experimental tube, and an alumina lattice was placed on it to hold the sample-packed bed. The position of the inner tube was so adjusted that the sample-packed bed remained in the hot zone of the furnace. Then, about 60 g of the sample was placed in the reaction tube so that a 50-mm-thick packed bed was obtained. Moreover, in order to ensure uniform gas flow, a 20-mm-thick layer of alumina balls (2 mm in diameter) was set above and below the sample. The sample temperature was measured by the thermocouple at three positions—the top, center, and bottom of the packed bed—and confirmed to be uniform. In the experiment, high-purity CO, CO2, H2, and N2 gases were used for controlling the atmosphere. A mixture of CO, CO2, H2, H2O, and N2 gases were used for controlling the oxygen partial pressure for analysis of reaction rate. Water-saturated N2 was generated by passing N2 gas through a heated water bubbler. A balance was installed below the reaction tube, so that weight changes in the entire reaction tube, including the sample, could be measured during the reduction experiment.

2.3. Composition of the Gas Phase

For the reduction of the sinter by a reducing gas, three systems were employed: CO/CO2/N2, H2/H2O/N2, and CO/CO2/H2/H2O/N2 gas mixtures. For investigating the relationship between the gas composition and the reduction behavior, the sinter was reduced by the gas mixture under three different levels of oxygen partial pressure. Partial pressures of oxygen in the reducing gas were chosen as CO/CO2 ratios saturated with C and saturated doubly Fe/FeO, and middle of them. Moreover, the H2/H2O ratios were decided to be the same as the oxygen partial pressure of the CO/CO2 system. To study the synergistic effect of mixing on reduction, the ratio of CO+CO2/H2+H2O was employed as 1/1. When preparing a CO/CO2/H2/H2O mixture, identical volumes of CO/CO2 and H2/H2O mixtures, which had the same oxygen partial pressures were mixed. The total pressure of the inlet gas was 1 atm; 0.5 atm was attributed to N2, and the other 0.5 atm comprised the gas mixture mentioned above. Since the oxygen partial pressures in the CO/CO2 and H2/H2O systems are the same, the water-gas-shift reaction does not proceed in the CO/CO2/H2/H2O mixture, without reduction reaction of sinter. The standard free energy change for the reaction between CO/CO2 and H2/H2O and the standard free energy of formation of FeO are listed in Table 2.14,15) The selected gas compositions for the experiments at 1 073 K, 1 173 K, and 1 273 K are shown in Table 3.

2.4. Experimental Procedure

In order to prevent oxidation of the sample, the sample temperature was increased at the rate of 300 K/h, with N2 gas flow at the rate of 500 ml/min, in the reaction tube. The sample was heated to 1 073, 1 173, or 1 273 K and maintained at this level until the temperature was uniform. Then, the reducing gas was introduced into the reaction tube at a total flow rate of 500 ml/min, and the sample was exposed to this gas atmosphere for a specific length of time. After the reduction experiment, the tube was cooled under N2 gas flow. The variation in the sample weight and the reduction degree can be measured every second by the electronic balance. The sample was taken out from the reaction tube, maintaining arrangement of the particles by the following procedures, in order to observe the packed bed of arbitrary reduction rates. The packed bed was fixed by the epoxy resin in the reaction tube after cooling, and the packed bed was taken out. The lump of the sinter-packed bed was first

Table 1. Chemical composition (mass%) of sinter.

<table>
<thead>
<tr>
<th>T-Fe</th>
<th>FeO</th>
<th>M-Fe</th>
<th>CaO</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>58.28</td>
<td>8.09</td>
<td>0.42</td>
<td>9.57</td>
<td>4.55</td>
<td>1.70</td>
<td>1.28</td>
</tr>
</tbody>
</table>

Table 2. Standard free energies of formation.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Standard free energy of formation [cal/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>yFe + ( \frac{1}{2} ) O2 = FeO</td>
<td>( \Delta G_f^\circ = -62452 + 15.127T )</td>
</tr>
<tr>
<td>( \frac{3}{4} ) FeO + ( \frac{5}{4} ) Fe = ( \frac{7}{4} ) O2</td>
<td>( \Delta G_f^\circ = -67430 - 24.017T + 15.488T \log T )</td>
</tr>
<tr>
<td>3Fe + 2O2 = Fe3O4</td>
<td>( \Delta G_f^\circ = -256677 + 68.746T )</td>
</tr>
<tr>
<td>CO + 1/2O2 = CO2</td>
<td>( \Delta G_f^\circ = -67828 + 21.2676T - 1.5399 \times 10^{-4}T^2 )</td>
</tr>
<tr>
<td>H2 + 1/2O2 = H2O</td>
<td>( \Delta G_f^\circ = -58262 + 11.5146T - 7.27961 \times 10^{-4}T^2 )</td>
</tr>
</tbody>
</table>
sliced into two vertically, and then, each part was further sliced into three along the vertical direction. The surface of the vertical plane was polished for the Scanning Electron Microscope analysis.

3. Experimental Results

3.1. Measurement of Reduction Rate Constants

Iron ore was reduced by the gas mentioned above at 1 073, 1 173, or 1 273 K. The reduction behavior of the sinter in CO/CO₂/N₂, H₂/H₂O/N₂, or CO/CO₂/H₂/H₂O/N₂ is shown in Fig. 2. The vertical axis denotes the reduction degree of the iron ore, under the assumption that the gangue was not reduced. The Reduction degree \( R \) is defined as

\[
R = 1 - \frac{W_{\text{sample}} - W_{\text{Fe}} - W_{\text{gang}}}{W_{\text{int.}} - W_{\text{Fe}} - W_{\text{gang}}}. \quad \text{(1)}
\]

where \( W_{\text{sample}} \), \( W_{\text{int.}} \), \( W_{\text{Fe}} \), and \( W_{\text{gang}} \) denote the weight of the sample, the initial weight of the sample, the weight of iron in the sample, and the weight of gangue in the sample, respectively.

3.2. Reduction Behavior of Sinter Reduced by CO

The reduction behavior of the sinter reduced by CO is shown in Fig. 2(a). c1–3, c4–6, and c7–9 indicate the results obtained at 1 073, 1 173, and 1 273 K, respectively. \( R \) increases with a decrease in the oxygen partial pressure when the temperature is constant. Since the oxygen partial pressure is equal to the atmosphere at Fe/FeO equilibration, the \( R \) values for conditions c1, c4, and c7 were constant at 0.3. Under other conditions, the reaction rates decreased for \( R > 0.3 \), and \( R \) increased linearly.

3.3. Reduction Behavior of Sinter Reduced by H₂

The reduction behavior of the sinter reduced by H₂ is shown in Fig. 2(b). The lines representing \( R \) indicate slight fluctuations since the total weight of the reaction tube changes because of the condensed water dripping from the gas outlet tube and evaporating at the upper side of packed bed. Lower part of the fluctuation of line is including the influence of the condensed water weight. Although the h7...
experiment was conducted several times, the reproducibility of the \( R \) curve was poor because of the influence of moisture, and hence, this curve is not shown in the figure. However, the final \( R \) value obtained from the weight change in the sample after the experiment was about 0.3. The \( h_7 \) sample reduced to FeO, like the \( h_1 \) and \( h_4 \) samples. As observed in the CO reduction, \( R \) increased with decreasing oxygen partial pressure at the same temperature. In the CO reduction, the inflection point of the reduction curve was seen at \( R=0.3 \); however, in the \( H_2 \) reduction, the inflection point was seen at \( R=0.1 \) and 0.3, which corresponded to the reduction of \( Fe_2O_3 \) to \( Fe_3O_4 \) and FeO, respectively, implying that the rate of reduction from \( Fe_2O_3 \) to FeO was significantly high.

3.4. Reduction Behavior of Sinter Reduced by CO/CO\(_2\)/H\(_2\)/H\(_2\)O/N\(_2\) Mixture

As shown in Fig. 2(c), the reduction rate is significantly high and relatively high below \( R=0.1 \) and 0.3, respectively. A comparison of the reduction curves obtained in the CO, \( H_2 \), and mixed gas experiments at 1 073 K, 1 173 K, and 1 273 K is shown in Figs. 3(a), 3(b), and 3(c). Same numerical number of sample are same initial oxygen potential each other. The reduction curves in the three cases are similar, and the influence of the gas species on the reduction behavior is weaker than that of temperature or oxygen partial pressure. However, at the same oxygen partial pressure, the reduction proceeds in the order mixed gas \( \geq H_2 \geq CO \). The reduction rate in the case of \( H_2 \) is slightly higher than that in the case of CO, as mentioned in some literature. Meanwhile, the reduction rate in the case of the CO/\( H_2 \) mixture is also slightly higher than in the case of \( H_2 \). In particular, the difference in \( R \) is significant at low oxygen partial pressures, implying the synergetic effect of the mixing gases on the reaction rate. The \( H_2/CO \) mixture might accelerate the reaction by the generation of a refined structure or a water-gas shift reaction.

3.5. Texture of Reduced Sinter

The sinter packed bed after 50% reduction at 1 173 K was used for SEM analysis. The center of each part was chosen as the observation position. SEM images of the samples are shown in Fig. 4. The samples reduced by CO, \( H_2 \), and the CO/H\(_2\) mixture are indicated as a–c, d–f, and g–i, respectively. The upper, middle, and lower parts of the packed bed are denoted by a, d, and g; b, e, and h; and c, f and i, respectively. The black area indicates a resin.

Under any condition, the reaction degree in the lower part is higher than that in the upper part. In the lower part, iron exists as \( Fe/FeO \), while in the upper part, iron mainly exists as \( FeO/Fe_3O_4 \). In the lower part, \( FeO \) (gray) is surrounded by \( Fe \) (white).

Although the structure of iron changes with the reducing gas species and a layer of dense \( Fe \) is observed in the sample reduced by CO (c), a rough \( Fe \) layer with small pores is seen in the sample reduced by \( H_2 \) (f) and the mixed gas (i). The sample reduced by the mixed gas has a thick \( Fe \) layer with high porosity. \( FeO \) exists inside the dense \( Fe \) layer, as seen in the lower part (c).

In the sample reduced by \( H_2 \) (e), the \( Fe \) layer is discontinuous, with \( FeO \) inside it. In the sample reduced by the mixed gas (f), \( FeO \) occupies a large area and the \( Fe \) layer is only partial.

In the upper part, metallic \( Fe \) is not observed. A fine gray \( FeO \) area exists around the continuous dense \( Fe_3O_4 \) phase in samples (a) and (d). In the sample reduced by the mixed gas (g), the \( Fe_3O_4 \) phase is divided into smaller grain and
the FeO region is distributed irregularly.

In the early stages of the reaction, a dense and continuous FeO layer was generated by CO and H₂ reduction. In CO reduction, a dense Fe layer would be formed from FeO, while in H₂ reduction, a porous Fe layer would be formed. On the other hand, in the mixed gas reduction, discontinuous Fe₃O₄ was initially formed, and then, a thick Fe layer of fine structure was formed on the surface of FeO₃. Further research would be needed to clarify the relationship of the synergistic effect of reducing gas and mechanism of structural change. From the relationship between the structure and the reduction rate, it can be said that reduction of the iron ore layer with a fine structure proceeds faster than that of the layer with a dense structure. Moreover, when using the conditions with H₂, the iron ore becomes fine-structured with a large specific surface area. In particular, the grain size of the sample reduced by the mixed gas is small. The reduction behavior in Fig. 3(c) can be explained from the specific surface area.

4. Analysis of Reduction Behavior by Numerical Model

4.1. Reaction Model of Sinter Packed Bed

4.1.1. Constitution of Reduction Model

In the case of the sample mentioned in section 3.5, a multistage reaction, i.e., Fe₂O₃→Fe₃O₄→FeO→Fe, was observed, and the reduction progressed in the position exposed to the gas phase. In the present study, an unreacted core model with three interfaces⁸ was employed for the analysis of reduction in the gas phase. Further research would be needed to clarify the relationship of the synergistic effect of reducing gas and mechanism of structural change. From the relationship between the structure and the reaction rate, it can be said that reduction of the iron ore layer with a fine structure proceeds faster than that of the layer with a dense structure. Moreover, when using the conditions with H₂, the iron ore becomes fine-structured with a large specific surface area. In particular, the grain size of the sample reduced by the mixed gas is small. The reduction behavior in Fig. 3(c) can be explained from the specific surface area.

4.1.2. Reaction Model of Reaction of Packed Bed

The reactions in the sinter iron ore are shown as follows.

3Fe₂O₃(s) + CO(g) = 2FeO(s) + CO₂(g) ............ (1)

Fe₃O₄(s) + CO(g) = 3FeO(s) + CO₂(g) ............ (2)

FeO(s) + CO(g) = Fe(s) + CO₂(g) ............ (3)

3Fe₂O₃(s) + H₂(g) = 2FeO(s) + H₂O(g) ............ (4)

Fe₃O₄(s) + H₂(g) = 3FeO(s) + H₂O(g) ............ (5)

FeO(s) + H₂(g) = Fe(s) + H₂O(g) ............ (6)

Hara’s model⁹ was modified by changing the reaction and the reaction rate constant, and a reaction model of the sinter packed bed reduced by CO and H₂ was constructed. Since the grain size of the sintered iron ore was small, gas diffusion in the fine grains was not considered in our calculation. Therefore, the reaction rate in the CO/CO₂ or H₂/H₂O atmosphere was derived as

\[
v_{\text{ore}}^{\text{CO}} = \frac{\pi d_{\text{ore}}^2}{R \times T} \times (P_{\text{CO}} - P_{\text{CO}}^*) \\
\times (1 - R_{\text{ore}})^{2/5} \times k_{\text{ ore}} \times \left(1 + \frac{1}{K_{\text{ CO}}^{\text{ ore}}} \right) \quad \text{[mol/h]} \]

where \( v_{\text{ore}} \), \( R \), \( T \), \( d_{\text{ore}} \), \( P \), \( P^* \), \( k_{\text{ ore}} \), and \( K_{\text{ CO}}^{\text{ ore}} \) denote the reaction rate of the ore particles, gas constant, temperature, pressure, reaction rate of the ore particles, reaction rate of iron oxide, and equilibrium constant derived from the standard free energy change for each reaction, respectively. The effect of the boundary film is weaker than that of the other factors and is hence ignored.

Considering the mole number, the reduction rate of the ore particle is rewritten as

\[
dR_{\text{ore}} = \frac{6 \times M_{\text{FeO}_{1.5}}}{d_{\text{ore}} \times \pi \times \rho_{\text{FeO}_{1.5}}} \times (v_{\text{ore}}^{\text{CO}} + v_{\text{ore}}^{\text{H₂}}) \quad \text{[1/h]} \]

where \( d_{\text{ore}} \), \( M_{\text{FeO}_{1.5}} \), and \( \rho_{\text{FeO}_{1.5}} \) denote the mean diameter of the ore, molar weight, and specific gravity of FeO₁.₅, respectively.

If the \( R \) value for the Fe₂O₃→Fe₃O₄, Fe₃O₄→FeO, and FeO→Fe stages are represented as \( R_1 \), \( R_2 \), and \( R_3 \), respectively, the \( R \) value of the whole ore is expressed as

\[
R = 0.1111R_1 + 0.1889R_2 + 0.7000R_3 \quad [-] \]

where \( R \) is essentially equal to that estimated by Eq. (1).

4.1.3. Mathematical Model and Various Reaction Rates

Although the aim of this research was analysis of the packed bed, the reaction rate constant was determined by referring to the experimental data for the single particles. The effective diffusion coefficient \( D_e \) in a particle is expressed as follows, using the diffusion coefficient \( D_G \),

\[
D_{\text{ore}} = \delta_{\text{ore}} \cdot D_G 
\]

Here, \( \delta_{\text{ore}} = 0.15 \), \( \delta_e = 0.20 \), and \( \delta_{\text{ore}} = 0.2 \) were employed as the coefficients \( \delta \) for the reduction of Fe₂O₃, Fe₃O₄ and FeO, respectively.¹⁰ The reduction rate constant in the literature and the present experimental results were compared, and the reaction rate constant for our sample was derived using parameter fitting by trial and error.

4.2. Calculation Results

Reaction rate constants for the reduction of iron ore in the literature²⁻¹³ were used in the present model, and the reaction behavior was analyzed. There are a few experimental results for the reaction rate constant corresponding to the reduction of sintered iron ore by CO/CO₂ gas and H₂/H₂O gas under the same conditions. Moreover, in a mixed gas, the water-gas shift reaction affects the reduction of iron oxide. Some water gas-shift reaction rate constants have already been reported, under conditions where iron and iron oxide coexist. Because of the catalytic effect of iron, it is difficult to carry out a direct comparison of the values under different conditions.
Here, the iron oxide reduction behaviors observed when using CO/CO₂ gas and H₂/H₂O gas were compared.

4.2.1. Reduction Behavior of the Sinter Reduced by CO/CO₂ Gas

The reported reaction rates constant for the reduction of iron ore by CO⁷⁻³ are summarized in Table 4. The calculation result depending on reported reduction rate constants, is shown in Fig. 5. The calculation results are higher⁵ or lower⁶ as compared with present experimental results. Reduction behavior was simulated for the conditions c3, c6, and c9 in Table 3. According to the calculation results at 1 173 K and 1 273 K, the reaction rate constant does not have any notable influence on the reduction rate. Moreover, the calculated reduction rate is larger than the experimental result, notably in the low-temperature region. However, some experimental values are larger than the calculated values in the early stage of the reduction. Therefore, when the reported reaction rate constant was used, the reduction rate for the conversion from FeO to Fe was overestimated in the present model. In this research, since a 3-mm sinter is employed, the influence of porosity on the reaction area is significant, and reactions with the characteristics of a homolytic model and an unreacted core model would proceed.

4.2.2. Reduction Behavior of the Sinter Reduced by H₂/H₂O Gas

The reported reaction rate constant of iron ore reduced by H₂⁶⁻¹¹ is summarized in Table 5. The calculation result depending on reported reduction rate constants, the comparatively high value ¹⁰ and the low value ¹¹ is shown in Fig. 6 as compared with an experimental result. The analysis method is the same as that adopted for the reduction by CO/CO₂, as mentioned in 4.2.1. The calculated curve shows a reaction rate higher than the experimental measurement.

![Image](image-url)

**Table 4.** Chemical reaction rate constants, k₁ₐ, k₂ₐ, and k₃ₐ for the CO reduction of iron oxide.

<table>
<thead>
<tr>
<th>Chemical reaction rate constant of reduction [cm/sec]</th>
<th>Temp. range (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>exp(6.88 – 16 000/RT)⁶</td>
<td>973–1 273</td>
</tr>
<tr>
<td>exp(3.61 – 12 600/RT)⁴</td>
<td>1 073–1 273</td>
</tr>
<tr>
<td>exp(6.22 – 14 300/RT)⁴</td>
<td>773–1 273</td>
</tr>
<tr>
<td>exp(3.16 – 12 000/RT)⁶</td>
<td>973–1 373</td>
</tr>
<tr>
<td>exp(12.5 – 27 200/RT)⁷</td>
<td>1 073–1 273</td>
</tr>
<tr>
<td>exp(5.34 – 12 200/RT)⁴</td>
<td>1 073–1 273</td>
</tr>
<tr>
<td>exp(1.04 – 7 200/RT)⁴</td>
<td>1 073–1 273</td>
</tr>
<tr>
<td>exp(4.74 – 10 800/RT)⁴</td>
<td>1 073–1 273</td>
</tr>
<tr>
<td>exp(2.09 – 9 560/RT)⁴</td>
<td>1 073–1 273</td>
</tr>
<tr>
<td>exp(7.82 – 17 600/RT)⁷</td>
<td>1 073–1 273</td>
</tr>
<tr>
<td>exp(3.39 – 8 560/RT)⁵</td>
<td>1 073–1 273</td>
</tr>
<tr>
<td>exp(6.69 – 16 500/RT)⁶</td>
<td>1 073–1 273</td>
</tr>
<tr>
<td>exp(3.27 – 8 110/RT)⁶</td>
<td>1 073–1 273</td>
</tr>
<tr>
<td>exp(5.42 – 14 700/RT)⁵</td>
<td>773–1 273</td>
</tr>
<tr>
<td>exp(7.44 – 16 600/RT)⁷</td>
<td>1 073–1 273</td>
</tr>
</tbody>
</table>

R = 1.9872 (cal/K·mol)

**Table 5.** Chemical reaction rate constants, k₁₂, k₂₁, and k₃₂ for H₂ reduction of iron oxide.

<table>
<thead>
<tr>
<th>Chemical reaction rate constant of reduction [cm/sec]</th>
<th>Temp. range (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2 × 10⁵ exp(−15 900/RT)⁸</td>
<td>973–1 223</td>
</tr>
<tr>
<td>4.0 × 10⁵ exp(−13 200/RT)⁹</td>
<td>973–1 223</td>
</tr>
<tr>
<td>exp(6.56 – 15 100/RT)¹⁰</td>
<td>1 073–1 273</td>
</tr>
<tr>
<td>exp(8.70 – 16 300/RT)¹¹</td>
<td>1 073–1 273</td>
</tr>
<tr>
<td>exp(4.49 – 7 980/RT)⁶</td>
<td>1 073–1 273</td>
</tr>
<tr>
<td>1.6 × 10⁵ exp(−22 000/RT)⁷</td>
<td>1 073–1 273</td>
</tr>
<tr>
<td>2.2 × 10⁵ exp(−6 650/RT)⁸</td>
<td>973–1 223</td>
</tr>
<tr>
<td>8.0 × 10⁵ exp(−8 000/RT)⁹</td>
<td>973–1 223</td>
</tr>
<tr>
<td>exp(6.51 – 12 000/RT)¹⁰</td>
<td>973–1 273</td>
</tr>
<tr>
<td>exp(8.92 – 17 200/RT)¹¹</td>
<td>1 073–1 273</td>
</tr>
<tr>
<td>exp(2.09 – 9 560/RT)⁴</td>
<td>1 073–1 273</td>
</tr>
<tr>
<td>2.3 × 10³ exp(−17 000/RT)⁵</td>
<td>1 073–1 273</td>
</tr>
<tr>
<td>4.1 × 10³ exp(−14 000/RT)⁹</td>
<td>973–1 223</td>
</tr>
<tr>
<td>6.8 × 10³ exp(−14 000/RT)⁹</td>
<td>973–1 223</td>
</tr>
<tr>
<td>exp(10.4 – 19 000/RT)¹⁰</td>
<td>1 073–1 273</td>
</tr>
<tr>
<td>exp(11.85 – 23 200/RT)¹¹</td>
<td>1 073–1 273</td>
</tr>
<tr>
<td>exp(5.42 – 14 700/RT)⁴</td>
<td>1 073–1 273</td>
</tr>
<tr>
<td>2.0 × 10³(−15 200/RT)⁶</td>
<td>1 073–1 273</td>
</tr>
</tbody>
</table>

R = 1.987 [cal/K·mol]

![Image](image-url)
Even when the reaction rate constant is changed in the temperature range 1 073–1 273 K, variation in the reduction curve is small. Moreover, the calculated $R$ value is higher than the experimental value. If these reaction rate constants are used for the present experimental conditions, the gas supply rate must be appropriately controlled. The experimental reaction rate is lower than that calculated using the model.

### 4.3. Determination of the Reaction Rate Constants

The reduction behavior derived from the reported reaction rate was compared with the reduction rate obtained from the present experiment. In order to derive a reaction rate constant for the present sample, parameter fitting was used based on this difference.

#### 4.3.1. Reduction Rate Constant of the Sinter Reduced by CO Gas

As shown in Fig. 5, reaction degree in the present experiment is lower than that derived from the reaction rate constant in the literature. In order to represent the experimental result, parameter fitting was carried out; the obtained reaction rate constants for sinter reduction in the present experiment are represented by Eqs. (12)–(14).

$$k_1^{CO} = \exp \left( 9.087 - 7.564/T \right) \text{[m/h]} \quad \ldots \ldots \quad (12)$$

$$k_2^{CO} = \exp \left( 8.255 - 7.410/T \right) \text{[m/h]} \quad \ldots \ldots \quad (13)$$

$$k_3^{CO} = \exp \left( 8.349 - 8.129/T \right) \text{[m/h]} \quad \ldots \ldots \quad (14)$$

where the unit of the reaction rate constant is [m/h]; $k_1^{CO}$, $k_2^{CO}$, and $k_3^{CO}$ denote the reduction between Fe$_2$O$_3$/Fe$_3$O$_4$, Fe$_3$O$_4$/FeO, and FeO/Fe, respectively.

The variation in $R$ obtained using the reaction rate constants determined from Eqs. (12)–(14) in the present model is shown in Fig. 7. At the reaction degree of 0.2, the maximum deviation between the calculated and experimental $R$ values was observed; the difference was about 0.03. Therefore, the reaction rate constant obtained from the present study can express the actual measurement well.

A comparison of the reaction rate constants in the literature and that derived from the present study is shown in Fig. 8. Although the values of $k_1^{CO}$ and $k_2^{CO}$ are within the range of distribution of the literature values, $k_3^{CO}$ is much lower than the literature value. Since the sinter particles used in present experiment are small, when the reported value is employed for the calculation, the derived reaction rate would be overestimated in the FeO reduction stage. Although the influence of particle diameter is included in Eqs. (7) and (8), it will be necessary to adjust the reaction rate constant when the particle size of the sintered ore is

---

Fig. 7. Comparison calculated and experimental reduction behavior of sinter reduced by CO a) at 1 073 K, b) 1 173 K and c) 1 273 K.

Fig. 8. Comparison of reaction rate constant of sinter reduced by CO.
much larger than that of the experimental sample.

4.3.2. Reduction Rate Constant of the Sinter Reduced by H$_2$ Gas

As shown in Fig. 6, the reduction rate when using H$_2$, as obtained from the present model using the reported value, is higher than that determined experimentally. Based on this difference, the reaction rate constant that represents the present experimental result was derived. The obtained reaction rate constants are expressed by Eqs. (15)–(17).

\[ k_{1^H2} = \exp(11.33 - 9.539/T) \] m/h \hspace{1cm} (15)

\[ k_{2^H2} = \exp(9.808 - 8.722/T) \] m/h \hspace{1cm} (16)

\[ k_{3^H2} = \exp(6.173 - 5.359/T) \] m/h \hspace{1cm} (17)

where the unit of the reaction rate constant is [m/h]; $k_{1^H2}$, $k_{2^H2}$, and $k_{3^H2}$ denote the reduction between Fe$_2$O$_3$/Fe$_3$O$_4$, Fe$_3$O$_4$/FeO, and FeO/Fe, respectively. The variation in $R$ obtained by the rate constants estimated from Eqs. (15)–(17) using the present model is shown in Fig. 9.

The reduction curve derived from the model agrees with the experimental results. In the early stage of H$_2$ reduction, the difference between the experimental and calculated values is larger than that during CO reduction. The water vapor generation during H$_2$ reduction might cause a measurement error.

Figure 10 shows a comparison of the reaction rate constants obtained using Eqs.(15)–(17) with those in the literature. The values of $k_{1^H2}$, $k_{2^H2}$, and $k_{3^H2}$ are smaller than those in the literature. The reason for this is the same as in the case of CO reduction.


5.1. Reaction Behavior of Iron Ore in CO/CO$_2$/H$_2$/H$_2$O/N$_2$ Mixture

When iron ore is reduced by CO and H$_2$ simultaneously, the water gas shift reaction would influence the reduction reaction. Here, the influence of the water gas shift reaction is investigated by comparing the reduction reaction rate for CO or H$_2$ reduction obtained using the developed model with experimental results for CO and H$_2$ reduction.

Firstly, in order to avoid the influence of the water gas shift reaction, its reaction rate was assumed to be 0, and the reaction behavior was simulated using the developed model. The reduction curve is shown in Fig. 11.

The calculation results agreed well with experimental results for CO or H$_2$ reduction separately. However, the reaction ratio derived from the reaction rate constants of literature was lower than that of experimental result of CO and H$_2$ reduction. In particular, at the stage of FeO reduced...
to Fe of condition ch3 and ch6, the difference is significant. This shows that the reduction reaction cannot be solely predicted by summing the reduction rates for CO and H2.

5.2. Influence of the Water Gas Shift Reaction on the Reduction of Iron Ore

The water gas shift reaction between CO/CO2 and H2/H2O gas is represented as

$$ \text{H}_2\text{O} + \text{CO} = \text{H}_2 + \text{CO}_2 \quad \text{..........................} \quad (18) $$

The reaction rate constants of the water gas shift reaction\textsuperscript{6,17} are summarized in Table 6. The coexistence phase in Table 6 denotes the solid phase that exists with the gas phase. Although atmospheric pressure dependence is present in each reaction, since this experiment was carried out under 1 atm, the reaction rate under 1 atm was calculated. Both values\textsuperscript{6,17} have a reaction rate constant of coexistence of Fe larger than that of iron oxide, and it can be seen that the catalytic effect of metallic iron is larger than that of iron oxide. In the experiment, since the main solid phases were FeO, the calculation that introduced a shift reaction between CO/CO2/H2/H2O with water gas shift reaction\textsuperscript{17} of FeO coexistence was performed. Here, after changing the CO/CO2 and H2/H2O ratios according to Eqs. (7) and (8), the ratio of CO/CO2/H2/H2O was changed depending on the water gas shift reaction rate.

Figure 12 shows a comparison of the calculation results with and without the shift reaction. A comparison of the calculation results with and without the water gas shift reaction shows that the reduction rate with the reaction is higher than that without that by about 0.03 at 1 073 K. Meanwhile, the influence of the shift reaction is small at lower oxygen partial pressure at higher temperatures. Because the initial oxygen potentials of CO/CO2 and H2/H2O mixture are

![Image](https://example.com/image1.png)

**Fig. 11.** Comparison calculated and experimental reduction behaviors of sinter reduced by CO and H2 a) at 1 073 K, b) 1 173 K and c) 1 273 K.

![Image](https://example.com/image2.png)

**Fig. 12.** Comparison of reduction behavior between calculated lines with and without shift reaction at 1 073 K to 1 273 K.

<table>
<thead>
<tr>
<th>Water gas shift reaction constant (mol/s·cm(^3)·atm(^{-2}))</th>
<th>Coexistence Phase</th>
<th>Temp. range(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.35×10(^{-8})exp((-1.750/RT))\textsuperscript{6}</td>
<td>Fe</td>
<td>973–1 223</td>
</tr>
<tr>
<td>1.83×10(^{-7})exp(1.87×10(^{-3})RT)\textsuperscript{6}</td>
<td>FeO</td>
<td>973–1 223</td>
</tr>
<tr>
<td>93.32×exp((-30 620/RT))\textsuperscript{17}</td>
<td>Fe</td>
<td>973–1 273</td>
</tr>
<tr>
<td>1.827×10(^{-3})exp(32.8/RT)\textsuperscript{17}</td>
<td>FeO</td>
<td>973–1 373</td>
</tr>
<tr>
<td>1.798×10(^{-3})exp((-331/RT))\textsuperscript{17}</td>
<td>Fe(_2)O(_3)</td>
<td>1 073–1 273</td>
</tr>
</tbody>
</table>

R = 1.9872 (cal/K·mol)
same each other, the influence of shift reaction did not appear as a significant difference in the small packed bed like experimental conditions. The reaction behavior cannot be completely reproduced only by water gas shift reaction, and the water gas shift reaction does not only affect the H2 reduction. For further improvement in accuracy, the influence of hydrogen on the structural changes of iron ore must be investigated.

6. Conclusions

The reduction behavior of a sinter packed bed was investigated. Further, a mathematical model for analyzing the reduction of a packed bed was developed, and the model was used to derive the reaction rate constant of the sinter based on the experimental results. The influence of the water gas shift reaction on the reduction reaction in a packed bed was discussed by comparing the reduction reaction in CO/CO2/N2, H2/H2O/N2, and a CO/CO2/H2/H2O/N2 mixture. The following conclusions were obtained.

(1) Reduction rate of iron ore reduced by gas mixtures of the same oxygen partial pressure is increased in the following order: CO/CO2/H2/H2O/N2>H2/H2O/N2>CO/CO2/N2.
(2) The reaction rate constants of the sinter reduced by CO and H2 were obtained using Eqs. (12)–(17).

\[
\begin{align*}
    k_1^{CO} &= \exp(9.087 - 7564/7) \ [\text{m/h}] \\
    k_2^{CO} &= \exp(8.255 - 410/7) \ [\text{m/h}] \\
    k_3^{CO} &= \exp(8.349 - 129/7) \ [\text{m/h}] \\
    k_1^{H2} &= \exp(11.33 - 9539/7) \ [\text{m/h}] \\
    k_2^{H2} &= \exp(9.808 - 8722/7) \ [\text{m/h}] \\
    \text{and} \\
    k_3^{H2} &= \exp(6.173 - 5359/7) \ [\text{m/h}]
\end{align*}
\]

(3) Structural refinement of the iron oxide reduced by H2 was observed. The reduction rate would be enhanced by the enlargement of the specific surface area due to the H2 reduction.

(4) The effect of the water gas shift reaction was discussed using the developed mathematical model. Although the water gas shift reaction enhanced the reduction reaction, its influence on the reduction reaction of the sinter was small.

(5) In higher temperature region, the reduction reaction of the iron ore was accelerated by the addition of H2 to the reducing gas.

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