Influence of CaO and SiO2 on the Reducibility of Wüstite Using H2 and CO Gas

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CaO- (0–20 mass%) and SiO2-containing (0–30 mass%) wüstite (‘FeO’) compacts were isothermally reduced at 1 273 K under CO and H2 gas. Prior to reduction, the phase of dicalcium ferrite (Ca2Fe2O5) and fayalite (Fe2SiO4) was equilibrated with ‘FeO’ at 1 273 K under 50%CO/50%CO2 and identified using X-ray diffraction and scanning electron microscopy. The rate of reduction for CaO-containing ‘FeO’ compacts under both H2 and CO increased up to the vicinity of 2.5 mass% CaO, and then decreased with higher CaO dependent on the formation of an intermediate phase of dicalcium ferrite. For SiO2-containing ‘FeO’, the rate decreased with SiO2 additions. When the dense fayalite is present reduction using CO was limited, while considerable reduction was observed using H2. The reduction was affected by three distinct reduction mechanisms of interfacial chemical reaction, gaseous mass transport, solid state diffusion of oxygen or a combination of these individual mechanisms termed the mixed control. The contribution of each mechanism with the content of CaO or SiO2 affecting the reduction behavior was determined. The compact porosity increased when CaO was added to approximately 2.5 mass% and subsequently decreased with higher CaO, but continuously decreased with SiO2 additions. The ratio of the effective diffusivity (De) to molecular interdiffusivity (D) was highest at the vicinity of 2.5 mass% CaO and thus the maximum reduction rate was obtained when the porosity was highest.

KEY WORDS: H2 reduction; wüstite; CaO; SiO2; Ca2Fe2O5; Fe2SiO4; solubility; reduction mechanism; effective diffusivity.

1. Introduction

The pressing need for stronger environmental regulations, particularly on CO2 emissions, has left the iron-making technologies confronted with the difficult task of balancing environmental issues and higher productivity with decreased raw materials quality. This has led to considerable interest in CO2 emissions from blast furnace (BF) operation, which is responsible for more than 90% of the iron produced around the world1) but is strongly dependent on good quality coke as a reductant and heat source. Furthermore, although the BF is by far the most energy efficient reaction system for iron-making, current systems require not only the BF but also a coke oven and pelletization/sintering plants, which add to the total environmental cost. For this reason, much effort has been devoted to finding alternatives, including not only the electric arc furnace (EAF; produces steel from scrap)2) and direct reduced iron (DRI; produced by MIDREX, HYL, and fluidized bed FINMET processes)3) but also the utilization of H2 instead of carbon, which affords more environmentally friendly products.

For example, several studies have focused on the effect of using H2-containing reducing gas in the BF on the carbon consumption rate from the mass and heat balances (using the basic concept of the RIST operating diagram) for the consumption of CH4,4) and H2.5) Furthermore, the kinetics of H2 utilization in the reduction reaction, one of the major reactions inside the BF, have been also reported for various starting materials such as hematite (Fe2O3),7–10) magnetite (Fe3O4),11) and wüstite (hereinafter referred to as ‘FeO’)12,13)—the constituent phases of iron ore charged into the BF. However, in addition, the effects of impurities such as SiO2 and CaO on the reducibility of iron ores can be expected to significantly differ under H2 than under CO. The researches relevant to the effects of SiO2 and CaO are summarized below.

El-Geassy and coworkers found that during the reduction of Fe2O314) and ‘FeO’15) under CO and H2 the reducibility depended on the form of SiO2—crystalline α-SiO2 or amorphous. The reduction rate was lower with amorphous SiO2 than with crystalline SiO2. Shigematsu et al.16) observed the reduction rate of ‘FeO’ plates with H2 below 1 003 K decreased due to the small amount of SiO2 dissolved in ‘FeO’ rather than formation of complex oxides such as fayalite. In addition, above 1 473 K, the reduction of ‘FeO’ is retarded by formation of dense fayalite on ‘FeO’.17) The effects of SiO2 on the lattice parameters,18) porosity19) of SiO2-containing ‘FeO’ were elucidated to understand the relation between reduction rate and mechanism. El-Geassy

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studied the influence of CaO on the reducibility of Fe₂O₃ \(^{20,21}\) and found that the reduction mechanism changed with the stage (early, intermediate, and later) and the step \((\text{Fe₂O₃} \rightarrow \text{Fe₃O₄}, \text{Fe₃O₄} \rightarrow \text{FeO}, \text{and} \ '\text{FeO}' \rightarrow \text{Fe})\) of reduction because of the structural changes caused by CaO. Studies on the effect of solutes on the reduction rate under \(\text{H₂},^{16,22}\) \(\text{CO},^{23}\) and \(\text{H₂–CO}^{17}\) showed that the reduction increased with the amount of CaO dissolved. Takahashi et al.\(^{22,23}\) concluded that the reason for the increase is the increase of porosity produced because CaO particles prevent sintering. Inami et al.\(^{24}\) showed that under a CO–CO₂ gas mixture, the lattice parameters of CaO-containing 'FeO' increased with CaO addition up to the solubility limit of CaO in 'FeO' and then became constant. Beyond the solubility limit, Jeon et al.\(^{25}\) and Fukuyama et al.\(^{26}\) also empirically confirmed the formation of dicalcium ferrite from 'FeO' under the controlled oxygen potential where 'FeO' is stable at 1 273 K.

Despite these several studies, however, there is still controversy behind the roles of CaO and SiO₂, especially in distinguishing between the effect of solutes and co-existing phases (such as fayalite or dicalcium ferrite). Further, previous studies used a limited range of additive concentrations (CaO: \(\sim\)5 mass%, SiO₂: \(\sim\)11 mass%). In present study, the reduction behavior of 'FeO' under H₂ was investigated at 1 273 K using thermo-gravimetric analysis (TGA) for a wider range of CaO (0–20 mass%) and SiO₂ (0–30 mass%) concentrations, which was compared with those under CO. In addition, a pre-treatment step was performed before reduction to generate the phase equilibrated with 'FeO' under the given composition, thus making the conditions very similar to the real reduction process. Moreover, for a better understanding, the reduction mechanisms and their contributions are also considered together with the morphological changes.

### Table 1. Experimental conditions in present study.

<table>
<thead>
<tr>
<th>No.</th>
<th>Chemical composition of compact (mass%)</th>
<th>Constituent phases: developed before reduction by CO and H₂</th>
<th>Condition of reduction</th>
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<td>'FeO' 100 0</td>
<td>1 273 K</td>
</tr>
<tr>
<td>2</td>
<td>0 100</td>
<td></td>
<td></td>
</tr>
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<td>3</td>
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<td>'FeO' 100 0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>70 0 30 Fe₂SiO₄</td>
<td>'FeO' 100 0</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>59 10 30 'FeO' + Fe₂SiO₄</td>
<td>'FeO' 100 0</td>
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<td>7</td>
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<tr>
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<tr>
<td>13</td>
<td>39 7.5 2.5 'FeO' + Ca₂Fe₂O₅</td>
<td>'FeO' 100 0</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>39 7.5 2.5 'FeO' + Ca₂Fe₂O₅</td>
<td>'FeO' 100 0</td>
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</tbody>
</table>

2. Experimental

2.1. Apparatus and Procedure

Reagent grade CaO or SiO₂ powder was added to 'FeO'

<table>
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<td>39 7.5 2.5 'FeO' + Ca₂Fe₂O₅</td>
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Fig. 1. Schematic representation of the experimental (a) steps and (b) apparatus for thermo-gravimetric analysis.

The mixtures were held at 1 773 K for 5 h in a flow of high-purity (99.9999%) Ar gas. The samples were quenched and then crushed into powders with a particle size of 100 μm. These powders were pressed in a cylindrical mould.
under a force of 12,000 N. To minimize the effect of size, all the produced compacts had the same size (13 mm in diameter and 10 mm ± 0.1 mm in height). These compacts were placed inside a TGA apparatus in Fig. 1(b) under high-purity Ar gas and heated to 1273 K. Before reduction, the compacts were maintained at 1273 K for 4 h under 50%CO–50%CO2 to obtain the phase that equilibrate with ‘FeO’ under the given conditions, which constitutes STEP III in the schematic in Fig. 1(a). To confirm the formed phase, immediately after STEP III, the compacts were quenched in high-purity He and then identified by X-ray diffraction (XRD). The compacts were then isothermally reduced at 1273 K under H2 and CO, as shown in Table 1. During reduction, the mass loss of the compacts due to the removal of oxygen was continuously recorded at 1 Hz using the TGA apparatus. Preliminary tests indicated that a reducing gas flow rate of 450 cm3/min at standard condition was sufficient to minimize the effects of bulk gas mass transfer around the compacts. After reduction, some samples were quenched in He and examined using a scanning electron microscope (SEM) and an automatic porosimeter.

2.2. Identification of Phase Equilibrated with ‘FeO’ before Reduction

Prior to reduction by CO and H2, a pre-treatment step (STEP III in Fig. 1(a)) was introduced to obtain the phase equilibrated with ‘FeO’ under 50%CO–50%CO2 at 1273 K. From the XRD results (Fig. 2(a)) and the phase diagram of ‘FeO’-CaO shown in Fig. 3(a),27 the CaO-containing compacts contained dicalcium ferrite (Ca2Fe2O5), except for the compact with 2.5 mass% CaO, which had no Ca2Fe2O5. Jeon et al.25 and Fukuyama et al.26 also found that Ca2Fe2O5 formed from ‘FeO’ under the same range of CO–CO2 mixture concentrations as those used here. They also suggested that the direct formation reaction for Ca2Fe2O5 from ‘FeO’ and CaO was as follows:

\[
2\text{FeO} + 2\text{CaO} + \frac{1}{2}O_2 = \text{Ca}_2\text{Fe}_2\text{O}_5 \quad \text{.......... (1)}
\]

where extra oxygen (\(\frac{1}{2}O_2\)) is taken from the atmosphere during formation. Fayalite (Fe2SiO4) in Fig. 3(b)28 was also found as a constituent phase in all the SiO2-containing compacts, whose XRD patterns are shown in Fig. 2(b). The SEM
micrographs for Ca$_2$Fe$_2$O$_5$ and Fe$_2$SiO$_4$ formed from ‘FeO’ during STEP III provide more evidence, as shown in Figs. 4(a) and 4(b), respectively.

3. Results and Discussion

3.1. Effect of CaO and SiO$_2$ on the Reducibility of ‘FeO’ Compacts

Compacts of pure ‘FeO’ and those with 2.5, 10, and 20 mass% CaO were isothermally reduced at 1 273 K under CO and H$_2$ gas. The reduction curves under CO and H$_2$ are shown in Figs. 5(a) and 5(b), respectively, where the reduction degree $R$ is defined as follows:

$$R \% = \frac{\Delta W_o}{\Delta W_i} \times 100$$

where $\Delta W_o$ is the total weight loss by removed oxygen and $\Delta W_i$ is the initial weight of removal oxygen in the compact. The values of $\Delta W_o$ for the CaO-containing compacts should be determined by considering both oxygen removal in ‘FeO’ and the extra oxygen from the atmosphere in Eq. (1). Under both CO and H$_2$, the experimental results indicated that the rate of reduction increased with 2.5 mass% CaO. However, CaO content from 2.5 to 10 mass% resulted in a decrease in the rate of reduction, which contradicts the results of previous studies.$^{16,22,23}$ This tendency was more pronounced as CaO content exceeded more than 10 mass%, which may be speculated to be a result of the different role of CaO dissolved as a solute (free CaO) or as an intermediate multi-component phase details of which will be discussed in later sections.

For SiO$_2$-containing ‘FeO’ compacts, as shown in Figs. 6(a) and 6(b), the rate of reduction decreased with increasing SiO$_2$ content under both CO and H$_2$, although the effect was more obvious under H$_2$. At 30 mass% SiO$_2$, the compact was scarcely reduced under CO compared with H$_2$, probably due to the phase of Fe$_3$SiO$_4$. 

Fig. 4. SEM micrographs of the phase equilibrated with ‘FeO’ in (a) 10 mass% CaO - ‘FeO’ and (b) 10 mass% SiO$_2$ - ‘FeO’ compacts during STEP III.

Fig. 5. Reduction curves of CaO-containing ‘FeO’ compacts under reducing gas of (a) CO and (b) H$_2$.
The effects of CaO and SiO\textsubscript{2} additions on the reduction behavior was more obvious at the later stages of reduction compared to early stages. Thus, the apparent rate constant at 60% reductions was taken as the reference for comparison as CaO or SiO\textsubscript{2} content was varied, which was shown in Fig. 7. The apparent rate constant ((mol·g)/(s·cm\textsuperscript{2}·atm)) of reduction was obtained from the tangent of the fraction of oxygen removed as a function of time and the following equation.

\[ k_{app} = - \frac{dO}{dt} \begin{bmatrix} A \times \frac{1}{P_{H_2} or CO} \times \frac{1}{P_{H_2} or CO} \end{bmatrix} \]  … (3)

where \( dO/dt \) is the amount of oxygen removed per unit time (mol/s), \( A \) is the specific area (cm\textsuperscript{2}/g), \( P_{H_2} or CO \) is the initial partial pressure of the reducing gas (atm), \( P_{H_2} or CO \) is obtained from the FeO/Fe equilibrium (atm).

3.2. Mechanism and Kinetics of Reduction
Several mathematical formulae have been derived to distinguish the reduction mechanisms affecting the reduction rate. The grain model derived by Szekely et al.\textsuperscript{29} seems to be the most applicable mathematical model in heterogeneous gas-solid reaction assuming long cylindrical compacts.\textsuperscript{30} The detailed derivations of these formulae has been provided in previous published literature\textsuperscript{29} and are beyond the scope of this work. Only the simplified forms of the grain models are expressed in the following equations. A plot of these models as a function of time will result in a linear slope if the apparent mechanisms are affecting the rate of reduction.

(a) Interfacial chemical reaction:
\[ g(F) = 1 - (1 - F) \frac{1}{t} = t' = k_2 \cdot t = Y \]  ……… (4)

(b) Gaseous mass transport through the product layer:
\[ p(F) = X + (1 - F) \cdot \ln(1 - F) = 2 \cdot F_g \cdot F_p \cdot t' / \sigma^2 \]  … (5)

(c) Mixed control (interfacial chemical reaction + gaseous mass transport) reaction:
\[ t' = g(F) + \sigma^2 \cdot p(F) = k_3 \cdot t = Y \]  ……… (6)

Here, \( F \) is the fractional reduction degree at a given reduction time \( t \) (s); \( F_g \) and \( F_p \) are the shape factors for grains and compacts (=1, 2, and 3 for flat plates, cylinders, and spheres), respectively; \( t' \) is dimensionless time; \( \sigma \) is the gas–solid reaction modulus; \( \sigma \) is the generalized gas–solid reaction modulus (\( \sigma^2 \approx 1 \)); and \( k_1, k_2, k_3 \) are constants (s\textsuperscript{-1}).

The mathematical conversion formulae in Eqs. (4), (5), and (6) were applied to the reduced fraction (F) as a function of time for pure ‘FeO’ and CaO- and SiO\textsubscript{2}-containing ‘FeO’ compacts to determine the reduction mechanisms, as shown in Figs. 8(a)–8(j). From the results of applying the mathematical modeling, it seems that the reduction behavior is affected by three distinct controlling mechanisms of interfacial chemical reaction, gaseous mass transport, solid state diffusion of oxygen, or a combination of these individual mechanisms termed the mixed control, as shown in Table 2.

It is speculated that the reduction mechanism for all CaO-containing compacts follow Type I, where the reduction is initially controlled by interfacial chemical reaction and changes to the mixed control reaction (I) as significant product layer is formed and the resistance to gas mass transfer becomes important. In addition, the regions controlled by the interfacial chemical reaction under CO are much wider than those under H\textsubscript{2}, which stems from the lower rate constant of CO at the reaction interface compared to H\textsubscript{2}.

For the 2.5 and 10 mass% SiO\textsubscript{2}-containing ‘FeO’ compacts under CO, the reduction follows a Type I reduction
behavior, where the mechanism changes from the initial interfacial chemical reaction to a mixed control (I) of interfacial chemical reaction and gaseous mass transport. However, with further reduction solid state diffusion of oxygen inside the Fe$_2$SiO$_4$ phase becomes a factor under H$_2$ reduction as previously observed from the micrographs shown in Fig. 4(b) and thus the mixed control (II) is observed in the reduction plots. For the 30 mass% SiO$_2$ under CO, the reduction follows a Type III reduction behavior and the final reduction degree was approximately 18%, where a single dominant mechanism of interfacial chemical reaction was rate controlling. However, for the 30 mass% SiO$_2$ under H$_2$ gas, the reduction follows a Type II reduction behavior and the final reduction degree was approximately 78%, where the mechanism changes from the initial interfacial chemical reaction.

Table 2. Types of controlling mechanisms affecting the reduction behavior.

<table>
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<th>Type I</th>
<th>Type II</th>
<th>Type III</th>
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<tr>
<td>1 Interfacial Chemical Reaction (ICR)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>2 Gaseous Mass Transport (GMT)</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>3 Solid State Diffusion (SSD)</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>

Reduction mechanism steps during reduction:
1. Interfacial chemical reaction (ICR)
2. Mixed (I)
3. Mixed (II)

Fig. 8. Application of mathematical formulae deduced from grain model on the reduction of (a) 10 mass% CaO - FeO under CO, (b) 10 mass% CaO - FeO under H$_2$, (c) 2.5 mass% CaO - FeO under CO, (d) 2.5 mass% CaO - FeO under H$_2$, (e) pure FeO under CO, (f) pure FeO under H$_2$, (g) 10 mass% SiO$_2$ - FeO under CO, (h) 10 mass% SiO$_2$ - FeO under H$_2$, (i) 30 mass% SiO$_2$ - FeO under CO, (j) 30 mass% SiO$_2$ - FeO under H$_2$. 

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reaction to a mixed control (I) of interfacial chemical reaction and gaseous mass transport followed by a mixed control (II) of interfacial chemical reaction, gaseous mass transport, and solid state diffusion. This higher reduction degree using H2 for 30% SiO2-containing 'FeO' indicates that H2 has a higher permeability for the Fe2SiO4 phase compared to CO, which was also verified by the SEM micrographs at 30 mass% SiO2 after CO and H2 reduction as shown in Figs. 9(a) and 9(d), respectively, which are remarkably different from those for pure 'FeO' (Figs. 9(b) and 9(e)) and CaO-containing 'FeO' (Figs. 9(c) and 9(f)). For a SiO2 content of 30%, the compacts are mostly Fe2SiO4 and iron nuclei formed only on the surface of the Fe2SiO4 phase using CO, but iron nuclei were found both on the surface and internally in the Fe2SiO4 phase under H2 reduction. Therefore, as the H2 penetrates into Fe2SiO4 further reduction is possible and the mixed control (II) involving solid-state diffusion of oxygen can be a factor in governing the reduction behavior of 30 mass% SiO2-'FeO' compacts under H2 when gaseous mass transport becomes less dominant and additional reduction mechanism such as solid state diffusion becomes important.

To quantify the contributions of each reduction mechanism to the reduction behavior, the kinetic parameters $k_1$ and $k_2$ were plotted, as shown in Fig. 10. It should be noted that $k_1$ and $k_2$ were obtained from the plots for the gaseous mass transport and interfacial chemical reaction in the mixed control (I) region, respectively. The approximate values of $k_1$ and $k_2$ were comparable suggesting a mixed control is rate controlling. In Fig. 10(a), $k_2$ decreases with increasing CaO or SiO2 content under both CO and H2, which indicates that the gaseous mass transport can become an important factor in determining the overall rate controlling mechanism. Thus, the effect of gaseous mass transport in the mixed control (I) becomes more dominant. It should be noted that although $k_2$ continues to decrease with CaO and SiO2 additions, $k_1$ does not continuously decrease with CaO additions.

But is convex with CaO additions showing a maximum between 2.5 mass% and 5 mass% CaO and decreases above 5 mass% as shown in Fig. 10(b). This indicates that the
increase in \( k_1 \), which represents a higher contribution of gaseous mass transport within the mixed control (I) region, is the reason why the compact in the vicinity of 2.5 mass% CaO has the largest apparent rate constant (at 60% reduction; Fig. 7) under CO or \( H_2 \). This could be closely related with the pore characteristics inside the compacts, which are discussed in detail in the next section.

3.3. Relation between Porosity and Effective Diffusivity

The effect of CaO on the porosity of the CaO-containing compacts after reduction by \( H_2 \) was plotted as a function of CaO or SiO\(_2\) content in Fig. 11(a). It should be noted that only compacts fully reduced by \( H_2 \) were used to measure the porosity as this minimized the effect of unreduced ‘FeO’. The measured porosity of fully reduced CaO-containing ‘FeO’ increased up to the vicinity of 2.5 mass% CaO, which is the same as seen in the previous results\(^{22,23} \) but decreased at higher CaO concentrations. One of the reasons for this could be the change in the lattice parameter of the CaO-containing ‘FeO’. The lattice parameter increases with the CaO content but becomes nearly constant after the solubility limit of CaO in ‘FeO’ is exceeded—the solubility limit for CaO in ‘FeO’. In addition, it is speculated that the porosity increase is responsible for the decrease in gaseous mass transport and subsequently the apparent rate constant at 2.5 mass% CaO. Beyond the solubility limit, such as at 10 and 20 mass% CaO, although the lattice parameter does not change with CaO content, the decrease in the mass fraction of ‘FeO’, which contributes to porosity on reduction from ‘FeO’ to Fe, explains in the decrease in porosity. The porosity of reduced SiO\(_2\)-containing compacts decreased with the SiO\(_2\) content, which could originate from the increase in mass fraction of the dense Fe\(_2\)SiO\(_4\) phase\(^{39} \) and subsequent decrease in ‘FeO’.

To quantify the effects of pore structure on the reduction behavior, especially on gaseous mass transport of the reducing gas, the ratio of the effective diffusivity (\( D_e, \text{cm}^2/\text{s} \)) to the molecular interdiffusivity (\( D, \text{cm}^2/\text{s} \)) of the reducing gas, i.e., \( D_e/D \), was plotted as a function of CaO or SiO\(_2\) content with the results of Turkdogan\(^{7} \) et al. and McKewan\(^{21} \) as shown in Fig. 11(b). The \( D_e/D \) is a dimensionless parameter and is a property of a given porous material that characterizes the pore structure. For a long, cylindrical geometry, \( D_e \) can be obtained from Eq. (7)\(^{33} \) which was derived from the slope of the straight line \( F + (1-F)\cdot \ln(1-F) = \frac{4\cdot D_e}{\rho \cdot r_0^2 \cdot R \cdot T} \left( p^{\text{in}} - p^{\text{eq}} \right) \cdot t = k_1 \cdot t \),

\[
\frac{D_e}{D} = \frac{\left( \frac{T^{3/2}}{P \cdot \delta_{12}^{3/2} \cdot \Omega^{1/2}} \right) \left( \frac{1}{M_1} + \frac{1}{M_2} \right)^{1/2}}{1}, \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ ld
mining the influence of CaO and SiO₂ on gaseous mass transport in the mixed control reaction (I) and subsequent reducibility of ‘FeO’ under CO and H₂.

4. Conclusions

CaO- (0–20 mass%) and SiO₂-containing (0–30 mass%) wüstite (‘FeO’) compacts containing their equilibrium phases were isothermally reduced at 1 273 K under CO and H₂ gas. Prior to reduction, the compacts were kept at 1 273 K for several hours to obtain the phases such as dicalcium ferrite (Ca₂Fe₂O₅) or fayalite (Fe₂SiO₄) that are equilibrated with ‘FeO’. The results obtained are summarized as follows:

(1) The rate of reduction for CaO-containing ‘FeO’ compacts under both CO and H₂ increased with 2.5 mass% added CaO but was lower at 10 mass% CaO and beyond. This can be attributed by the distinctly different influences of CaO on the reducibility in the regions below and above the solubility limit of CaO in ‘FeO’, where there exists dissolved CaO and formation of Ca₂Fe₂O₅, respectively. For SiO₂-containing ‘FeO’ compacts, the rate of reduction decreased with the SiO₂ content. At 30 mass% SiO₂, in particular, scarcely any reduction occurred under CO due to the dense Fe₂SiO₄ phase, although it was considerably reduced under H₂. The rates and reducibility under H₂ were significantly higher than those under CO for both CaO- and SiO₂-containing compacts.

(2) For CaO-containing compacts, the reduction mechanism under both CO and H₂ changes from an interfacial chemical reaction (I) (interfacial chemical reaction + gaseous mass transport) to a mixed control (I) region despite a decrease in k₂ (contribution of interfacial chemical reaction). For the SiO₂-containing compacts, the decrease in both k₁ and k₂ in the mixed control (I) region resulted in the decrease in the rate with increasing SiO₂ content.

(4) The porosity for fully reduced CaO-containing ‘FeO’ under H₂ increased up to the vicinity of solubility limit of CaO due to the increase of lattice parameter and then decreased with further CaO addition. For the SiO₂-containing ‘FeO’, the porosity decreased with an increase in SiO₂ content. These changes in porosity were similar to those in the Dₚ/D₀ ratio and k₁.

REFERENCES