1. Introduction

While recycling and biomass energies are attracting attention as countermeasures for global warming and other environmental problems, the dependence on fossil energies remains high. The use of coal as an energy source causes atmospheric pollution through the release of carbon dioxide and sulfur oxide emissions and, therefore, requires an enormous amount of environmental control investment. Although the steel industry has already installed many desulfurization units in its production processes, it is required to further improve the desulfurization efficiency of all production processes because the industry uses large quantities of coal. It is particularly important to improve the desulfurization efficiency of the blast furnace process, which is capable of capturing into the slag phase and discharging, in a stable form, approximately 85% of sulfur in a hot strongly reductive atmosphere.

Discussions regarding the desulfurization reaction in blast furnaces have mostly focused on the reaction between the slag and metal in the blast furnace hearth. However, Tsuchiya et al. referred to the possibility of a desulfurization reaction through the vapor phase and Kodama et al. studied the evaporation of slag components and reported the abundance of magnesium oxide evaporation. This evaporation seems to take place after magnesium oxide has been reduced because the boiling point of magnesium alone (boiling point: 1 090°C, melting point: 648.8°C) is lower than that of magnesium oxide (boiling point 3 600°C, melting point: 2 830°C).

Yang et al., who are studying the desulfurization of molten iron using the magnesium gas generated from carbon and magnesium oxide in the steelmaking process, report that this desulfurization is highly effective.

We studied the possibility of desulfurization using the magnesium gas generated by reducing the mixture of pulverized coal and magnesium oxide in the high-temperature region in the vicinity of the blast furnace tuyeres.

2. Thermodynamic Study of Desulfurization Reaction

In this study, the desulfurization reaction path was considered as follows: First, the magnesium oxide injected through the tuyeres becomes magnesium gas on being reduced in the hot strongly reducing atmosphere and the resulting magnesium gas forms magnesium sulfide by reaction with the sulfur in the molten iron. By dividing this desulfurization process into a magnesium gas producing reaction and a desulfurization reaction by the magnesium gas, the desulfurization effect of the magnesium oxide flux was confirmed through laboratory experiment. A thermodynamic study on the desulfurization reaction in which SiO gas resulting from the reduction of SiO₂ produces a silicon sulfide gas by reaction with the sulfur in the molten iron revealed that the possibility of desulfurization of the molten iron by the silicon sulfide gas is not negligible.

KEY WORDS: environmental measures; blast furnace; desulfurization; serpentine.
\[
\text{MgO (s) + C (s) \rightarrow Mg (g) + CO (g)} \quad \text{(1)}
\]
\[
\Delta G_{(1)}^{0} = 696.957 + 29.83 T \log T - 432.62T \quad [\text{J/mol}]
\]
\[
\text{Mg (g) + \text{S} = MgS (s)} \quad \text{(2)}
\]
\[
\Delta G_{(2)}^{0} = -437.020 + 185.47T \quad [\text{J/mol}]
\]

The free energy change in the reaction expressed by Eq. (1) can be defined as follows:
\[
\Delta G_{(1)} = \Delta G_{(1)}^{0} + RT \ln K_{(1)} \quad \text{(3)}
\]
\[
K_{(1)} = \frac{P_{\text{Mg}} \cdot P_{\text{CO}}}{a_{\text{MgO}} \cdot a_{\text{C}}} \quad \text{(4)}
\]

While \(\Delta G_{(1)}^{0} = 0\) in the equilibrium condition, \(P_{\text{Mg}}\) at a given temperature can be obtained by defining the furnace conditions as \(P_{\text{CO}} = 0.15\) [MPa] and \(a_{\text{C}} = 1\) and giving \(a_{\text{MgO}}\). The following equation formulated based on the report of Kume et al.\(^{14}\) was used for determining the activity of magnesium oxide.
\[
\gamma_{\text{MgO}} = 1.542 \cdot (\%\text{CaO}) + 1.544 \cdot (\%\text{SiO}_{2}) + 1.583 \cdot (\%\text{Al}_{2}O_{3}) + 1.352 \cdot (\%\text{MgO}) - 151.96 \quad \text{at 1 600°C} \quad \text{(5)}
\]

In order to consider the temperature dependence, Eq. (6), obtained by the regular solution approximation, was used.
\[
T \cdot \ln \gamma = T_{0} \cdot \ln \gamma_{0} \quad \text{(6)}
\]

**Figure 1** shows the \(P_{\text{Mg}}\) at given temperatures \(T\) and under the furnace conditions derived by using Eqs. (3) to (6). The free energy change in the reaction expressed by Eq. (2) is described by Eq. (7).
\[
\Delta G_{(2)} = \Delta G_{(2)}^{0} + RT \ln K_{(2)} \quad \text{(7)}
\]
\[
K_{(2)} = \frac{a_{\text{MgS}}}{P_{\text{Mg}} \cdot a_{\text{S}}} \quad \text{(8)}
\]

Then, \(a_{\text{S}} = 0.3\) was obtained by substituting the sulfur concentration in the hot metal in front of the tuyeres and the activity coefficient, which are respectively approximately 0.1 mass% and approximately 3, in Eq. (9).
\[
a_{\text{S}} = f_{\text{S}} \cdot \text{mass%S} \quad \text{(9)}
\]

The activity of MgS in the slag was evaluated as described below.
\[
2\text{MgO (s) + S}_{2} (g) \rightarrow 2\text{MgS (s) + O}_{2} (g) \quad \text{(10)}
\]
\[
\Delta G_{(10)}^{0} = 493 100 + 59.66T \log T - 282T \quad [\text{J/mol}]
\]

\[
K_{(10)} = \frac{a_{\text{MgS}}^{2} \cdot P_{\text{O}_{2}}}{a_{\text{MgO}}^{2} \cdot P_{\text{S}_{2}}} \quad \text{(11)}
\]

Here, the following equation was derived from the definition of the sulfide capacity \(C_{\text{s}}\) that expresses the desulfurization capacity of the slag.
\[
\frac{P_{\text{O}_{2}}}{P_{\text{S}_{2}}} = C_{\text{s}}^{2} \times (\text{mass%S})^{2} \quad \text{(12)}
\]

The relationship between the activities of magnesium sulfide and magnesium oxide was derived by substituting Eq. (12) in Eq. (11).
\[
a_{\text{MgS}} = \frac{a_{\text{MgO}} \cdot (\text{mass%S}) \cdot K_{(10)}^{0.5}}{C_{\text{s}}} \quad \text{(13)}
\]
\[
\gamma_{\text{MgS}} = \frac{a_{\text{MgO}} \cdot (\text{mass%S}) \cdot K_{(10)}^{0.5}}{C_{\text{s}} \cdot X_{\text{MgS}}} \quad \text{(14)}
\]

\(C_{\text{s}}\) was determined by using the following equation that employs optical basicity \(\Lambda\).\(^{15}\)
\[
\log C_{s} = 12.6 \Lambda - 12.3 \quad \text{(15)}
\]
\[
\Lambda = 1.0 \cdot X_{\text{CaO}} + 0.78 \cdot X_{\text{MgO}} + 0.61 \cdot X_{\text{Al}_{2}O_{3}} + 0.48 \cdot X_{\text{SiO}_{2}} \quad \text{(1 500°C)} \quad \text{(16)}
\]

By using the above equation, \(\gamma_{\text{MgS}}\) at 1 500°C and \(a_{\text{MgS}}\) were obtained. Considering the temperature dependence by using Eq. (6), \(a_{\text{MgS}}\) and the equilibrium partial pressure of magnesium between 1 500°C and 2 100°C were also determined. The equilibrium partial pressure of magnesium was determined not only with the activity of magnesium sulfide in the slag but also with the assumption that the activity of magnesium sulfide is unity. Figure 1 shows the obtained partial pressures together with the equilibrium partial pressure of magnesium described earlier.

The equilibrium partial pressure of magnesium in the magnesium oxide reducing reaction, with the blast furnace conditions considered, at 1 600°C was as high as \(10^{-4.8}\) [MPa]. In terms of equilibrium, the partial pressure of magnesium is presumed to be higher in the vicinity of the tuyeres where the temperature is still higher.

The equilibrium partial pressure of magnesium in the desulfurization reaction differed greatly depending on whether magnesium sulfide exists alone (\(a_{\text{MgS}} = 1\)) or magnesium sulfide coexists with the slag (\(a_{\text{MgS}} = 10^{-3.18}\) to \(10^{-3.10}\) at 1 500 to 1 900°C). It seems that the desulfurization reaction proceeds when magnesium sulfide coexists with the partial pressure of magnesium in the magnesium oxide reducing reaction is lower than the partial pressure of magnesium in the magnesium oxide reducing reaction.

### 3. Magnesium Gas Producing Reaction Experiment

The desulfurization reaction by way of magnesium gas seems to comprise a reaction to produce magnesium gas from magnesium oxide and a reaction to desulfurize molten
iron with the produced magnesium gas. Thermodynamically, it was revealed that desulfurization might take place if the magnesium gas producing reaction occurs in the presence of the slag. However, no finding has yet been obtained as to how far the magnesium gas producing reaction from the mixture of magnesium oxide and carbon proceeds in a hot strongly reductive atmosphere at 1 600°C or above simulating the raceway of the blast furnace. Therefore, a gasification reaction experiment was conducted by using mixtures of magnesium oxide and carbon.

3.1. Experimental Method

The weight reduction associated with the gas producing reaction was determined on-line and the measured weight reduction was used as the rate of gas producing reaction. The specimens were prepared by using a magnesium oxide reagent (99% pure and particle median diameter = 15 μm) as the source of magnesium oxide and the chippings of a graphite crucible (particle median diameter = 97 μm) as the source of carbon. As the experiment was conducted in a system where only magnesium oxide and carbon were present, the rate of weight reduction seemed to represent the rate of the magnesium gas producing reaction. Figure 2 shows the apparatus used in the experiment. The predetermined quantities of the magnesium oxide reagent and graphite crucible chippings were weighed, mixed and put in the graphite crucible. In the temperature raising process, the temperature was controlled by a thermocouple fastened directly below the crucible and raised from room temperature to a range between 1 600 and 1 900°C at a rate of 1 K/s. While the temperature was elevated, carbon monoxide gas was supplied from below (at a rate of 1 NL/min) to provide a reductive atmosphere. The change in the weight of the specimen in the crucible was determined by using a thermobalance.

3.2. Experimental Results

In this experiment, the average of the weight reduction rate during the period (5 min) during which weight reduction became stable 2 min after the temperature was held constant was taken as the magnesium gas producing reaction rate. As the specimen ratio might affect the magnesium gas producing reaction, the magnesium oxide/carbon ratio (weight fraction) was varied and the weight reduction at each ratio was measured. Then it was discovered that carbon exists in a sufficiently large quantity with respect to magnesium oxide when the magnesium oxide/carbon ratio is not greater than 1 and the magnesium gas producing reaction does not depend on the carbon ratio. Figure 3 shows the results obtained when temperature was varied at a magnesium oxide to carbon ratio of 1 and the specimen weight was 0.56 g. From the obtained results, it became obvious that weight reduction becomes increasingly active beyond approximately 1 600°C and the speed of weight reduction increases exponentially with increasing temperature. Figure 3 also shows the results with the tableted specimens used in the desulfurization experiment described later. It seems that the tableted specimens produce had less influence, although the speed of weight reduction was somewhat slower.

Now that the existence of exponential temperature dependence has been confirmed (Fig. 4), it seems that the speed of weight reduction shows the speed of the reaction.
The obtained results led to a calculation revealing that the activation energy of the weight reduction reaction was 362 [kJ/mol]. This activation energy is almost equal to 385 [kJ/mol] derived from the magnesium gas desulfurization experiment conducted by Tsuchiya et al. 1

3.3. Analysis of Accretion on the Suspension Wires

When high-sulfur coal was used as the carbon source, white and black accretions were found on the suspension wires (Fig. 5). Scanning electron-energy dispersion spectroscopic (SEM-EDS) analysis revealed that Structure 3a contains magnesium, silicon and sulfur (Fig. 6) and Structure 3b contains magnesium, silicon and aluminum.

4. Molten Iron Desulfurization Experiment with Magnesium Gas

It became clear that magnesium oxide is reduced by carbon and increases the speed of the gasification reaction at temperatures higher than 1600°C. Molten iron was desulfurized with the magnesium gas generated from the tableted specimen and the effect of desulfurization was quantitatively evaluated.

4.1. Experimental Method

A mixture of serpentine (Table 1), magnesium oxide reagent and carbon source was tableted and heated in an electric furnace. The gas generated when the specimen was held at high temperature was brought into contact with the surface of the molten iron by using a carrier gas (carbon monoxide) and induced desulfurization by a gas–metal reaction. After the gas–metal reaction was allowed to continue for a given time, the sulfur concentration in the sampled molten iron was quantitatively assayed. As shown in Fig. 7, magnesium gas arose from the tablets in the upper crucible (Eq. (1)), while magnesium sulfide was formed and desulfurization occurred in the lower crucible where the magnesium gas reacted with the sulfur in the molten iron (Eq. (2)). In this experiment, it was particularly important to bring the magnesium gas generated in the upper crucible into contact with the molten iron. In order to ensure this contact, the path of the gas flow was confined by an alumina tube so that the produced magnesium gas was stably in contact with the surface of the molten iron. Figure 8 shows the dimensions of the graphite crucible used in the experiment. The crucible was divided into an upper and a lower segment that are joined together by threads. Seven holes were perforated in the upper crucible in order to deliver the gas generated from the tablets to the lower crucible. An alumina crucible containing molten iron was placed in the lower segment and the molten iron was allowed to react with the gas generated in the upper segment. Four 5 mm diameter holes were perforated in the side face of the crucible as paths for the gas flow. An alumina tube having an outside diameter of 15.6 mm was inserted in the upper crucible (of graphite) having an inner diameter of 16 mm and fastened together by using a heat-resistant adhesive (zirconia refractory). The temperature was raised from room temperature to 1800°C at a rate of 1 K/s while supplying nitrogen gas (at 1 NL/min) so as to prevent the oxidation of the reaction tube. While tablets (0.2 g × 4) were charged through the alumina tube, carbon monoxide was supplied into the reaction tube (at 1 NL/min) to produce a reducing atmosphere. After given periods of time (30 or 60 min), the specimens were taken out and rapidly cooled in air. After scraping off the surface and crushing, the specimens were subjected to chemical analysis.

4.2. Test Specimen

The tablets (0.2 g and 5 mm diameter) were prepared by

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**Table 1. Chemical composition of serpentine.**

<table>
<thead>
<tr>
<th>Component</th>
<th>mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>T.Fe</td>
<td>5.18</td>
</tr>
<tr>
<td>FeO</td>
<td>2.56</td>
</tr>
<tr>
<td>CaO</td>
<td>0.90</td>
</tr>
<tr>
<td>SiO₂</td>
<td>39.52</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.54</td>
</tr>
<tr>
<td>MgO</td>
<td>39.14</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.006</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.003</td>
</tr>
<tr>
<td>MnO</td>
<td>0.12</td>
</tr>
<tr>
<td>S</td>
<td>0.013</td>
</tr>
<tr>
<td>C.W.</td>
<td>12.44</td>
</tr>
</tbody>
</table>

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![Fig. 5. Microphotograph of the accretion on the suspension wire.](image)

![Fig. 6. Analytical results of the accretion on the suspension wire.](image)

![Fig. 7. Positioning of the specimen.](image)
pressing a 2 : 1 mixture of the magnesium oxide flux (magnesium reagent or serpentine) and carbon source (coke or VM-free coal). By assuming the composition in front of the tuyeres, the molten iron was prepared by pre-melting a mixture of electrolytic iron, iron sulfide reagent and carbon. Tables 2 and 3 show the results of their chemical assays.

4.3. Experimental Results

Figure 9 shows the results of the experiment. The sulfur concentration in the molten iron was decreased in the blank test, in which no tablet was charged. This means sulfur forms some compounds in a gas phase and some desulfurization reactions occur in a gas phase. Although more sulfur was charged, the sulfur concentration in the molten iron was lower in the test charged with the tablets than in the blank test. Despite the variations, both of the magnesium oxide reagent and serpentine proved to have desulfurization effects. The tablets prepared with the use of serpentine proved to have a greater desulfurization effect. Differences between the carbon sources were not clear.

5. Discussion

It seems that the pure magnesium oxide reagent provides higher equilibrium partial pressure of magnesium and generates magnesium gas more vigorously. At the same time, it also seems that the great desulfurization effect of the tablets of serpentine was due to the silicon oxide in serpentine that has an effect on the desulfurization reaction. The following assumptions were studied regarding the promotion of desulfurization by serpentine.

The equilibrium partial pressures of magnesium resulting from the use of the magnesium oxide reagent and serpentine were compared under the common conditions that $P_{\text{CO}} = 0.101$ [MPa] and $a_c = 1$. For the calculation, the magnesium oxide reagent was made by assuming that the reagent was a pure substance that does not produce a compound of magnesium oxide and magnesium sulfide and that $a_{\text{MgO}} = 1$ and $a_{\text{MgS}} = 1$. It was further assumed that the serpentine approximately comprises, except the water of crystallization, 50% magnesium oxide and 50% silicon oxide, and has a composition similar to the one described in the paper of Kume et al. with the activity of magnesium oxide assumed to be 0.25. The sulfide capacity of the magnesium oxide–silicon oxide system at 1 650°C was cited from the literature as being $10^{-4}$. By using the above parameters, the equilibrium partial pressure of magnesium was calculated and the possibility of desulfurization was studied. Figure 10 shows the results obtained, from which it seems that serpentine provides a greater difference in the equilibrium partial pressure of magnesium, if slag phase were formed by reduction of serpentine. However, little slag phase was formed during the experiment. So there might be other reasons for the great desulfurization effect of serpentine.

Here, the possibility of desulfurization by the silicon sul-
order approximation between 1 500 and 2 100°C.

The magnesium desulfurization reaction was confirmed by the magnesium gas, the desulfurization in the molten iron. By dividing this desulfurization reaction, the possibility of desulfurization of the molten iron by the silicon sulfide gas is not negligible.

This study on desulfurization promotion technology by the injection of fluxes comprising magnesium oxide and silicon oxide revealed that desulfurization takes place not only as magnesium sulfide but also in the form of other compounds. While identification of such compounds remains a problem, the desulfurization technology is cost-effective and requires less capital investment. This technology may apply to high-sulfur coals that have been undesirable in the steel industry.

6. Conclusion

This paper presents a study on desulfurization technology in the steel industry, with attention focused on the removal of sulfur that forms acid rain, which has been creating various global problems. The study was confined to the technology that injects a mixture of serpentine and pulverized coals. Thermodynamically, a magnesium gas producing reaction occurs when magnesium oxide is turned into a hot strongly reducing atmosphere and the resulting magnesium gas forms magnesium sulfide by reaction with the sulfur in the molten iron. By dividing this desulfurization process into a magnesium gas producing reaction and a desulfurization reaction by the magnesium gas, the desulfurization effect of the magnesium oxide flux was confirmed through laboratory experiment.

In the measurement of weight reduction in a pure system comprising a magnesium oxide reagent and carbon, the weight loss exponentially increased at temperatures above 1 600°C. Accordingly, it seems that there is a good possibility that the magnesium gas producing reaction occurs in the blast furnace raceway where the temperature is higher than 2 000°C. When the magnesium reagent and coal were heated to 1 800°C, accretions comprising magnesium, silicon, and sulfur were found on the suspension wires, and they proved that silicon has an effect on the desulfurization reaction.

The experiment on the desulfurization of molten iron by the magnesium gas revealed that the magnesium reagent and serpentine have desulfurization effects. Serpentine exhibited a greater desulfurization effect and, therefore, it seemed that the silicon oxide contained in it has an effect on the desulfurization reaction. A thermodynamic study on the desulfurization reaction in which the SiO gas resulting from the reduction of SiO₂ produces a silicon sulfide gas by reaction with the sulfur in the molten iron revealed that the possibility of desulfurization of the molten iron by the silicon sulfide gas is not negligible.

Table 4 shows the $P_{SiS}/P_{SiO}$ derived from Eqs. (17) to (19). In the equilibrium condition, not only the partial pressure of the silicon oxide gas but also that of the silicon sulfide gas increases. In terms of equilibrium, the desulfurization effect of the silicon sulfide gas does not seem to be negligible.

### Table 4. $P_{SiS}/P_{SiO}$ at different temperatures.

<table>
<thead>
<tr>
<th>°C</th>
<th>$P_{SiS}/P_{SiO}$</th>
<th>$P_{SiO}$</th>
<th>$P_{SiS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>-3.50</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>1600</td>
<td>-2.46</td>
<td>1.92</td>
<td></td>
</tr>
<tr>
<td>1700</td>
<td>-1.53</td>
<td>3.12</td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>-0.70</td>
<td>4.96</td>
<td></td>
</tr>
<tr>
<td>1900</td>
<td>0.06</td>
<td>7.54</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>0.74</td>
<td>11.01</td>
<td></td>
</tr>
</tbody>
</table>

REFERENCES

13) Recommended Equilibrium Values for Steelmaking Reactions, Compiled by the Steelmaking Committee 19 of the Japan Society for the Promotion of Science, Tokyo, 33.