Influence of Slag Basicity and Temperature on Fe and Mn Distribution between Liquid Fe–Mn–Ca–O–S Matte and Molten Slag

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We have proposed a novel process for recycling Mn wasted in steelmaking slag via sulfurization to separate P from Mn. For clarifying the efficient recovery of Mn from steelmaking slag, the influences of slag basicity and temperature on the distributions of Mn and Fe between the Fe–Mn–Ca–O–S matte and FeO–MnO–MgO–P2O5–SiO2–CaO slag were investigated. The distributions of Fe and Mn between the matte and the slag increased with an increase in the slag basicity. Moreover, when log $P_{S2}$ ($P_{S2}$: partial pressure of S) was more than $-2$, the Mn distribution increased to be more than 10 as the slag basicity increased beyond 1.7. Even though the effects of slag basicity and $P_{S2}$ on the Mn content in the matte were small, the behavior of Mn in the matte was dependent on temperature. In order to understand the behavior of Mn and Fe in steelmaking slag and matte, the relationship between the activity coefficient ratio of MnS and FeS ($\gamma_{MnS}/\gamma_{FeS}$) and the mole fraction ratio of MnS and FeS for the matte was investigated. To evaluate $\gamma_{MnS}/\gamma_{FeS}$ for the matte, the activity coefficient ratio of MnO and FeO ($\gamma_{MnO}/\gamma_{FeO}$) was estimated using an empirical formula and the RS model, and the mole fractions of MnS and FeS in the matte were calculated on the basis of mass balance. The results revealed that the values of $\gamma_{MnS}/\gamma_{FeS}$ for the Fe–Mn–S–O matte were about twice those for the Fe–Mn–Ca–S–O matte. Moreover, $\gamma_{MnS}/\gamma_{FeS}$ for the Fe–Mn–Ca–S–O matte decreased with an increase in temperature.

KEY WORDS: recycling; sulfurization; steelmaking slag; matte; manganese; phosphorus; slag basicity; activity coefficient; manganese sulfide; iron sulfide.

1. Introduction

Mn plays a key role in improving the mechanical and chemical properties of steel products. In spite of the growing consumption and important role of Mn for high-grade steel products, no recycling strategy for realizing stable Mn resources has been investigated yet. The authors have proposed a recycling process to recover Mn from steelmaking slag because in Japan, the amount of Mn wasted in steelmaking slag is similar to the amount consumed in steelmaking process.1–4,12) Steelmaking slag commonly contains oxides of P,5) which is a harmful element that adversely affects the properties of steel products. Therefore, the separation of P from Mn is necessary to recover Fe–Mn alloys from steelmaking slag. The P content in the matte was below 0.1 mass%. The separation of P from Mn was achieved by the sulfurization of slag. In addition, the distribution of Mn between the matte and slag increased when the partial pressure of sulfur was higher than $-10^{-2.5}$.4) Even though commercial steelmaking slag contains CaO, the slag in our previous study did not include CaO to keep the matte composition simple. Therefore, an equilibrium relation between the matte and molten slag that includes CaO should be established for clarifying the efficient recovery of Mn from steelmaking slag.

In the present study, the influences of slag basicity and temperature on the distributions of Mn and Fe between the Fe–Mn–Ca–O–S matte and FeO–MnO–MgO–P2O5–SiO2–CaO slag were investigated. Furthermore, in order to clarify the behavior of Mn and Fe in steelmaking slag and matte, the activity coefficient ratio of MnS and FeS was evaluated.

2. Experimental Procedure

The experimental equipment used in the present study is described elsewhere in detail.1,2) The experimental procedure is concisely outlined here. Approximately 5 g of the FeS–MnS–CaS matte powder was put on 5 g of the slag powder.
in a MgO crucible. The prepared sample was then heated at
1 573, 1 623, 1 673, and 1 723 K for 24 h, after which the sample
was quenched in water. In the preliminary experiments, the Mn, Fe, and Ca content in the matte and slag became con-
stant after 24 h of heat treatment at desired temperatures. Tables 1 and 2 list the initial compositions of the matte and slag. As shown in Table 1, the effect of slag basicity on the Fe and Mn distributions between the matte and slag was investigated using four types of slag with different CaO content. Moreover, as shown in Table 2, the effect of temperature on the Fe and Mn distributions between the matte and slag was investigated using only one type of slag. The slag was prepared from a mixture of reagent-grade MnO, MgO, Ca3(PO4)2, SiO2, CaO, Fe, and Fe2O3 powders. The appropriate content of FeO in the slag was obtained by mixing the Fe and Fe2O3 powders, the mole ratio of which was carefully
maintained at 1:1. CaO in the slag was prepared using a
CaCO3 powder calcined at 1 273 K for more than 3 h in air.

During the equilibrium experiments at different tempera-
tures, the partial pressures of O2 and S2 (PO2 and PS2, respec-
tively, atm) in the furnace were controlled using a CO–CO2–
SO2 mixing gas. As listed in Table 3, log P02 and log P03, which were calculated using FactSage,6) were varied in the ranges −1.4–−6.0 and −9.9–−13, respectively.

The Fe, Mn, Ca, Mg, Si, and P content in matte were ana-
lyzed using inductively coupled plasma atomic emission
spectroscopy (ICP–AES). For the analysis of the slag, the Fe,
Mn, Mg, Ca, and P concentrations were analyzed using ICP–
AES and the SiO2 concentration was analyzed by the alkali-
fusion and gravimetric methods. Inert gas fusion-infrared
absorptiometry was employed to measure the O content in the
matte. A combustion-infrared spectrometer was used to eval-
uate the S content in the slag and matte. The microstructures
and compositions of the matte and slag were analyzed by observations of an electron probe micro analyzer (EPMA).

### 3. Results

#### 3.1. Suspension Behaviors of Slag in Matte and Matte in Slag

Figure 1 shows the mineralogical microstructures of the
matte and slag for log P02 and log P03, values of −9.9 and −1.4,
respectively. Figures 1(a) and 1(c) show the pictures of the
matte and slag for a CaO/SiO2 ratio in the slag of unity (see M-S2 in Table 1). Figures 1(b) and 1(d) show the pictures of the
matte and slag with a CaO/SiO2 ratio of 1.5 (see M-S3 in
Table 1).

| Table 1. Initial compositions of matte and slag for various CaO/ SiO2 ratios at 1673 K. |
|-----------------|-----------------|-----------------|-----------------|
| **Temp.** | **Slag** | **Matte** |
| **Slag type** | CaO | SiO2 | FeO | MnO | MgO | P2O5 | CaO/SiO2 | FeS | MnS | CaS |
| S1 | 21 | 41 | 12 | 12 | 9 | 5 | 0.5 | 80 | 20 | |
| 1 673 K | S2 | 31 | 31 | 12 | 12 | 9 | 5 | 1.0 | 70 | 21 | 9 |
| S3 | 33 | 22 | 16 | 7 | 17 | 5 | 1.5 | |

| Table 2. Initial compositions of matte and slag for constant CaO/ SiO2 ratio at various temperatures. |
|-----------------|-----------------|-----------------|-----------------|
| **Temp.** | **Slag** | **Matte** |
| **Slag type** | CaO | SiO2 | FeO | MnO | MgO | P2O5 | CaO/SiO2 | FeS | MnS | CaS |
| 1 573 K | S1 | 33 | 33 | 8 | 6 | 13 | 7 | 1.0 | 84 | 14 | 2 |
| 1 623 K | S2 | 30 | 30 | 10 | 6 | 17 | 7 | 1.0 | 79 | 17 | 4 |
| 1 673 K | S3 | 33 | 34 | 12 | 7 | 9 | 5 | 1.0 | 75 | 22 | 3 |
| 1 723 K | S4 | 31 | 38 | 5 | 2 | 20 | 5 | 0.8 | 67 | 26 | 7 |

| Table 3. Gas flow rate and partial pressure. |
|-----------------|-----------------|-----------------|
| **Temp.** | **No.** | **Partial pressures (atm)** | **Gas flow rate (10−6 m3/min)** |
| **(K)** | | logP02 | logP03 | logPSO2 | CO | CO2 | SO2 | Ar−1%SO2 |
| M | −9.9 | −1.4 | −3.1 | 128 | 0.1 | 11.7 |
| O | −10.1 | −3.9 | −4.6 | 102 | 18.3 | 10.2 |
| P | −10.0 | −5.0 | −5.0 | 115 | 22.9 | 2.6 |
| Q | −11.0 | −1.9 | −4.5 | 135 | 1.3 | 3.9 |
| R | −11.0 | −3.9 | −5.5 | 112 | 6.7 | 11.2 |
| V | −13.0 | −4.0 | −7.5 | 129 | 0.6 | 10.3 |
| W | −13.0 | −5.0 | −8.0 | 136 | 0.8 | 3.0 |
| X | −13.0 | −6.0 | −8.5 | 138 | 0.9 | 0.8 |

The units of Partial pressure and gas flow rate has been revised in Table 3.

Fig. 1. Mineralogical microstructures of matte and slag under log P02 and log P03 of −9.9 and −1.7.
the typical compositions of each phase in the slag. Phases (A) and (B) indicate the matrix oxide phase. Phase (C) shown in Fig. 1(d) is the MgO-FeO phase. Phase (D) is the suspended sulfides phase only in which S was detected in the slag, as shown in Table 5.

Table 6 lists the chemical analysis results for the matte and slag. Since the conventional analysis methods could not be used to separate the compositions that originated from the suspended particles, the results listed in Table 6 indicate the concentration of not only each composition in the matte or slag but also the compositions that originated from the suspended particles. In order to investigate the effect of slag basicity on the accurate distribution ratios of Fe and Mn between the matte and slag, it was necessary to obtain the true compositions of the matte and slag by subtracting the composition of the suspended phase from the analyzed composition value.

The relation between the analyzed value, real content in matte, and content that originated from suspended slag can be expressed by the following equation:

\[ \{M\}_{\text{Analyzed}} = \{M\}_{\text{Matte}} + \{M\}_{\text{SP}} \]  

where \( \{M\}_{\text{Analyzed}} \) denotes the analyzed value of an element present in the matte.

### Table 4. Typical composition of each phase in matte.

| No. | Composition/mass% |
|-----|------------------|
|     | Fe   | Mn   | Ca   | S    | O    | Mg   | Si   | P    |
| 1   | Mn-rich sulfide| 41.5 | 20.8 | 1.2  | 36   | 0.5  | 0    | 0    |
| 2   | Fe-rich sulfide| 58.0 | 5.6  | 0.8  | 34.4 | 1.6  | 0.0  | 0.2  |
| 3   | Ca-rich oxysulfide| 44.3 | 3.8  | 19.3 | 20.8 | 11.8 | 0    | 0    |
| 4   | Fe-Mg rich oxysulfide| 60.5 | 9.5  | 1.7  | 38   | 19   | 2.1  | 0.1  |
| 5   | Suspended oxide in matte| 8.3  | 3.9  | 24.6 | 2.2  | 34.3 | 9.7  | 15.2 |

### Table 5. Typical composition of each phase in slag.

| No. | Composition/mass% |
|-----|------------------|
|     | Fe   | Mn   | Ca   | S    | O    | Mg   | Si   | P    |
| A   | Slag 1| 1.6  | 2.4  | 25.4 | 15.9 | 13.4 | 2.3  | 39.0 |
| B   | Slag 2| 0.8  | 1.1  | 36.3 | 14.4 | 6.3  | 3.7  | 37.4 |
| C   | MgO-FeO| 6.5  | 2.5  | 0.1  | 53.5 | 30  | 37.4 |
| D   | Suspended sulfide in slag| 48.6 | 11.6 | 3.1  | 0    | 0    | 2.6  | 34.0 |

### Table 6. Analyzed results for matte and slag.

| Sample no. | Temp. (K) | Slag type | Partial pressures | Matte/mass% | Slag/mass% |
|------------|-----------|-----------|-------------------|-------------|------------|
| M-S1       | S1        | 52.80     | 12.40             | 0.75       | 0.50       | 31.15   | 3.86   |
| M-S2       | S2        | 49.11     | 14.46             | 2.87       | 0.46       | 27.98   | 4.56   |
| M-S3       | S3        | 47.46     | 12.18             | 7.54       | 0.93       | 20.92   | 4.74   |
| O-S1       | S1        | 54.86     | 11.80             | 0.79       | 0.36       | 27.54   | 4.80   |
| O-S2       | S2        | 50.42     | 14.40             | 3.40       | 0.81       | 24.21   | 6.16   |
| O-S3       | S3        | 47.30     | 12.15             | 7.59       | 1.74       | 25.17   | 2.53   |
| P-S1       | S1        | 55.71     | 11.58             | 0.85       | 0.21       | 29.57   | 5.81   |
| P-S2       | S2        | 49.91     | 14.29             | 2.98       | 0.38       | 31.50   | 4.39   |
| P-S3       | S3        | 48.50     | 12.20             | 7.27       | 1.20       | 26.56   | 5.09   |
| Q-S3       | S3        | 54.10     | 11.58             | 0.85       | 0.21       | 29.57   | 5.81   |
| R-S3       | S3        | 49.91     | 14.29             | 2.98       | 0.38       | 31.50   | 4.39   |
| V-S1       | S1        | 55.36     | 10.80             | 0.73       | 0.21       | 28.09   | 4.92   |
| V-S2       | S2        | 50.87     | 14.03             | 2.41       | 0.30       | 28.92   | 5.30   |
| V-S3       | S3        | 46.61     | 12.35             | 8.10       | 1.55       | 26.38   | 5.18   |
| W-S1       | S1        | 51.64     | 10.59             | 0.95       | 0.26       | 27.88   | 4.55   |
| W-S2       | S2        | 51.41     | 13.52             | 2.44       | 0.36       | 26.93   | 5.14   |
| W-S3       | S3        | 48.54     | 12.82             | 7.61       | 1.00       | 25.29   | 5.08   |
| X-S1       | S1        | 51.47     | 12.33             | 0.96       | 0.50       | 29.46   | 5.21   |
| X-S2       | S2        | 52.57     | 14.03             | 3.09       | 0.29       | 26.06   | 4.99   |
| X-S3       | S3        | 47.78     | 12.37             | 7.22       | 1.42       | 31.68   | 3.94   |

### Table 6 (continued).

| Sample no. | Temp. (K) | Slag type | Partial pressures | Matte/mass% | Slag/mass% |
|------------|-----------|-----------|-------------------|-------------|------------|
| T1-M-S2    | 1573     | 2        | 55.70             | 9.36       | 1.7       | 0.12     | 31.06   | 4.01 |
| T2-M-S2    | 1623     | 2        | 52.50             | 11.35      | 2.75      | 0.27     | 25.41   | 4.11 |
| T3-M-S2    | 1673     | 2        | 48.96             | 13.62      | 3.87      | 0.33     | 24.68   | 4.56 |
| T4-M-S2    | 1723     | 2        | 44.95             | 14.52      | 6.43      | 0.73     | 23.22   | 4.17 |
| T1-X-S2    | 1573     | 2        | 58.30             | 10.20      | 1.5       | 0.19     | 32.46   | 3.97 |
| T2-X-S2    | 1623     | 2        | 52.77             | 11.54      | 2.22      | 0.19     | 31.35   | 3.65 |
| T3-X-S2    | 1673     | 2        | 51.66             | 13.67      | 3.17      | 0.52     | 30.11   | 4.99 |

\( W_{\text{SP}} \): Suspended amount of slag within matte by calculating Si contents in matte

\( W_{\text{M}} \): Suspended amount of matte within slag by calculating S contents in slag

\( (\text{Si})^{**} \): Calculated contents of Si in slag were originated from \( \text{SiO}_2 \) concentration analyzed by the alkali-fusion and gravimetric methods
M in the matte, as shown in Table 6; \{M\}_{\text{Matte}} denotes the accurate concentration of M in the matte; and \{M\}_{\text{SP}} denotes the concentration of M due to the suspended slag. In Eq. (1), it is simplified to eliminate the term for total weight of matte from both sides. In addition, the sum of weight in left side of Eq. (1) can be equal to total weight of matte because the weight of suspended oxide particle is considered to be very small than that of matte. From Table 4, it can be seen that Si and P were detected only in the suspended phase (5), as shown in the matte images in Fig. 1. It is reasonable to assume that the real Si content in the matte is zero. This assumption can be expressed by following equation:

\[ [\text{Si}]_{\text{Matte}} = 0 \]  

(2)

From Eq. (2), the analyzed concentration of Si in the matte in Table 6 \([\text{Si}]_{\text{Analyzed}}\) was equal to the Si concentration due to the suspended slag \([\text{Si}]_{\text{SP}}\). Moreover, the concentrations of suspended oxide particles can be calculated on the basis of the composition of the suspended phase (5) (Table 4) and the Si content in the matte (Table 6):

\[ [\text{Si}]_{\text{Analyzed}} = [\text{Si}]_{\text{SP}} = W_{\text{SP}} \times \frac{[\text{Si}]_{\text{SP}}}{100} \]  

(3)

where \(W_{\text{SP}}\) denotes the mass percent of suspended slag particles in the matte and \(<\text{Si}>_{\text{SP}}\) denotes the Si content in suspended slag (mass%) particles as obtained by the EPMA analysis (Table 4). Finally, the concentration of M in the matte can be obtained by the following equation:

\[ \{M\}_{\text{Matte}} = \{M\}_{\text{Analyzed}} - W_{\text{SP}} \times \frac{\{M\}_{\text{SP}}}{100} \]  

(4)

where \(<M>_{\text{SP}}\) is the M content in suspended slag particles (mass%) as obtained by the EPMA analysis (Table 4). The calculated values of \(W_{\text{SP}}\) are listed in Tables 6 and 7.

By the same procedure, the analyzed value of M in the slag (Table 6) was separated into the true concentration of M in the slag and the concentration of M due to the suspended matte particles in the slag. In this case, the analyzed S concentration in the slag (Table 6) was considered to be equal to the S concentration due to the suspended matte particles. The mass percent of the suspended matte particles in the slag \(W_{\text{SP}}\) was also estimated. Table 7 lists the matte and slag compositions.

Figure 2 shows \(W_{\text{SP}}\) values for the Fe–Mn–O–S matte and Fe–Mn–Ca–O–S matte as a function of the \(%\text{Mn} + \%\text{Ca}\)_{Matte}/\(%\text{Fe}\)_{Matte} ratio in the matte at 1673 K. The results for the Fe–Mn–O–S matte were taken from one of our previous studies. In most cases, \(W_{\text{SP}}\) was less than 4 mass%. In the case of the Fe–Mn–O–S matte, the amount of suspended slag particles decreased with an increase in the \(%\text{Mn}\)_{Matte}/\(%\text{Fe}\)_{Matte} ratio. In contrast, the concentration of suspended

### Table 7.

| Sample no. | Temp. (K) | Slag Type | Partial pressures | Matte/mass% | Slag/mass% |
|-----------|----------|-----------|-------------------|-------------|------------|
|           |          |           | \(\log \text{P}_{\text{O}}\) | \(\log \text{P}_{\text{S}}\) | \{Fe\} | \{Mn\} | \{Ca\} | \{Mg\} | \{Si\} | \{O\} | \{P\}_{\text{Matte}} | \{FeO\} | \{MnO\} | \{MgO\} | \{P2O5\} | \{CaO\} | \{SiO2\} | \(W_{\text{SP}}\) |
| M-S1      | 1005     | S1        | 0.43              | 0.56            | 2.88 | 0.25 | 1.27 | 1.66 | 3.01 | 4.01 | 0.62 | 3.17 | 0.90 | 21.16 | 4.18 | 36.45 | 4.59 |
| M-S2      | 1005     | S2        | 0.43              | 0.56            | 2.88 | 0.25 | 1.27 | 1.66 | 3.01 | 4.01 | 0.62 | 3.17 | 0.90 | 21.16 | 4.18 | 36.45 | 4.59 |
| M-S3      | 1005     | S3        | 0.43              | 0.56            | 2.88 | 0.25 | 1.27 | 1.66 | 3.01 | 4.01 | 0.62 | 3.17 | 0.90 | 21.16 | 4.18 | 36.45 | 4.59 |

\(W_{\text{SP}}\) : Suspended amount of slag within matte by calculating Mg and Si contents in matte

\(W_{\text{SP}}\) : Suspended amount of matte within slag by calculating S contents in slag

\([P]_{\text{Matte}}\) means the difference between \([P]_{\text{Analyzed}}\) and \([P]_{\text{SP}}\) (values are represented as a negative number.)
slag particles in the Fe–Mn–Ca–S–O matte was 2–4 mass% with no dependence on the \( \% \text{Mn} + \% \text{Ca} / \% \text{Fe} \) Matte ratio. Figure 3 shows the relation between the analyzed values of P (Table 6, \( \{\text{P}\}_{\text{Analyzed}} \)) and the true P concentrations in the matte (Table 7, \( \{\text{P}\}_{\text{Matte}} \)) at 1 673 K. We have reported that the analyzed P content in the Fe–Mn–S–O matte was due to the suspended oxide particles in that matte because \( \{\text{P}\}_{\text{Matte}} \) was close to zero. Moreover, in the case of the Fe–Mn–Ca–O–S matte, \( \{\text{P}\}_{\text{Matte}} \) was also close to zero. This implies that P was not distributed in the matte. Therefore, the sulfurization of molten slag containing P and Mn can separate Mn from P. However, it is necessary to decrease the suspension of slag in the matte because the analyzed P content in the matte is due to suspended slag particles in the matte.

Figure 4 shows the relation between the slag basicity and concentration of suspension in the slag at 1 673 K. The values of suspension in the FeO–MnO–MgO–P\(_2\)O\(_5\)–SiO\(_2\) slag were again taken from one of our previous studies. The slag basicity was determined by the following equation:

\[
\text{Slag basicity} = \frac{\% \text{CaO} + \% \text{MgO}}{\% \text{SiO}_2} \quad \text{...(5)}
\]

For slag basicity below unity, the concentration of suspended matte particles in the slag decreased as the slag basicity increased. For slag basicity between 1.0 and 1.8, the concentration of suspended matte particles in the slag was almost constant at approximately 6 mass%. For slag basicity over 1.8, the concentration of suspended matte particles in the slag increased with an increase in the slag basicity. The relation between the slag basicity and suspension in the slag will be discussed on the basis of the change in the slag viscosity in Sec. 4.1.

Figure 5 shows a comparison between \( W_{\text{SP}}^{*} \) and \( W_{\text{SP}}^{**} \) as a function of temperature. The slag basicity ranged from 1.21 to 1.56 and \( \{\% \text{Mn} + \% \text{Ca}\}_{\text{Matte}} / \{\% \text{Fe}\}_{\text{Matte}} \) ranged from 0.19 to 0.46. Even though the \( W_{\text{SP}}^{\ast} \) value for the slag increased with an increase in temperature, the effect of temperature on \( W_{\text{SP}}^{\ast} \) seems to be small.

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Figure 6 shows the relation between the slag basicity and concentration of suspension in slag at 1 673 K. The values of suspension in the FeO–MnO–MgO–P\(_2\)O\(_5\)–SiO\(_2\) slag were again taken from one of our previous studies. The slag basicity was determined by the following equation:

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\]

For slag basicity below unity, the concentration of suspended matte particles in the slag decreased as the slag basicity increased. For slag basicity between 1.0 and 1.8, the concentration of suspended matte particles in the slag was almost constant at approximately 6 mass%. For slag basicity over 1.8, the concentration of suspended matte particles in the slag increased with an increase in the slag basicity. The relation between the slag basicity and suspension in the slag will be discussed on the basis of the change in the slag viscosity in Sec. 4.1.

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For slag basicity below unity, the concentration of suspended matte particles in the slag decreased as the slag basicity increased. For slag basicity between 1.0 and 1.8, the concentration of suspended matte particles in the slag was almost constant at approximately 6 mass%. For slag basicity over 1.8, the concentration of suspended matte particles in the slag increased with an increase in the slag basicity. The relation between the slag basicity and suspension in the slag will be discussed on the basis of the change in the slag viscosity in Sec. 4.1.

Figure 5 shows a comparison between \( W_{\text{SP}}^{*} \) and \( W_{\text{SP}}^{**} \) as a function of temperature. The slag basicity ranged from 1.21 to 1.56 and \( \{\% \text{Mn} + \% \text{Ca}\}_{\text{Matte}} / \{\% \text{Fe}\}_{\text{Matte}} \) ranged from 0.19 to 0.46. Even though the \( W_{\text{SP}}^{\ast} \) value for the slag increased with an increase in temperature, the effect of temperature on \( W_{\text{SP}}^{\ast} \) seems to be small.
As shown in Fig. 7, both distribution ratios increased with increase in the slag basicity. When log PS$_2$ was more than $-2$ (M and Q in Fig. 7(a)), $L_{Fe(M/S)}$ was larger than that for low PS$_2$ values. Furthermore, when log PS$_2$ and slag basicity were more than $-2$ and 1.7 (M and Q in Fig. 7(b)), respectively, $L_{Mn(M/S)}$ increased to become 10 or higher. According to one of our previous studies,$^4$ $L_{Mn(M/S)}$ and $L_{Fe(M/S)}$ increased with increasing PS$_2$, which was larger than $-10^{-2.5}$. However, the overall value of $L_{Mn(M/S)}$ was lower than that of $L_{Fe(M/S)}$ because of the low basicity of the slag. Figure 7 revealed that $L_{Mn(M/S)}$ became larger than $L_{Fe(M/S)}$ when slag basicity and PS$_2$ were more than 2.8 and $-10^{-2}$, respectively. Figure 8 shows the effect of slag basicity on the $\%$Mn/$\%$Fe + $\%$Ca ratio for the Fe–Mn–Ca–O–S matte. When PS$_2$ was lower than $-10^{-2}$, the $\%$Mn$_{Matte}/\%$Fe + $\%$Ca$_{Matte}$ ratio increased slightly with an increase in the slag basicity. For higher PS$_2$ values, the change in $\%$Mn$_{Matte}/\%$Fe + $\%$Ca$_{Matte}$ seemed constant against increasing basicity of the slag, the maximum value of which was smaller than 0.3.

3.3. Influence of Temperature on Fe and Mn Distributions between Fe–Mn–Ca–S–O Matte and Molten Slag

Figure 9 shows the influence of temperature on the Fe, Mn, and Ca content in the matte. The Fe content in the matte decreased as the temperature increased, although the Ca content in the matte increased with an increase in temperature. Furthermore, the Mn content in the matte increased at temperature increased. When the effect of temperature on the Mn content in the matte is compared with the effect of slag basicity on that the Mn content (Fig. 6), it becomes clear that the Mn content depends on temperature.

Figures 10(a) and 10(b) show the effect of temperature on $L_{Fe(M/S)}$ and $L_{Mn(M/S)}$, respectively, with the slag basicity in the range 1.21–1.56. $L_{Fe(M/S)}$ increased as temperature increased as shown in Fig. 10(a). In addition, at 1 673 K, the values of $L_{Fe(M/S)}$ in Fig. 10(a) were slightly larger than those of in Fig. 7(a) because of the different composition of matte as represented in Tables 1 and 2. In the case of equilibrium between the matte without CaS and the slag, the CaO in slag was moved to the matte as formation of CaS. In order to achieve the effective sulfurization of steelmaking slag, we thought that the CaS content in matte is also important to increase the distribution ratio of Mn and Fe. On the other hand, when PO$_2$ and PS$_2$ were high, as shown by the solid line in Fig. 10(b), $L_{Mn(M/S)}$ increased with an increase in temperature. However, when log PO$_2$ and log PS$_2$ were low, the effect of temperature on $L_{Mn(M/S)}$ was small.

Figure 11 shows the effect of temperature on the $\%$Mn/$\%$Fe + $\%$Ca ratio for the Fe–Mn–Ca–O–S matte. The $\%$Mn$_{Matte}/\%$Fe + $\%$Ca$_{Matte}$ ratio increased with an
increase in the temperature. However, the effect of $P_{O_2}$ and $P_{S_2}$ was small.

4. Discussion

4.1. Relation between Slag Viscosity and Suspended Matte in Molten Slag

Figure 12 shows the relation between slag viscosity ($\log \mu$) and $W_{SP}$ as a function of the slag basicity at 1673 K. The slag viscosities were calculated using the Iida model\(^7\)\(^8\) by the following equations:

\[
\mu_{slag} = A \mu_0 \exp \left( \frac{E}{B_i} \right) \quad \text{(7)}
\]

where $\mu_0$ is the viscosity of non-network forming for each slag; $B_i$ is the modified basicity index; $A$ and $E$ are equal to 0.4919 and 4.717, respectively, at 1673 K.

As shown in Fig. 4, when the slag basicity was less than unity, $\mu_{slag}$ increased as the slag basicity decreased or as the SiO$_2$ content in the slag increased. Generally, chains or rings of the network structure in silicate melts are dependent on the SiO$_2$ content in the slag. The slag viscosity thus increases as these chains or rings in the slag increase. Hence, $W_{SP}$ increased because of the increase in the slag viscosity.

When the slag basicity ranged from 1.0 to 1.8, $W_{SP}$ was almost constant at approximately 6 mass% because of low slag viscosity. However, as shown in Fig. 1(d), phases such as MgO–FeO were formed in the slag with a high CaO content at 1673 K. Although the slag viscosity calculated using the Iida model was low, the crystalline phases in the slag increased the slag viscosity. Therefore, $W_{SP}$ would increase with increasing slag basicity because of the solid phases in the slag.

As shown in Fig. 2, $W_{SP}$ for the Fe–Mn–Ca–O–S matte was 2–4 mass% with no dependence on the $%\text{Mn} + %\text{Ca}\text{}/%\text{Fe}$ ratio. Even though the suspension of slag particles in the matte was generally influenced by various properties such as surface tension, viscosity and temperature etc., it was thought that an increase in the Ca content in the matte decreased the matte density. The density of a mixture ($\rho_{\text{mixture}}$) can be derived as follows:\(^9\)

\[
\rho_{\text{mixture}} \left( \text{kg} / \text{m}^3 \right) = \frac{\sum_{i=1}^{N} M_i x_i}{V_m} \quad \text{(11)}
\]

\[
V_m \left( \text{m}^3 / \text{mol} \right) = \sum_{i=1}^{N} V_i x_i \quad \text{(12)}
\]

where $V_m$ is the molar volume of the mixture; $M_i$ and $x_i$ are the molar weight and mole fraction of a component $i$, respectively; and $V_i$ is the partial molar volume of $i$ and is generally assumed to be equal to the molar volume of a pure compo-
The mole fractions of FeS, MnS, MnO, FeO, and CaS in the matte are given in Table 8. The calculation method for each mole fraction will be discussed in Sec. 4.2. Figure 13 shows a comparison between the ρmixture values for the matte and the suspended slag in each matte as function of the [%Mn + %Ca]/[%Fe] ratio at 1 673 K. For the calculation of the suspended slag density, we used the slag composition of Table 7 as the composition of the suspended slag because the suspended slag particle in matte was originated from the bulk of slag equilibrated with each matte. In the case of the Fe–Mn–O–S matte, the change in ρmixture of matte was small as the [%Mn]/[%Fe] ratio increased. On the other hand, ρmixture of matte for the Fe–Mn–Ca–O–S matte decreased as the [%Mn + %Ca]/[%Fe] ratio increased. Therefore, the density difference between matte and the suspended slag decreased as the [%Mn + %Ca]/[%Fe] ratio increased and this phenomena would affect the suspension of slag particles in the Fe–Mn–Ca–O–S matte.

### Table 8. Mole fractions of MnS, MnO, FeS, FeO, and CaS in Fe–Mn–Ca–O–S matte and activity ratios of MnO/FeO in slag.

| Sample No. | Temp. (K) | Slag Type | Partial pressures | Empirical formula | RS Model** | \[\frac{\text{MnO}_{\text{slag}}}{\text{FeO}_{\text{slag}}}\] | \[\frac{\text{MnS}_{\text{slag}}}{\text{FeS}_{\text{slag}}}\] |
|------------|-----------|-----------|------------------|------------------|-----------|-------------------|-------------------|
| M-S1       | 1673      | S1        | logP_{O2} | logP_{S2} | α | N_{CaS} | N_{MnS} | N_{MnO} | N_{FeS} | N_{FeO} | αMnO(l)/αFeO(l) | γMnS/γFeS | αMnO(l)/αFeO(l) | γMnS/γFeS |
| M-S2       | 1673      | S2        | −9.9     | −1.4     | 3.70 | 0.80 | 0.048 | 0.18 | 0.05 | 0.53 | 0.19 | 0.09 | 0.78 | 0.28 | 2.50 |
| M-S3       | 1673      | S3        | 3.49     | 0.81 | 0.139 | 0.15 | 0.04 | 0.48 | 0.19 | 0.08 | 0.77 | 0.25 | 3.19 | 0.10 | 0.97 |
| O-S1       | 1673      | S1        | 3.62     | 0.78 | 0.003 | 0.15 | 0.04 | 0.60 | 0.21 | 0.08 | 1.06 | 0.25 | 2.06 | 0.25 | 2.06 |
| O-S2       | 1673      | S2        | −10.1    | −3.9    | 2.39 | 0.72 | 0.054 | 0.17 | 0.06 | 0.45 | 0.27 | 0.09 | 0.75 | 0.25 | 2.06 |
| O-S3       | 1673      | S3        | 3.00     | 0.79 | 0.135 | 0.15 | 0.04 | 0.45 | 0.22 | 0.32 | 2.87 | 0.21 | 1.95 | 0.21 | 1.95 |
| P-S1       | 1673      | S1        | 3.31     | 0.77 | 0.005 | 0.13 | 0.04 | 0.63 | 0.19 | 0.09 | 1.34 | 0.27 | 3.81 | 0.34 | 3.55 |
| P-S2       | 1673      | S2        | −10.0    | −5.0    | 3.84 | 0.80 | 0.050 | 0.17 | 0.04 | 0.59 | 0.15 | 0.11 | 1.11 | 0.34 | 3.55 |
| P-S3       | 1673      | S3        | 3.09     | 0.79 | 0.133 | 0.15 | 0.04 | 0.44 | 0.24 | 0.24 | 2.09 | 0.29 | 2.50 | 0.10 | 0.95 |
| Q-S3       | 1673      | S3        | −11.0    | −1.9    | 3.80 | 0.82 | 0.148 | 0.16 | 0.03 | 0.51 | 0.15 | 0.14 | 1.36 | 0.25 | 2.06 |
| R-S3       | 1673      | S3        | −11.0    | −3.9    | 2.64 | 0.77 | 0.143 | 0.16 | 0.05 | 0.43 | 0.22 | 0.31 | 2.58 | 0.25 | 2.06 |
| V-S1       | 1673      | S1        | 3.36     | 0.77 | 0.006 | 0.13 | 0.04 | 0.63 | 0.20 | 0.15 | 2.23 | 0.21 | 3.07 | 0.45 | 4.67 |
| V-S2       | 1673      | S2        | −13.0    | −4.0    | 3.00 | 0.76 | 0.038 | 0.16 | 0.05 | 0.55 | 0.19 | 0.07 | 0.70 | 0.17 | 1.42 |
| V-S3       | 1673      | S3        | 2.75     | 0.78 | 0.152 | 0.15 | 0.04 | 0.41 | 0.24 | 0.21 | 1.74 | 0.17 | 1.42 | 0.40 | 3.99 |
| W-S1       | 1673      | S1        | 3.96     | 0.80 | 0.009 | 0.14 | 0.03 | 0.64 | 0.18 | 0.15 | 2.12 | 0.34 | 4.80 | 0.10 | 0.95 |
| W-S2       | 1673      | S2        | −13.0    | −5.0    | 2.92 | 0.76 | 0.041 | 0.16 | 0.05 | 0.52 | 0.23 | 0.15 | 1.45 | 0.40 | 3.99 |
| W-S3       | 1673      | S3        | 2.90     | 0.78 | 0.140 | 0.16 | 0.04 | 0.40 | 0.26 | 0.24 | 1.82 | 0.21 | 1.55 | 0.45 | 5.85 |
| X-S1       | 1673      | S1        | 3.40     | 0.77 | 0.006 | 0.15 | 0.04 | 0.63 | 0.17 | 0.12 | 1.57 | 0.45 | 5.85 | 0.72 | 5.76 |
| X-S2       | 1673      | S2        | −13.0    | −6.0    | 3.96 | 0.81 | 0.053 | 0.18 | 0.04 | 0.49 | 0.23 | 0.32 | 2.54 | 0.72 | 5.76 |
| X-S3       | 1673      | S3        | 4.18     | 0.83 | 0.135 | 0.15 | 0.03 | 0.52 | 0.16 | 0.26 | 2.72 | 0.30 | 3.12 | 0.45 | 10.25 |

Empirical formula* and RS model** were reported in Ref. [11] in Table 8.

Fig. 13. Comparison of ρmixture of matte and slag as function of [%Mn + %Ca]/[%Fe] ratio at 1 673 K.

In order to understand the behavior of Mn and Fe in the molten slag and matte, the activity coefficient ratio of MnS/FeS in the matte was evaluated. When the matte and slag are considered to be a pure sulfide and pure oxide, respectively, the equilibrium of Fe and Mn between the matte and slag is expressed by following equations:

\[
\Delta G_{\text{MnS}}^{\text{FeO}} (J/mol) = 58 490 – 25.735 T \quad \ldots\ldots (13)
\]
\[ K_{(13)} = \frac{a_{\text{MnO}} \cdot a_{\text{FeS}}}{a_{\text{FeO}} \cdot a_{\text{MnS}}} \]  

where \( K_{(13)} \) is an equilibrium constant; \( a_{\text{FeO}} \) and \( a_{\text{MnO}} \) are the activities of FeO and MnO in the slag; and \( a_{\text{FeS}} \) and \( a_{\text{MnS}} \) are the activities of FeS and MnS in the matte. From Eq. (14), the activity coefficient ratio of MnS and FeS (\( \gamma_{\text{MnS}}/\gamma_{\text{FeS}} \)) can be obtained as follows:

\[ \frac{\gamma_{\text{MnS}}}{\gamma_{\text{FeS}}} = \frac{1}{K_{(13)}} \frac{\gamma_{\text{MnO}} \cdot N_{\text{MnO}}}{\gamma_{\text{FeO}} \cdot N_{\text{FeO}}} \cdot \frac{N_{\text{FeS}}}{N_{\text{MnS}}} \]  

where \( N_{\text{FeO}} \) and \( N_{\text{MnO}} \) are the mole fractions of FeO and MnO in the slag; and \( N_{\text{FeS}} \) and \( N_{\text{MnS}} \) are the mole fractions of FeS and MnS in the matte.

On the basis of Eq. (15), it is considered that two factors are necessary to evaluate \( \gamma_{\text{MnS}}/\gamma_{\text{FeS}} \) for the matte. The first factor is the activity coefficient ratio of MnO and FeO in the slag—\( \gamma_{\text{MnO}}/\gamma_{\text{FeO}} \). In order to obtain \( \gamma_{\text{MnO}} \) and \( \gamma_{\text{FeO}} \) for the molten slag equilibrated with the matte, the authors have investigated \( \gamma_{\text{MnO}} \) and \( \gamma_{\text{FeO}} \) for a FeO–MnO–MgO–P2O5–SiO2–CaO slag system on the basis of the equilibrium of this slag system with Ag at 1673 K. The measured values of \( \gamma_{\text{MnO}} \) and \( \gamma_{\text{FeO}} \) were evaluated by an empirical model, regular solution (RS) model, and FactSage. Since the slag composition in the present study was similar to that of the FeO–MnO–MgO–P2O5–SiO2–CaO slag in Ref. [11], the empirical formula and RS model of Ref. [11] can be used to calculate the values of \( \gamma_{\text{MnO}} \) and \( \gamma_{\text{FeO}} \) for the FeO–MnO–MgO–P2O5–SiO2–CaO slag equilibrated with the Fe–Mn–Ca–O–S matte. \[ N_{\text{FeS}}/N_{\text{MnS}} \] is required for the evaluation of \( \gamma_{\text{MnS}}/\gamma_{\text{FeS}} \) in the matte. Therefore, the second factor is \( N_{\text{FeS}}/N_{\text{MnS}} \). However, \( N_{\text{FeS}} \) and \( N_{\text{MnS}} \) for the Fe–Mn–Ca–O–S matte were difficult to measure owing to the lack of an analytical method for evaluating the accurate mole fractions of sulfide from the oxysulfide matte. Therefore, in the case of the Fe–Mn–O–S matte, we have reported that the mole fractions of MnS, MnO, FeS, and FeO were calculated on the basis of the mass balance of Fe, Mn, O, and S in the matte. The calculation method of the mole fraction of sulfide in the oxysulfide matte is briefly explained here. The mole fractions of Mn, Fe, Ca, S, and O in the Fe–Mn–Ca–O–S matte obtained by general analysis methods were designated as \( N_{\text{Fe}} \), \( N_{\text{Mn}} \), \( N_{\text{Ca}} \), \( N_{\text{S}} \), and \( N_{\text{O}} \), respectively. When the \( N_{\text{Fe}}/N_{\text{Mn}} = \alpha \) (\( \alpha \) is a stoichiometric ratio of MnS, MnO, FeS, and FeO for the matte as obtained from Eq. (15) and \( a_{\text{FeO}}/a_{\text{MnO}} \) for the slag as calculated using the empirical formula and RS model.

\[ \frac{N_{\text{FeS}}}{N_{\text{MnS}}} = \frac{N_{\text{Fe}}}{N_{\text{Mn}}} = \alpha \]  

Further, on the basis of the mass balance of S, the mole fraction of S as FeS (\( N_{\text{FeS}}/N_{\text{Fe}} \)) is calculated using Eq. (18) and \( N_{\text{FeS}} \) is obtained using Eq. (19), assuming a stoichiometric ratio for FeS.

\[ N_{\text{S as FeS}} = N_{\text{T.S}} - N_{\text{CaS}} - N_{\text{FeS}} \]  

In the case of the Fe–Mn–Ca–S–O matte, the weight percent of Ca in the matte was less than 7.18 mass% (Table 7). Therefore, since the mole fraction of Ca (\( N_{\text{Ca}}/N_{\text{T.Ca}} \)) in the matte was small, the mole fraction of CaO (\( N_{\text{CaO}} \)) in the matte could be regarded as zero. Then, the mole fraction of CaS (\( N_{\text{CaS}} \)) is given by Eq. (20):

\[ N_{\text{CaS}} = N_{\text{Ca}} + N_{\text{CaS}} = 2N_{\text{T.Ca}} \]  

where \( N_{\text{Ca}} \) and \( N_{\text{CaS}} \) are the mole fractions of Ca and Ca in calcium sulfide (CaS).

Table 8 lists the calculated mole fractions of MnS, MnO, FeS, FeO, and CaS for the Fe–Mn–Ca–O–S matte; \( \alpha \) values listed here are calculated using Eq. (21). In this table, \( \gamma_{\text{MnS}}/\gamma_{\text{FeS}} \) for the matte as obtained from Eq. (15) and \( a_{\text{FeO}}/a_{\text{MnO}} \) for the slag as calculated using the empirical formula and RS model.
are also represented.

Figure 15 shows a comparison between the $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ values for the matte as a function of $[\text{NMnS} + \text{NCaS}]_{\text{Matte}}/[\text{NFeS}]_{\text{Matte}}$ at 1673 K. The results of $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ in Fe–Mn–O–S matte were calculated using only the empirical formula for the values of $d_{\text{MnS}}/d_{\text{FeS}}$. In the case of the Fe–Mn–S–O system, when the empirical formula was used to calculate the $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ ratio, the $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ ratio was almost constant when the $\text{N}_{\text{MnS}}/\text{N}_{\text{FeS}}$ ratio was increased. The $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ Value for the Fe–Mn–Ca–S–O matte was also constant against any changes in the $[\text{NMnS} + \text{NCaS}]_{\text{Matte}}/[\text{NFeS}]_{\text{Matte}}$ ratio even though the CaFe–Mn–Ca–S–O matte was also constant against any changes in the mass% to 7.18 mass%. However, the values of the $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ content in the Fe–Mn–Ca–S–O matte increased from 0.15 formula listed in Table 8. In the case of the RS model, it was estimated using the empirical formula and the steel steel slag were investigated. The following conclusions were obtained:

1. About 2–4 mass% slag particles were suspended in the Fe–Mn–Ca–S–O matte.
2. The distribution ratio of Fe and Mn between the matte and slag increased as the slag basicity increased. When log $P_S$ was more than -2, the Mn distribution increased to be more than 10 as the slag basicity increased beyond 1.7.
3. The Fe and Mn distribution ratios between the matte and slag and the Mn content in the matte increased as temperature increased. Furthermore, the effect of temperature on the increase in the Mn content in the matte was larger than that of the slag basicity and $P_S$.
4. The ratio of the activity coefficients for MnS and FeS in matte ($\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$) was investigated. To evaluate $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ for the matte, $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ was estimated using the empirical formula and the steel model and $\text{NMnS}$ and $\text{NFeS}$ for the Fe–Mn–Ca–S–O matte were calculated on the basis of mass balance. The results revealed that the values of $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ for the Fe–Mn–S–O matte were about twice those for the Fe–Mn–Ca–S–O matte; moreover, $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ decreased as temperature increased.

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