Sulfur Partitions between Carbon-saturated Iron Melt and Na2O-SiO2 Slags*

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Synopsis

The sulfur partitions between carbon-saturated iron melt and Na2O-SiO2 slags with the Na2O/SiO2 molar ratio of 3/2, 1/2, 2/3 and 1/3 have been measured at 1 250 and 1 350 °C. The sulfide capacities $C_s$ defined by Richardson and Fincham,14) has obtained sulfide capacities in the melts produced under a reducing atmosphere. Nagashima15) has obtained sulfide capacities in the melts in Na2O-SiO2 melts with the Na2O/SiO2 molar ratio of 0.9. Desulfurization and dephosphorization of the carbon-saturated iron melts (0.1 % P, 0.05 % S) by the sodium vapor produced by the reaction of NaCl with CaC2 investigated at 1 300 °C. Desulfurization was found to occur, but no dephosphorization was found.

I. Introduction

The fundamental researches on the external desulfurization of hot metal by soda ash have been reported a long time ago.1-5) The sulfur partitions, particularly, between carbon-saturated iron and Na2O-SiO2 slags have been studied by Körber and Oelsen,5,6) Oelsen,4) and Domalski et al.5) It was reported a long time ago.1-5) The sulfur partitions between carbon-saturated iron melt and Na2O-CaO-SiO2 melts at the constant silica content were also measured at 1 250 °C. The effect of time on the sulfur distribution was compared with that of Na2O in the plot of log (S)/(S) vs. (Na2O+ mCaO)/SiO2 ratio, thus resulting m=0.3. The significant amount of iron was observed in the slag phase after equilibration and the ratio of sulfur as FeS against total sulfur in slag was found to be maximum at the composition with the Na2O/SiO2 molar ratio of 0.9. Desulfurization and dephosphorization of the carbon-saturated iron melts (0.1 % P, 0.05 % S) by the sodium vapor produced by the reaction of NaCl with CaC2 investigated at 1 300 °C. Desulfurization was found to occur, but no dephosphorization was found.

II. Experiments

1. Materials

Electrolytic iron (C, S, Si, Mn=0.005 %, P=0.004 %) was melted in a graphite crucible for the preparation of Fe-C-S (S=0.25, 0.5, and 1.0 %) alloy by the addition of the required amount of reagent grade FeS. The mixture of analytical grade Na2CO3 and SiO2 (the Na2O/SiO2 molar ratio=3/2, 1/3) were melted in a platinum crucible and carbon-saturated iron at 1 250 and 1 350 °C and to compare these values with those of the previously reported sulfide capacities.

2. Procedure

SiC resistance furnace was employed and experi-
mental temperature (1 250 and 1 350 °C) was kept constant within ±2 °C by CHINO PID controller. In the experiments with the compositions of Na2O/SiO2=3/2, where the experimental time is less than 10 min, the temperature fluctuation was found to be ±4 °C. The temperature was measured with a Pt/Pt-13%Rh thermocouple on the crucible bottom. Argon gas with a flow rate of 200 ml/min was introduced after drying by phosphorus pentoxide and deoxidizing by copper net at 400 °C. Since sulfur partitions obtained in an argon atmosphere agreed well with those in a CO gas atmosphere (100 ml/min) within the limit of experimental errors, an argon atmosphere was chosen in the present experiments for the slags with Na2O/SiO2=3/2 and 1/1.

To confirm the attainment of equilibrium sulfur partitions, a fused magnesia crucible (21 mm I.D. and 45 mm height) containing 6-10 g of slag and 20 g of metal was used, while a graphite crucible (23 mm I.D. and 50 mm height) containing 8-10 g slag and 30 g of metal was used in the experiments of sulfur partitions. The stirring was made by an alumina rod (6 mm φ) for the determination of equilibrium sulfur partitions.

3. Chemical Analysis

Metallic iron was removed by magnetic separation after grinding under 60 mesh. Sodium was determined by the atomic absorption spectrochemical analysis (JIS-M-8204). The samples of Na2O/SiO2=3/2 and 1/1 were soluble in water and mineral acid, but those of Na2O/SiO2=2/3 and 1/3 are difficult to dissolve. In the latter samples, total sulfur was determined by gravimetric method of sulfur precipitated as barium sulfate (JIS-M-8217) and silica was determined gravimetrically by dehydration (JIS-M-8214) after dissolving the samples by alkali fusion mixture (Na2CO3+NaNO3). After the removal of silica by treating slag samples in hydrofluoric acid and perchloric acid, CaO was determined by titration with EDTA (JIS-M-8221) and/or by the atomic absorption spectrochemical analysis (JIS-M-8204) and/or by eriochrome-cyanine R method.

As described later, the chemical compositions are summarized in the present work on the assumption that total iron is present as FeS. The sum of the chemical compositions in the slags of Na2O/SiO2=3/2 was found to be 97 % at most, since the present slags become highly hygroscopic with an increase of Na2O content. Therefore, the concentrations of each slag component are corrected so that the sum of their concentrations may become 100 %. Sulfur and carbon in metal samples were analyzed by the coulometric titration method. Methylene blue method was also employed for the determination of sulfur less than 0.01 %, but no difference was observed within the limit of analytical errors. Silicon in metal was determined by the absorption spectrometry of molybdenum blue (JIS-G-1212).

III. Results and Discussion

1. Activities of Na2O

Using the stirrable transpiration technique, Sanders and Haller measured the activity of Na2O relative to the liquid standard state for Na2O-2SiO2 glass melt. They reported activities of Na2O at 1 250 and 1 350 °C as 6.56×10^-8 and 1.98×10^-7, respectively.

Kohsaka et al. measured the emf in the following type of a concentration cell given by Eq. (3). The emf is related to the activity of Na2O (aNa2O) in the Na2O-SiO2 system by Eq. (4), where aNa2O is the activities of Na2O in the reference melt of 0.4Na2O-0.6SiO2 and R and F are the gas and Faraday constants, respectively.

\[
E = -(RT/2F) \ln \left[ \frac{a_{Na2O}}{a_{Na2O}} \right]
\] ...........................(3)

Similarly, Frohberg et al. measured the ratio aNa2O/aNa2O in the Na2O-SiO2 melt. The emf’s at 1 250 °C referred to [0.4Na2O-0.6SiO2] melt obtained by Kohsaka et al. and Frohberg et al. are plotted against the SiO2 mole fraction in Fig. 1 by dotted- and double dotted-chain lines, respectively together with their lines referred to [0.33Na2O-0.67SiO2] melt. Yokokawa et al. measured the emf’s referred to the sodium metaphosphate Na2O·P2O5 at 800 °C in the Na2O-P2O5 melt. Their results are also indicated in Fig. 1 by a solid dotted-chain line together with the solid broken line referred to [0.67Na2O-0.33P2O5] melt. Furthermore, Yoko-

![Fig. 1. The emf’s referred to various reference melts of the Na2O-SiO2 and the Na2O-P2O5 systems at 1 250 °C.](image-url)
kawa and Kohsaka measured the temperature dependence of the emf between the 0.33Na2O·0.67SiO2 and the 0.67Na2O·0.33P2O5 melts. From their results, the emf's referred to [0.33Na2O·0.67SiO2] melt in the Na2O–P2O5 system are vertically shifted and plotted in Fig. 1 by the solid line.

In the present work, the activities of Na2O at 1250 and 1350 °C were calculated from the absolute activities of Na2O at the Na2O·2SiO2 composition described above and the activities ratios in the Na2O–SiO2 and the Na2O–P2O5 systems. These results are shown in Fig. 2 in which the activity of CaO in the CaO–SiO2 system at 1600 °C is also given for comparison. The activity of Na2O can be also estimated from the standard free energy of formations for Na2O·SiO2 (l) : 4G° = -58110 + 2.28T (cal) and Na2O·2SiO2 (l) : 4G° = -63270 + 2.08T (cal) and the previously reported SiO2 activities.

The activities of SiO2(l) at SiO2 mole fraction Xsio2 of 0.5 and 0.67 are reported to be 0.13 and 0.6, respectively by Callow at 1250 °C and those by Charles are 0.009 and 0.38, respectively. The activities of Na2O in the Na2O–SiO2 system were calculated at 1250 °C from these values and the thermodynamic data. Then, the activities of Na2O at Xsio2 = 0.5 and 0.67 are estimated to be 1.1 × 10^-7 and 6.6 × 10^-9, respectively by Callow and those are 1.6 × 10^-8 and 1.7 × 10^-8, respectively by Charles. These results are shown in Fig. 2 by open and filled triangles. Recently, activities of Na2O in Na2O–SiO2 melts have been measured between 1000 °C and 1100 °C using a galvanic cell employing sodium beta-alumina. The results obtained by extrapolation of these values to 1250 and 1350 °C are also indicated in Fig. 2.

The sodium vapor pressure due to the reduction of Na2O by carbon can be calculated from the activities of Na2O in the Na2O–SiO2 and the Na2O–P2O5 melts and the standard free energy for the following reaction:

\[
\text{Na}_2\text{O}(l) + C = 2\text{Na}(g) + \text{CO} \quad \text{..................(5)}
\]

\[
\Delta G^o = 107930 - 84.80T \quad \text{(cal)}
\]

Figure 3 shows logarithms of sodium vapor pressure under the C(\alpha_c=1)-CO(P_cO=1 atm) equilibrium plotted against mole fractions of SiO2 and P2O5. The sodium vapor pressure due to Eq. (6) was also calculated under the Fe(\alpha_f=0.82, assuming an ideal solution of Fe–C melt.)–FeO(\alpha_{fo}=1) equilibrium. It was found consequently that logarithm of the sodium vapor pressure was lower than the calculated lines given in Fig. 3 by \Delta \log P_{Na} = 1.44(1250 °C) and 1.57(1350 °C).

\[
\text{Na}_2\text{O}(l) + \text{Fe}(l) = 2\text{Na}(g) + \text{FeO}(l) \quad \text{..................(6)}
\]

\[
\Delta G^o = 79010 - 53.02T \quad \text{(cal)}
\]

These results suggest that if the suitable experimental time and slag compositions are chosen in the equilibrium experiment between carbon-saturated iron and Na2O–SiO2 slags, attainment of equilibration will be possible; that is, the change of composition due to the sodium vaporization loss will be negligible. The reaction given by Eq. (6) was previously pointed out by Carter and it is of particular importance in slags with high Na2O content.

2. Attainment of Equilibrium

To confirm the attainment of equilibrium, the sulfur equilibrium was approached to from larger and smaller contents of sulfur by using a magnesia crucible at 1250 °C. It was found that the equilibrium attained within 10 min for the slag of Na2O/SiO2=3/2 and 20 min for that of Na2O/SiO2=1/1, but it did not attain within 120 min for the slag of Na2O/SiO2=2/3 and
240 min for that of Na$_2$O/SiO$_2$=1/3. Therefore, the stirring by an alumina rod was made in a graphite crucible for 10, 20, 60, and 120 min corresponding to the slags with the compositions of Na$_2$O/SiO$_2$ and (Na$_2$O+CaO)/SiO$_2$=3/2, 1/1, 2/3, and 1/3, respectively.

3. Sulfur Partition

1. Na$_2$O-SiO$_2$ System

Figure 4 shows a plot of logarithms of the sulfur partition (S/\[S\]) against the Na$_2$O/SiO$_2$ molar ratio. The chemical compositions of slag and metal, and the sodium evaporation loss per unit time are summarized in Table 1. Since an alumina rod was used for stirring in the experiments using a graphite crucible, about 1 % Al$_2$O$_3$ was analyzed. This effect on desulfurization, however, can be negligible. The open circles and triangles indicated in Fig. 4 are the results for approaching sulfur to equilibrium from metal and the open squares and inverse triangles are those from slag. The temperature dependence of sulfur partition was not observed in this work. The results for a magnesia crucible are also included in Fig. 4, where the solid circles and squares denote the results for approaching sulfur to equilibrium from metal and slag, respectively. Figures on the symbols indicate MgO content. The sulfur partitions for slags of Na$_2$O/SiO$_2$=3/2 in a magnesia crucible are lower than those in a graphite crucible. This seems to be due to an increase of oxygen potential at slag/metal interface, judging from the decrease of carbon content in metal [3.88 % (No. 15), 4.14 % (No. 16)] listed in Table 1. Since the results in a magnesia crucible agree fairly well with those in a graphite crucible, the effect of MgO on desulfurization is negligible.

The sulfur partitions between carbon-saturated iron and the slags of Na$_2$O/SiO$_2$=0.53.2 have been studied in the temperature range 1 290 to 1 360 °C by Körber and Oelsen.2'3} Since they did not analyze sodium, but analyze only total iron, silica, and sulfur in slag after experiments, the Na$_2$O content was estimated from the following equation (7) on the assumption that the total iron is present as FeS and the remainder of sulfur is present as Na$_2$S.

\[
100 - (\% \text{ FeS}) + (\% \text{ SiO}_2) + (\% \text{ Na}_2\text{S}) = (\% \text{ Na}_2\text{O}) \]

Their results corresponding to the initial sulfur concentrations of 0.44, 0.87, and 1.43 % are compared with the present ones in Fig. 5. It appears from Fig. 5 that their relationship between log (S)/[S] vs. Na$_2$O/SiO$_2$ ratio is independent of the initial sulfur contents and their sulfur partitions obtained are lower than those of the present work. The possible explanation for this disagreement is due to that their experimental time is not sufficient to attain equilibrium in acidic region and to that in basic region, the Na$_2$O content was overestimated from Eq. (7).

The relationship between the sulfide capacity $C_s$ obtained by gas-slag equilibrium studies and the sulfur partition (S)/[S] can be derived by use of the thermodynamic data for the following reactions:

\[
\text{C} + \frac{1}{2}\text{O}_2 = \text{CO} \quad \text{.................................(8)}
\]
\[
\Delta G^0 = -26 700 - 20.95 T \text{ cal} \quad \text{.................................(9)}
\]
\[
\frac{1}{2}\text{O}_2 = \text{O} \quad \text{.................................(10)}
\]
\[
\Delta G^0 = -28 000 - 0.69 T \text{ cal} \quad \text{.................................(11)}
\]
\[
\frac{1}{2}\text{S}_2 = \text{S} \quad \text{.................................(12)}
\]
\[
\Delta G^0 = -31 520 + 5.27 T \text{ cal} \quad \text{.................................(13)}
\]

From Eqs. (9) and (10), we obtain,

\[
\log C_s = \log (S)/[S] + 284/T - 4.43 - \log f_s \quad \text{.................................(14)}
\]

Substituting $P_{\text{CO}}=1 \text{ atm}$ and $a_c=1$ into Eq. (8) we obtain from Eqs. (2) and (9)

\[
\log C_s = \log (S)/[S] + 284/T - 4.43 - \log f_s \quad \text{.................................(15)}
\]

The activity coefficient of sulfur ($f_s$) in carbon-saturated iron melt was calculated to be nearly unity by use of the data in the table given by Schenck and Steinmetz$^{35}$ (ess' = -0.028 and $e^{\text{max}} = 0.003$), although the reference of ess' is not listed. This also the $f_s$ in Eq. (13) was found to be negligible. In this work, the interaction parameter ess' of carbon-saturated iron melt was used for the value of Sherman and Chip-
assuming regular solution model. Consequently, the log $f_s$ at 1 250 and 1 350 °C was found to be 0.74 and 0.75, respectively.

By use of Eqs. (12) and (13), the sulfur partitions ($S$)/[$S$] at the oxygen potential of the $C(a_c=1)$-$CO$ ($P_{CO}=1$ atm) equilibrium were calculated from the sulfide capacities of Nagashima and Katsura$^{13}$ and Denier.$^{15}$ These results are shown in Fig. 6. The present sulfur partitions, which were obtained from slag/metal equilibrium using a graphite crucible are out of accord with those of Nagashima and Katsura and Denier. The reasons for this discrepancy are not clear at present.

Zhmoydin et al.$^{37}$ obtained the sulfide capacities were found to be 20 times as large as those obtained by Kor and Richardson,$^{38}$ who employed the gas-slag equilibration technique. They pointed out that the inadequate control of the CO pressure could be one of the explanations for such a large difference.

The oxygen potential at slag-metal interface determined by Si(asi)-SiO$_2$(asio$_2$) equilibrium was compared with that by $C(a_c=1)$-CO ($P_{CO}=1$ atm) equilibrium in the following.

$$\text{SiO}_2(l)+2C = Si+2CO \quad \text{………………(14)}$$

$$\Delta G^\circ = 140 580 -93.57 T^{28,33,39}$$

By use of the activities of SiO$_2$ in the Na$_2$O-SiO$_2$ system$^{29,30}$ and the activity coefficients calculated from the interaction parameters$^{30}$ assuming regular solution, silicon contents in metal were calculated at $a_c=1$ and $P_{CO}=1$ atm from Eq. (14). These results are given in Table 2 together with the experimentally determined values of silicon. Experimental numbers given in Table 2 correspond to those indicated in Table 1. Silicon contents particularly at 1 350 °C in the experiments of acidic slags were found to be different from those of the equilibrium values. Strictly speaking, the oxygen potential at slag-metal interface in the present work is not determined by the potential of $C$/$CO$, but the mixed potential of $C$-$CO$ and Si-$SiO_2$. However, it is considered to be dominated by $C(a_c=1)$-$CO(P_{CO}=1$ atm), because the equilibrium contents of silicon are low as shown in Table 2. Furthermore the sulfur partitions were measured by approaching to from larger and smaller content of sulfur in metal and these values were found to be in good accord with each other.

The results of Derici and Bell$^{40}$ are also shown in Fig. 6, but the details of the experimental method are unknown. The present sulfur partitions were converted to the sulfide capacities $C$ and $C_s$ by using Eqs. (12) and (13), as shown in Fig. 7 together with the previous measurements.

2. Na$_2$O-CaO-SiO$_2$ System

The sulfur partition between carbon-saturated iron and the Na$_2$O-CaO-SiO$_2$ melts at constant SiO$_2$ content were measured at 1 250 °C. The results obtained in the Na$_2$O-2SiO$_2$-3CaO-2SiO$_2$ and the Na$_2$O-SiO$_2$-CaO-SiO$_2$ pseudo-binary systems are shown in Fig. 8 and the chemical compositions of slag and metal are listed in Table 3. Since the sodium loss by evaporation was about 5 % at maximum, the
Fig. 6. Comparison of the present sulfur partition (S)/[S] in the Na₂O-SiO₂ slag-iron melt system with that obtained from the gas-slag equilibrium studies at 1 250 and 1 350 °C.

Table 2. Comparison of the silicon contents in metal between observation and calculation.

<table>
<thead>
<tr>
<th>No.</th>
<th>Na₂O/SiO₂ (mole ratio)</th>
<th>Sobs.</th>
<th>Steale.</th>
</tr>
</thead>
<tbody>
<tr>
<td>98</td>
<td>0.32</td>
<td>0.079</td>
<td>0.19</td>
</tr>
<tr>
<td>99</td>
<td>0.58</td>
<td>0.027</td>
<td>0.043</td>
</tr>
<tr>
<td>100</td>
<td>0.90</td>
<td>tr.</td>
<td>0.004</td>
</tr>
<tr>
<td>101</td>
<td>1.23</td>
<td>tr.</td>
<td>0.0002</td>
</tr>
<tr>
<td>151</td>
<td>0.36</td>
<td>0.124</td>
<td>0.19</td>
</tr>
<tr>
<td>105</td>
<td>0.31</td>
<td>0.256</td>
<td>3.38</td>
</tr>
<tr>
<td>106</td>
<td>0.56</td>
<td>0.083</td>
<td>1.09</td>
</tr>
</tbody>
</table>

Fig. 7. Sulfide capacities of the Na₂O-SiO₂, CaO-SiO₂, and CaO-CaF₂ systems.

Fig. 8. Logarithms of the sulfur partition (S)/[S] at 1 250 °C, P_CO = 1 atm in the 3Na₂O-2SiO₂-CaO-2SiO₂ pseudo-binary slag-iron melt and the Na₂O-SiO₂-CaO-SiO₂ pseudo-binary slag-iron melt systems.
It follows that logarithms of $C_t$ for Na$_2$O (I) CaO (I) are 3.44 (1 250 °C) and 0.23 (1 500 °C), respectively.

4. Transfer of Iron

It was found by Körber and Oelsen that the amount of sulfur per g Na$_2$CO$_3$ removed from carbon-saturated iron by soda ash or Na$_2$O-SiO$_2$ slags was dependent upon the initial sulfur content and Na$_2$O/SiO$_2$ ratios. The amount of removed sulfur predicted from the stoichiometric relation (Na$_2$CO$_3$ -> Na$_2$S) is 0.302 g (=32/106) per g Na$_2$CO$_3$, but the actual amount of removed sulfur was observed to be much greater, although it depends on the initial sulfur and Na$_2$O/SiO$_2$ ratios. Besides the significant amount of iron, which increased with increasing sulfur content in slag was analyzed in slag after magnetic separation. Accordingly, the observed iron in slag is considered to be due to the reaction given by Eq. (15). The most widely accepted mechanism for desulfurization under reducing conditions is given by Eqs. (15) to (17). The amount of iron oxide in the present work, therefore, will be determined by Eq. (17).

$$\text{Fe} + \text{S} = \text{FeS} \quad (15)$$
$$\text{Fe} + \text{S} + \text{Na}_2\text{O} = \text{Na}_2\text{S} + \text{FeO} \quad (16)$$
$$\text{FeO}(l) + \text{C} = \text{Fe}(l) + \text{CO} \quad (17)$$

$$\Delta G^° = 28 920 - 31.78 T \quad (18)$$

The oxygen potential in desulfurization by Na$_2$O–SiO$_2$ slags will be discussed in the following.

The activity of FeO at 1 250 °C was calculated to be $1.30 \times 10^{-3}$ by substituting the values of $P_{CO} = 1$ atm, $a_{Fe} = 1$ and $a_{FeO} = 0.82$ into Eq. (17). From this, FeO concentrations were obtained by using activity coefficients of FeO in the Na$_2$O-SiO$_2$ system, on the assumption that the activity coefficient of FeO is independent of total iron content in slag. These results are listed in Table 4 from which one may see that the amount of FeO at the Na$_2$O/SiO$_2$=1.3 and 0.9 are negligible, whereas those at the Na$_2$O/SiO$_2$=0.6 and 0.3 are not negligibly small as compared with iron content in slag. When the oxygen potential in the present work is determined by the Fe–FeO equilibrium on the assumption that total iron in slag is wholly present as FeO, the present sulfide capacity given in Fig. 7 deviates further from the other investigators' results.

The total iron in slag being present as FeS in the...
same way as Körber and Oelsen,2,3 the ratios of sulfur as FeS to the total sulfur are plotted against the Na2O/SiO2 molar ratios in Fig. 9 together with the results of Körber and Oelsen corresponding to the initial sulfur concentrations of 0.44, 0.87 and 1.43 %. Their data are considerably scattered regardless of the initial sulfur contents.

The present data correspond to the results for approaching sulfur to equilibrium from metal. Sulfur as FeS increases with increasing Na2O/SiO2 ratio and reaches maximum at the Na2O/SiO2=0.9 and then it decreases. The present results agree comparatively well with those of Körber and Oelsen in basic compositions, but do not agree with them in acidic compositions. According to kinetics studies on the sulfur transfer between carbon-saturated iron and Na2O-CaO-SiO2 slags by Schenck et al.4 it is reported that the iron content in slag abruptly increases at the initial stage and thereafter decreases to equilibrium value. The experimental time of Körber and Oelsen in acidic compositions (10'-20 min) is insufficient to attain equilibrium. The point of a magnesia crucible at the Na2O/SiO2=0.3 composition markedly deviates from the present curve given in Fig. 10. This is attributed to the assumption that the total iron is wholly present as FeS; that is, the amount of FeO given in Table 4 cannot be negligible as compared with the total iron listed in Table 1. In the case of approaching sulfur to equilibrium from slag, total iron content in slag was found to be much smaller and sulfur as FeS increases with decreasing Na2O/SiO2 ratios.

The desulfurization reaction between carbon-saturated iron and Na2O–SiO2 slags has been examined in the experiments using a magnesia crucible. If one considers T.Fe as FeS, then the desulfurization reaction by Na2O is represented by Eq. (18).

\[
\text{Na}_2\text{O} + \text{C} + \text{S} = \text{Na}_2\text{S} + \text{CO} \quad \cdots \cdots \cdot (18)
\]

5. Desulfurization of Sodium Vapor

Bahout et al.6 concluded from the results of soda ash injection treatments that the desulfurization by slag–metal reaction is more likely to occur, although the following reaction by gaseous sodium also occurs to a minor degree.

\[
2\text{Na}(g) + \text{S} = \text{Na}_2\text{S}(l) \quad \cdots \cdots \cdot (19)
\]

Since the sulfur removal occurs by the Na2O–SiO2 slag particles formed by desiliconization: Na2CO3+S\text{Na}_2\text{SiO}_3+C, to increase the Na2O content is necessary for improving desulfurization efficiency. Free carbon is precipitated as a product of the dephosphorization reaction46: Na2CO3+4/5P=Na2O +2/5P2O5+C as well as the desiliconization reaction. Such precipitated carbon and dissolved carbon in hot metal easily react with soda ash to produce gaseous sodium. The following experiments were carried out to study the desulfurization by gaseous sodium.

A graphite bell with an inner graphite crucible containing 10 g of the (2NaCl+CaC2) mixtures was immersed into a carbon-saturated iron melt (0.1 % P, 0.05 % S, 1 kg) at 1 300 °C. The sodium vapor pressures at 1 300 and 1 400 °C produced by the reaction of NaCl with CaC2 were calculated to be 1.32 atm and 2.65 atm, respectively by using the standard free energy for the following reaction.

\[
2\text{NaCl}(l)+\text{CaC}_{2}(s) = 2\text{Na}(g)+\text{CaCl}_{2}+2\text{CO} \quad \cdots \cdots \cdot (20)
\]

\[
\Delta G^\circ = 72 600 - 47.27T \quad \text{(cal)}
\]

As indicated in Fig. 10, sulfur in metal decreases with time. It was thus confirmed that the desulfurization by gaseous sodium occurred in the soda ash injection treatments, but the rate of sulfur removal was found to be lower than that by the Na2O–SiO2 slags. In contrast, the phosphorus removal by sodium gas [3Na(g)+P=Na3P] was not observed at all under the present experimental conditions due to the instability of the formation of Na3P.

6. Desulfurization of Hot Metal by Soda Ash

Desulfurization of Thomas pig iron by soda ash has been carried out in a ladle by Domalski et al.5 Desulfurization experiments in more basic compositions than the Na2O–SiO2 composition were made by the addition of lime to soda ash, while those in acidic compositions were made by the addition of iron oxide to desiliconize. The temperature dependence of sulfur partitions was not observed at around 1 200 °C. They did not take the effect of P2O5 content on sulfur partitions into consideration. Their results are shown in Fig. 11 together with the work of Bahout et al.6

\[
\text{Table 4. Estimated amount of iron oxide in the Na}_2\text{O–SiO}_2 \text{ system at 1 250 °C.}
\]

<table>
<thead>
<tr>
<th>Na2O/SiO2</th>
<th>0.3</th>
<th>0.6</th>
<th>0.9</th>
<th>1.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFeO</td>
<td>0.5</td>
<td>0.7</td>
<td>1.6</td>
<td>4.3</td>
</tr>
<tr>
<td>NFeO</td>
<td>0.003</td>
<td>0.002</td>
<td>0.0008</td>
<td>0.0003</td>
</tr>
</tbody>
</table>

\[
\text{Fig. 9. Sulfur as FeS against the total sulfur in the Na}_2\text{O–SiO}_2 \text{ slag–iron melt system at 1 250 and 1 350 °C.}
\]

\[
\text{Research Article}
\]
who did not also give any consideration to $P_2O_5$ content. In the laboratory scale experiments (4 kg) of soda ash treatments, Yamamoto et al.\textsuperscript{48} derived the linear relation between logarithm of $\frac{(S)}{[S]}$ and $\frac{(%Na_2O)}{[1.03(%SiO_2)+1.32 (%P_2O_5)]}$ in the temperature range 1300 to 1450 °C, although their experimental points are considerably scattered. The slags contain 6–9 % $P_2O_5$. Their sulfur partitions are plotted against the $Na_2O/SiO_2$ molar ratio in Fig. 11. It can be said that their sulfur partitions are lower than those of the present work, although our experiments were carried out in more acidic slag compositions.

The sulfur partitions in the oxygen potential of the Fe($\alpha_F=0.82$)-FeO($X_{reo}=0.01$) equilibrium were calculated from the values of the sulfide capacities $C_s$, the activity coefficient of FeO in the $Na_2O-SiO_2-FeO$ system\textsuperscript{49} and the free energy of formation of FeO ($\Delta_fG$),\textsuperscript{33} assuming that the carbon content in metal is under saturation. These results at 1250 and 1350 °C are indicated in Fig. 11 by broken lines. The oxygen potential at slag-metal interface in Yamamoto et al.’s experiments was estimated from sulfide capacities obtained in the present work. The oxygen pressure $P_{O_2}$ was found to be $2.8 \times 10^{-13}$–$2.4 \times 10^{-14}$ atm at 1350 °C in the composition $Na_2O/SiO_2=1.5$, which was higher than that determined by the $C(\alpha_C=1)$–CO($P_{CO}=1$ atm) equilibrium (i.e., $4.5 \times 10^{-17}$ atm). This is probably attributable to the fact that oxygen was blown with a lance in their experiments.

IV. Summary
The results obtained are summarized in the following.

1) Activities of $Na_2O$ in the $Na_2O-SiO_2$ and the $Na_2O-P_2O_5$ systems have been estimated at 1250 and 1350 °C from the activity of $Na_2O$ at the $Na_2O-SiO_2$ melt and the activity ratios of $Na_2O$ previously determined by the emf method. From these values the sodium vapor pressure due to the reaction of $Na_2O$ with carbon was calculated.

2) The sulfur partitions between carbon-saturated iron and the $Na_2O-SiO_2$ melts have been measured at 1250 °C at constant $SiO_2$ content. Logarithm of $\frac{(S)}{[S]}$ in the $3Na_2O.2SiO_2-3CaO.2SiO_2$ and the $Na_2O • SiO_2-CaO • SiO_2$ pseudo-binary systems decreases linearly with increasing $3CaO.2SiO_2$ and $CaO • SiO_2$ contents. The $Na_2O$ equivalent of $CaO$ for the sulfur partition was found to be 0.3.

3) The presence of FeS was confirmed by the findings that the amount of Fe in slag after experiments was much greater in comparison with that predicted from the content of FeO calculated in the $C(\alpha_C=1)$–CO($P_{CO}=1$ atm) equilibrium. The ratio of sulfur as FeS to total sulfur was maximum at the composition of $Na_2O/SiO_2=0.9$ (molar ratio).

4) The desulfurization by the gaseous sodium produced by the reaction of NaCl with CaC$_2$ was observed in carbon-saturated iron melt, but the dephosphorization reaction did not take place at all.

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REFERENCES

2) F. Köhler and W. Oelsen: Stahl u. Eisen, 58 (1938), 905.
3) F. Köhler and W. Oelsen: Stahl u. Eisen, 58 (1938), 943.