Desulfurizing Ability of the $CaO_{satd.}$-$CaCl_2$-CaF_2 Slags

JIAZHAN LIU and YOSHINAO KOBAYASHI

Desulfurizing ability of the CaO-$CaCl_2$-CaF_2 slags saturated with CaO has been investigated from the viewpoint of the sulfide capacity and CaO solubility. The CaO-$CaCl_2$-CaF_2 slags containing small amounts of Cu_2O and CaS were inserted in a CaO crucible with metallic copper. The CaO crucible was sealed in a nickel holder to prevent the evaporation of $CaCl_2$, then heated up and kept at temperatures from 1573 K (1300 °C) to 1673 K (1400 °C) for 24 hours, which enabled the system inside the CaO crucible to reach the equilibrium. As expected, the sulfide capacity derived from the data obtained as well as CaO solubility of the slag increase with an increase in temperature at a constant ratio of $CaCl_2/CaF_2$. The solubility of CaO increases by the replacement of CaF_2 with $CaCl_2$, whereas the sulfide capacity slightly decreases and the activity coefficient of CaS (γ_{CaS}) increases. This suggests that CaF_2 has stronger interaction with CaS than $CaCl_2$. The sulfur distribution ratio between carbon-saturated iron melts and the CaO-$CaCl_2$ slag has been calculated to be about 10 000 at 1573 K (1300 °C) using the sulfide capacity obtained, which value is still large enough even with the replacement of CaF_2 by $CaCl_2$.

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I. INTRODUCTION

IN the conventional hot metal desulfurization process, excessive solid lime is used as a desulfurizing agent and flux agent such as CaF_2 is added to promote CaO dissolution. The solid CaO does not directly participate in the desulfurization reaction, which is only due to the liquid slag coexisting with solid CaO.[1,2] For the desulfurizing ability of this liquid slag, two key factors should be considered: (1) sulfide capacity from a thermodynamic point of view and (2) solubility of CaO which ensures more chances for sulfur reacting with CaO from a kinetic point of view.

Over the years, in the practical hot metal pretreatment, an excellent desulfurization has been achieved using the CaO-CaF_2-based slags. However, it is strongly required to reduce the amount of CaF_2 in terms of environmental concern. Taniguchi *et al.*[3,4] proposed to directly use the carryover of a certain amount of blast furnace slag in the hot metal ladle as a flux agent and measured the sulfide capacity of the formed CaO-Al_2O_3-SiO_2-based slags. However, the value obtained is much lower than that of CaO-CaF_2-SiO_2 slags.[5] Besides that, it is well known that CaO-Al_2O_3-SiO_2 slags have limited solubilities of CaO and CaS;[6] therefore, fluxes having higher ability are required.

As a sort of flux agent, $CaCl_2$ is a candidate to replace CaF_2. Addition of $CaCl_2$ into CaO-based slags can effectively promote the melting of CaO, as reported elsewhere.[7] The research of Sakai *et al.*[8] confirmed that CaO-$CaCl_2$ slags have high sulfide capacity in the temperature range from 1273 K to 1523 K (1000 °C to 1250 °C). However, the sulfide capacity and CaO solubility in CaO-$CaCl_2$ based slags have not been clarified at hot metal desulfurization temperature which is usually over 1573 K (1300 °C), because the traditional experimental methods are not feasible due to the evaporation of $CaCl_2$ at higher temperature. Therefore, the present work aims to establish a new experimental method to finally investigate the effect of replacement of CaF_2 by $CaCl_2$ on the sulfide capacity and CaO solubility of CaO-$CaCl_2$-CaF_2 slags saturated with CaO in the temperature range from 1573 K (1300 °C) to 1673 K (1400 °C).

II. EXPERIMENTAL

A. *Experimental Principles*

The sulfide capacity of molten slags was originally defined on the basis of the gas/slag reaction (Eq. [1]) as shown in Eq. [2].

$$1/2S_2(g) + (O^{2-}) = 1/2O_2(g) + (S^{2-}) \qquad [1]$$

$$C_{S^{2-}} = \frac{K_1 \cdot a_{O^{2-}}}{f_{S^{2-}}} = (\text{pct S}) \cdot \left({}^{P_{O_2}}/{P_{S_2}}\right)^{1/2}, \qquad [2]$$

where $K_1, a_{O^{2-}}, f_{S^{2-}}$, P_i, and (pct S) are the equilibrium constant of Reaction [1], the activity of oxide ion, the Henrian activity coefficient of sulfide ion, the partial

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pressure of i, and the sulfur content on mass pct basis in slag, respectively. As shown in the definition, the sulfide capacity solely depends on slag composition and temperature.

For the present experiments, to suppress the loss dueto the severe evaporation of $CaCl_2$ above 1573 K (1300 °C), a gas–slag–metal equilibration technique was employed in a closed system to determine the sulfide capacity of slags. Copper was chosen as the reference metal which reflected the sulfur potential (P_{S_2}) and oxygen potential (P_{O_2}) derived from Eqs. [3] and [4] with the standard Gibbs energy for the dissolution reaction of gaseous sulfur and oxygen into the molten copper.[9,10]

$$1/2S_2(g) = [S]_{Cu}, \quad \Delta G^\circ = -103950 + 15.63T \text{ (J/mol)} \qquad [3]$$

$$1/2O_2(g) = [O]_{Cu}, \quad \Delta G^\circ = -66140 + 3.81T \text{ (J/mol)} \qquad [4]$$

CaS and Cu_2O were added into the slags as the source of sulfur and oxygen. The final Cu_2O content should be controlled as low as possible so as not to influence the property of CaO-$CaCl_2$-CaF_2 slags. A dense CaO crucible was used to contain the slag and copper and to make the slag saturated with CaO. The closed system in the experiments was supported by a nickel holder, which was carefully welded after inserting the CaO crucible. The reason for the choice of nickel holder in the present set-up instead of iron, molybdenum, or other metal holder with high melting point was the fact that nickel is relatively stable with oxygen, and thus the final oxygen potential in the closed system would not be regulated by the oxidation reaction of nickel.

B. *Experimental Procedure*

The slag samples were prepared by complete mixing of CaO calcined from $CaCO_3$, $CaCl_2$, CaF_2, Cu_2O, and CaS reagent powders. $CaCl_2$ is hygroscopic and the water absorbed by $CaCl_2$ would be the oxygen source at experimental temperature, which significantly increases the final equilibrium oxygen potential in the closed system. Thus, the slag powders were dehydrated at 873 K (600 °C) for 2 hours in a muffle furnace. Then, the powders were melted in a platinum crucible for 10 minutes at 1373 K (1100 °C) under argon atmosphere. After quenching the sample, 1 to 3 g of pre-melted slag and 3 g of copper were maintained in a dense CaO crucible (outer diameter: 19 mm, inner diameter: 15 mm, and height: 15 mm). After placing the CaO crucible into the nickel holder, the holder's lid was screwed on tightly and welded. To prevent the hydration of $CaCl_2$, the whole charging process was conducted in a glove box.

An $MoSi_2$ electric resistance furnace equipped with a proportional–integral–differential (PID) controller with a Pt–Pt/6 pct Rh thermocouple was used for all the experiments. Inside the furnace, an alumina reaction tube (outer diameter: 100 mm, inner diameter: 85 mm, and length: 1000 mm) was positioned. The temperature was controlled within ±2 K in the temperature even zone over a length of 50 mm. After reaching the target temperature, the nickel holder was placed in the center of the reaction tube under an argon atmosphere and held for 24 hours to reach equilibrium, which has been confirmed long enough by the preliminary experiments.

C. *Degrees of Freedom in the Closed System*

For a system in an invariant equilibrium state, the degree of freedom should be zero, which can be determined by the Gibbs phase rule. In the present study, the liquid CaO-$CaCl_2$-CaF_2-Cu_2O-CaS slags and copper in a CaO crucible have been equilibrated in a closed system given by a nickel holder. Accordingly, the number of the components is 8 due to the presence of calcium, copper, sulfur, chlorine, fluorine, oxygen, nitrogen, and nickel on element basis. The number of the phases is 5 due to the presence of liquid slag, molten metal, oxide and metal holder materials and gas phases. The temperature is constant. Consequently, the degree of freedom for this system is 4 and it can become zero by determining the initial content ratio of the slag components among $CaCl_2$, CaF_2, Cu_2O, and CaS. That is to say, the present system can reach the equilibrium, provided that the slag composition remains in a steady state throughout the experiments.

D. *Sample Analysis*

After equilibration, the nickel holder was quickly pulled out from the furnace and quenched with ice water. Then, the holder was cut open and the slag and copper samples were subjected to chemical analysis. The oxygen content in the metal and the sulfur content in both the slag and the metal were measured with LECO* oxygen analyser and sulfur analyser, respectively. The contents of calcium and copper were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). The CaO content of the slag was measured by neutralization titration. With the analysis results of overall calcium, CaO, CaS, and Cu_2O in the slag, the contents of $CaCl_2$ and CaF_2 were derived by calculation.

III. RESULTS AND DISCUSSION

A. *Equilibrium Time*

Preliminary experiments were carried out to determine the time required for equilibration. Figure 1 shows the change of CaO content and $L_S \cdot$ [pct O], where L_S is the sulfur distribution ratio between slag and metal, (pct S)/[pct S], with holding time for the system of 11.5CaO-87$CaCl_2$-1Cu_2O-0.5CaS slag (on mass pct basis) and molten copper in a CaO crucible which was

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placed in a closed nickel holder at 1573 K (1300 °C). The Henrian activity coefficients of oxygen and sulfur in the molten copper are both assumed to be 1, because the interaction between oxygen and sulfur is very small[9] and the content of other solute elements is extremely low. Hence, from the definition of sulfide capacity, it can be recognized that the desulfurization reaction reaches equilibrium when the value of $L_S \cdot$ [pct O] is constant. The CaO content and $L_S \cdot$ [pct O] become constant after about 16 hours, which confirms the attainment of equilibrium state in the closed system. For the main experiments, the holding time has been determined to be 24 hours. It is notable that for the two experiments with 32 hours of holding time, the final Cu_2O contents are quite different, 1.24 and 3.77 mass pct, respectively; but the CaO content and $L_S \cdot$ [pct O] are nearly the same, which indicates that the influence of a small amount of Cu_2O addition on the property of CaO-$CaCl_2$-CaF_2 slag can be neglected.

B. *Experimental Results*

The experimental results obtained in this study are listed in Table I. The mass ratio of $CaCl_2/CaF_2$ in the final slags does not change much throughout the experiments, which suggests that the evaporation of $CaCl_2$ had been successfully suppressed during the experiments. The oxygen content in copper after experiments confirms that the oxygen potential in the closed system was not regulated by the oxidation reaction of nickel.

C. *Solubility of CaO*

The solubility of CaO in CaO-$CaCl_2$, CaO-CaF_2, and CaO-$CaCl_2$-CaF_2 systems is shown in Figures 2 and 3, together with the results reported in the literature.[11–13] The CaO solubility of CaO-$CaCl_2$ system from 1573 K to 1673 K (1300 °C to 1400 °C) is located on the line extrapolated from the results by Wenz[11] for lower temperatures. For the CaO-CaF_2 system whose eutectic temperature is as high as 1633 K (1360 °C), the CaO solubility is smaller than that of CaO-$CaCl_2$ system. For the CaO-$CaCl_2$-CaF_2 system, CaO solubility increases with the replacement of CaF_2 by $CaCl_2$. At 1673 K (1400 °C), the CaO solubility is smaller than that obtained by Sano,[12] and the discrepancy becomes larger with an increase in $CaCl_2$ content. In Sano's experiment, because the evaporation of $CaCl_2$ had not been suppressed, some of the CaO once dissolved in the molten slag might have precipitated again and remained in the molten slag, which led to the final CaO content higher than the actual CaO solubility.

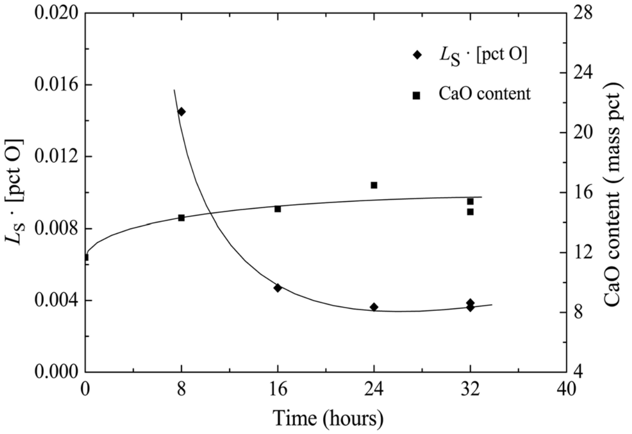

Fig. 1—Change of CaO content and $L_S \cdot$ [pct O] against time at 1573 K (1300 °C).

D. *Sulfide Capacity for the CaO-$CaCl_2$-CaF_2 Slags Saturated with CaO*

The sulfide capacity of CaO-$CaCl_2$-CaF_2 slags saturated with CaO from 1573 K to 1673 K (1300 °C to 1400 °C) is shown in Figure 4 as a function of $X_{CaCl_2}/(X_{CaCl_2}+X_{CaF_2})$. In the CaO-$CaCl_2$-$CaF_2$ slags, log $C_{S^{2-}}$, common logarithm of $C_{S^{2-}}$, increases with an increase in temperature and decreases with the replacement of CaF_2 by $CaCl_2$. An increase in the content of $CaCl_2$ from about 25 to 75 mol pct in the slag causes a decrease in $C_{S^{2-}}$, just by 1.5 to 1.8 times, indicating that the replacement of CaF_2 by $CaCl_2$ would not significantly influence the desulfurizing ability of CaO-$CaCl_2$-CaF_2 slags saturated with CaO. Figure 5 shows the sulfide capacity as a function of reciprocal temperature at a fixed $CaCl_2$ content in the slag. Linear relationships are observed, and the slopes of all the lines are almost the same.

The equilibrium reaction between CaO and CaS is as follows:[14]

$$\begin{gathered}\mathrm{CaO(s)}+1/2\mathrm{S_2(g)}=\mathrm{CaS(s)}+1/2\mathrm{O_2(g)}\\ \Delta G^\circ=92100-4.80T(\mathrm{J/mol})\end{gathered} \quad [5]$$

$$K_5=\gamma_{CaS}\cdot X_{CaS}\cdot P_{O_2}^{1/2}\Big/a_{CaO}\cdot P_{S_2}^{1/2}, \quad [6]$$

where K_5, a_{CaO}, γ_{CaS}, X_{CaS}, and P_i are the equilibrium constant of Reaction [5], the activity of CaO, the activity coefficient of CaS, the mole fraction of CaS, and the partial pressure of *i*. In the present work, slags are saturated with CaO; thus, a_{CaO} is unity. Considering Eq. [6], the enthalpy change for Reaction [5], ΔH_5°, can be expressed by Eq. [7] according to van't Hoff equation:

$$\frac{\partial\log\left(\gamma_{CaS}\cdot X_{CaS}\cdot P_{O_2}^{1/2}/P_{S_2}^{1/2}\right)}{\partial(1/T)}=-\frac{\Delta H_5^\circ}{2.303\mathrm{R}}. \quad [7]$$

Assuming that γ_{CaS} does not change with temperature, the value of ΔH_5° is given as 196 kJ/mol from the experimental data, which is larger than the reported value[14] of 92 kJ/mol. This indicates that γ_{CaS} considerably decreases with an increase in temperature.

The activity coefficient, γ_{CaS}, can be also calculated from Eq. [6]. Figure 6 shows the activity coefficient of CaS in the slag as a function of $X_{CaCl_2}/(X_{CaCl_2}+X_{CaF_2})$. γ_{CaS} increases with the replacement CaF_2 by $CaCl_2$ at

Table I. Analytical Composition of Final Slags, S and O Contents of Copper, and Calculated $C_{\mathrm{S}^{2-}}$

		Slag Composition (Mass Pct)					Metal Composition (Mass Pct)		
Run	Temperature, K (°C)	CaO	$CaCl_2$	CaF_2	Cu_2O	CaS	$[S]_{Cu}$	$[O]_{Cu}$	$\log C_{\mathrm{S}^{2-}}$
1	1573 (1300)	14.7	84.1	0	1.24	0.073	0.0706	0.0083	−1.78
2		13.9	50.1	35.1	0.67	0.177	0.1440	0.0086	−1.69
3		13.7	34.7	51.0	0.22	0.338	0.1462	0.0055	−1.61
4	1623 (1350)	14.4	83.4	0	1.95	0.193	0.1018	0.0075	−1.60
5		14.4	63.0	22.0	0.41	0.184	0.0931	0.0088	−1.54
6		14.3	49.8	34.8	0.93	0.115	0.1712	0.0348	−1.39
7		14.3	34.1	51.0	0.32	0.212	0.0942	0.0091	−1.33
8	1673 (1400)	15.6	83.1	0	1.02	0.241	0.0696	0.0067	−1.42
9		15.4	61.8	21.5	1.19	0.263	0.0833	0.0091	−1.33
10		14.8	49.6	34.9	0.29	0.439	0.0484	0.0037	−1.26
11		14.9	33.7	50.8	0.57	0.156	0.1047	0.0268	−1.19

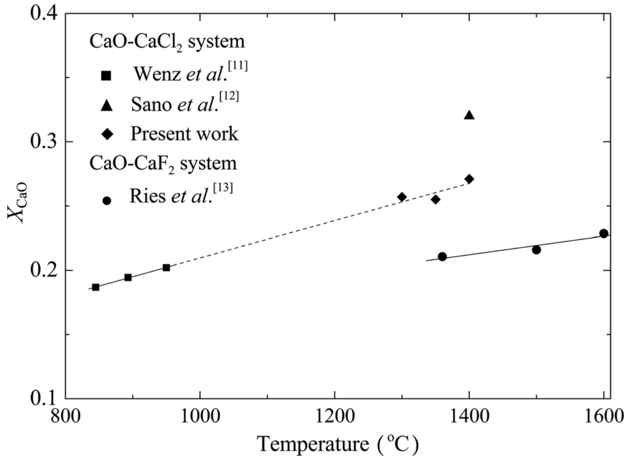

Fig. 2—Solubility of CaO in the CaO-$CaCl_2$ and CaO-CaF_2 slags.

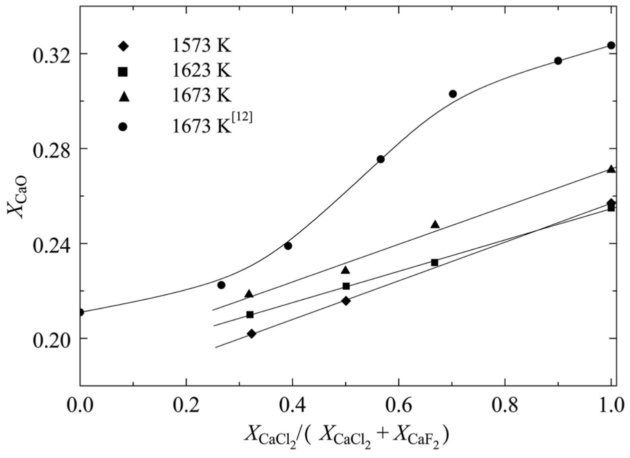

Fig. 3—Dependence of CaO solubility on the $CaCl_2$ content in the CaO-$CaCl_2$-CaF_2 slags.

each temperature, which suggests that CaF_2 has stronger interaction with CaS than $CaCl_2$.

Thermodynamic consideration has been made for the change in CaO solubility and $C_{\mathrm{S}^{2-}}$. The $a_{\mathrm{O}^{2-}}$ in the present work is determined by the reaction of (CaO) = (Ca^{2+}) + (O^{2-}) and can be expressed as follows:

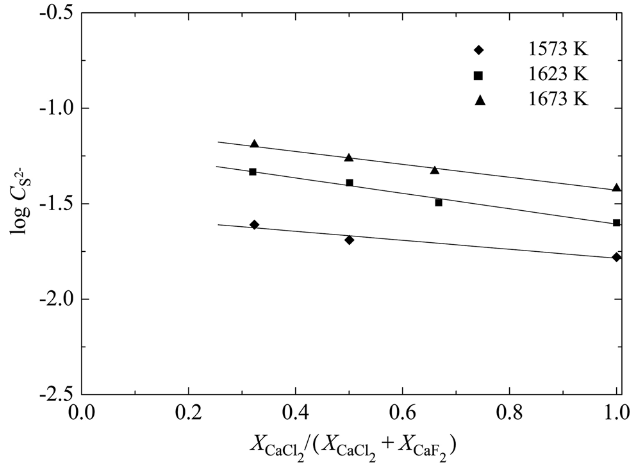

Fig. 4—Dependence of sulfide capacity on the $CaCl_2$ content in the CaO-$CaCl_2$-CaF_2 slags saturated with CaO.

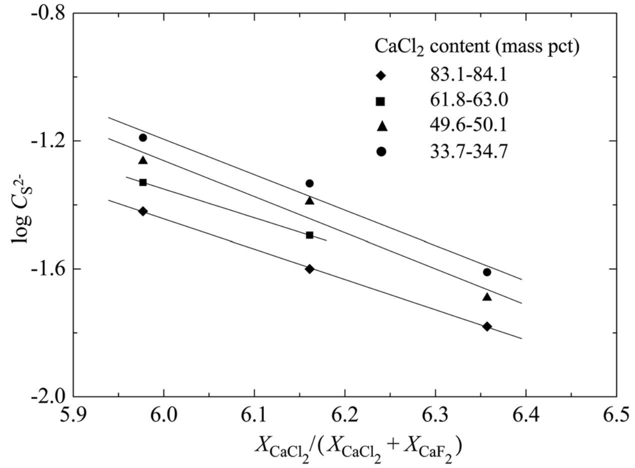

Fig. 5—Temperature dependence of sulfide capacity for the CaO-$CaCl_2$-CaF_2 slags saturated with CaO.

$$a_{\mathrm{CaO}}=a_{\mathrm{Ca}^{2+}}\cdot a_{\mathrm{O}^{2-}}=\left(\gamma_{\mathrm{Ca}^{2+}}\cdot X_{\mathrm{Ca}^{2+}}\right)\left(\gamma_{\mathrm{O}^{2-}}\cdot X_{\mathrm{O}^{2-}}\right)=1, \quad [8]$$

where $a_{\mathrm{Ca}^{2+}}$, γ_i, and X_j are the activity of calcium ion, the activity coefficient of i, and the mole fraction of j

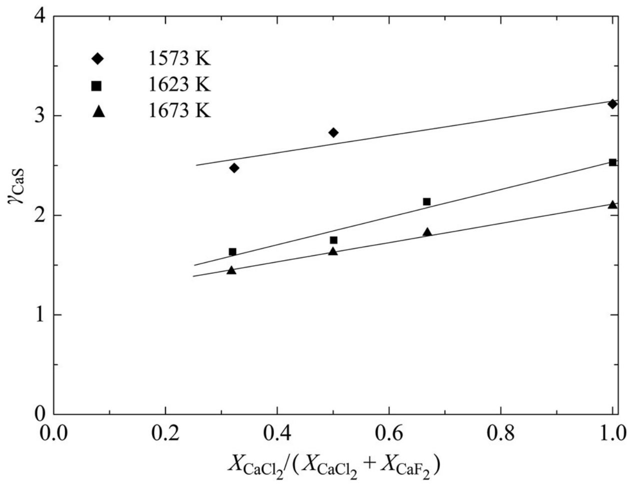

Fig. 6—Dependence of γ_{CaS} on the $CaCl_2$ content in the CaO-$CaCl_2$-CaF_2 slags saturated with CaO.

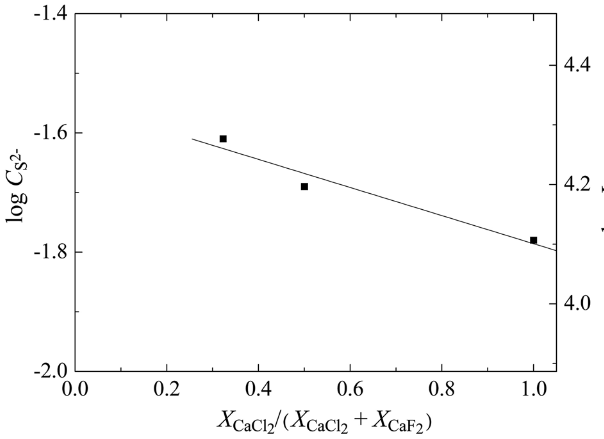

Fig. 7—Sulfide capacity and sulfur distribution ratio between slags and carbon-saturated iron melt at 1573 K (1300 °C).

in slag, respectively. Ca^{2+} is the only cation in the slag, and therefore $a_{Ca^{2+}}$ is constant, if Temkin model[15] is applied. Consequently, $a_{O^{2-}}$ is also constant and $C_{S^{2-}}$ is only influenced by temperature and $f_{S^{2-}}$ for the CaO-$CaCl_2$-CaF_2 slags saturated with CaO. As F^- is replaced by Cl^-, $\gamma_{O^{2-}}$ decreases because the radius of Cl^- is larger than that of F^- and, accordingly, the attractive force between Ca^{2+} and Cl^- is smaller than that between Ca^{2+} and F^-, leading to the reduction of total attractive force between Ca^{2+} and halide ion, which explains why CaO solubility increases with replacing CaF_2 by $CaCl_2$. In the present work, a decrease of $C_{S^{2-}}$ with replacing CaF_2 by $CaCl_2$ indicates the decrease of $\gamma_{S^{2-}}$, which may be caused by the increase of O^{2-} content because the attractive force between Ca^{2+} and O^{2-} is largest in the slag.

E. *Sulfur Distribution Ratio between Slag and Carbon-Saturated Iron Melts*

The experimentally obtained sulfide capacity can predict the sulfur distribution ratio between slag and metal which is more frequently and importantly used in the practical process, such as hot metal desulfurization. Eq. [9] shows the desulfurization reaction in carbon-saturated iron melts:

$$[S]_{Fe-C_{satd.}} + \left(O^{2-}\right) = 1/2O_2(g) + \left(S^{2-}\right). \qquad [9]$$

The sulfur distribution ratio L_S can be derived as shown in Eq. [12] by applying Eqs. [10] and [11] to the obtained sulfide capacity.[16,17]

$$1/2S_2(g) = [S]_{Fe-C_{satd.}}, \quad \Delta G^\circ = -125100 + 18.5T\,(\mathrm{J/mol}) \qquad [10]$$

$$\begin{gathered} C(s) + 1/2O_2(g) = CO(g), \\ \Delta G^\circ = -114391 - 85.77T\,(\mathrm{J/mol}) \end{gathered} \qquad [11]$$

$$L_S = \left(C_{S^{2-}} \cdot f_{S_{Fe-C_{satd.}}}/P_{CO}\right)\exp\left[\left(\Delta G^\circ_{10} - \Delta G^\circ_{11}\right)/RT\right], \qquad [12]$$

where $f_{S_{Fe-C_{satd.}}}$ is the activity coefficient of sulfur in carbon-saturated iron melts relative to 1 mass pct Henrian standard. At 1573 K (1300 °C), $f_{S_{Fe-C_{satd.}}}$ is 6.25[5] and L_S was calculated and is shown in Figure 7, by assuming P_{CO} = 1 atm. Even though L_S decreases with the replacement of CaF_2 by $CaCl_2$, the value of L_S for the CaO-$CaCl_2$ slag saturated with CaO is still as high as 10 000 at the temperature of 1573 K (1300 °C), which is satisfactory enough for the actual operation.

IV. CONCLUSIONS

The sulfide capacity and CaO solubility for the CaO-$CaCl_2$-CaF_2 slags saturated with CaO were determined at temperatures from 1573 K to 1673 K (1300 °C to 1400 °C) by equilibrating molten slag and molten copper in a CaO crucible. Furthermore, the sulfur distribution ratios between slags and carbon-saturated iron melts were derived using the obtained sulfide capacity. The specific findings are summarized as follows:

1. The CaO solubility and the sulfide capacity increase with an increase in temperature at a constant ratio of $CaCl_2/CaF_2$.
2. The CaO solubility increases by 4.5 to 5.5 mol pct and $C_{S^{2-}}$ decreases by the factor of 1.5 to 1.8 times with an increase in $CaCl_2$ content from about 25 to 75 mol pct.
3. The value of γ_{CaS} increases with a decrease in temperature and with the replacement of CaF_2 by $CaCl_2$, which indicates that CaF_2 has stronger interaction with CaS than $CaCl_2$.
4. The estimated sulfur distribution ratio between CaO-$CaCl_2$ slag saturated with CaO and carbon-saturated iron melts is as high as 10 000 at the temperature of 1573 K (1300 °C), which suggests the

feasibility of replacing CaF_2 by $CaCl_2$ in practical hot metal desulfurization.

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