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Study on sulphide capacity of CaO-SiO_2-Al_2O_3-MgO-Fe_tO slags

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Abstract: The sulphide capacity of CaO-SiO_2-Al_2O_3-MgO-Fe_tO slags was studied at 1773 K using gas-slag equilibrium techniques. Utilizing a Pt crucible, the slag was equilibrated with a mixture of gases, namely, CO, CO_2, SO_2 and N_2 to provide the partial pressure of oxygen and sulphur. It was shown that at fixed Fe_tO and Al_2O_3 contents and a fixed {(%CaO)+(%MgO)}/(%SiO_2) ratio, the sulphide capacity decreases with increasing MgO content. At a constant (%CaO)/(%SiO_2) ratio and constant MgO and Al_2O_3 contents, increasing the Fe_tO content of the slags also results in an increase of the sulphide capacity. The rising basicity of (%CaO)/(%SiO_2) from 1.0 to 1.4 at fixed MgO, Fe_tO and Al_2O_3 contents significantly increases the sulphide capacity.

Key words: CaO-SiO_2-Al_2O_3-MgO-Fe_tO slags; sulphide capacity; gas-slag equilibrium

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1. Introduction

In recent years, the COREX process has made rapid progress [1]. Several operating problems, however, have been encountered because of the shortage of plant operation data and experience [2-3]. First of all, the principal COREX slag composition consists of CaO, SiO_2, Al_2O_3, MgO, and Fe_tO. The physicochemical characteristics of COREX slags are somewhat different from those of blast furnace slags (typically CaO-SiO_2-Al_2O_3-MgO slags) and those of steelmaking slags (typically CaO-SiO_2-MgO-Fe_tO slags) [4-5]. Therefore, the knowledge of the sulphide capacity of COREX slags is valuable to the metallurgical process. This work investigates the sulphide capacity of CaO-SiO_2-Al_2O_3-MgO-Fe_tO slags at 1773 K using gas-slag equilibrium techniques.

2. Experimental principle

The principal equilibrium reaction of sulphur between the gas and slag phases is represented by the following equations:

$$\frac{1}{2}S_2+(O^{2-})=\frac{1}{2}O_2+(S^{2-}) \tag{1}$$

$$K_1=\frac{a_{S^{2-}}}{a_{O^{2-}}}\times(\frac{P_{O_2}}{P_{S_2}})^{\frac{1}{2}}=(\%S)\times(\frac{f_{S^{2-}}}{a_{O^{2-}}})\times(\frac{P_{O_2}}{P_{S_2}})^{\frac{1}{2}} \tag{2}$$

where K_1 is the equilibrium constant. Rearranging the thermodynamic parameters that can be determined experimentally in Eq. (2), the following relation can be obtained:

$$C_S=(\%S)\cdot(\frac{P_{O_2}}{P_{S_2}})^{\frac{1}{2}}=K_1\cdot(\frac{a_{O^{2-}}}{f_{S^{2-}}}) \tag{3}$$

The $C_S=(\%S)(P_{O_2})^{1/2}/(P_{S_2})^{1/2}$ has been defined as 'sulphide capacity' by Richardson and Fincham [6], where (%S) is the mass percentage of sulphur in slag, and P_{O_2} and P_{S_2} are the partial pressures of O_2 and S_2, respectively.

3. Experimental methods

3.1. Experimental materials

The chemical composition of the slags used in the present work is listed in Table 1. Fe_tO was prepared by sintering a reagent grade of Fe_2O_3 in an iron crucible under CO atmosphere for 24 h [7]. The stoichiometry of Fe_tO used in this work was found to be $Fe_{0.92}O$. Other oxide powders of reagent grade CaO, SiO_2, Al_2O_3 and MgO were calcined at 1173 K for 12 h before being thoroughly mixed with the required proportions in an agate mortar. The powder mixtures were premelted in a graphite crucible using an induction furnace. The pre-

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fused slags were ground into fine powders in an agate mortar and stored in desiccators before use. Chemical analysis of selected slags indicated that the composition agreed with the weight in amounts and that the slags did not pick up any carbon from the crucible during melting. The chemical composition of the slags in Table 1 is all the charged values, and the amount of prefused slags and Fe_tO were weighed and fixed to be used for the experiment according to the values listed in Table 1.

Table 1. Experimental results of the sulphide capacity (C_S) at 1773 K

No.	Composition of slags / wt%					(P_{O2}/P_{S2})	S / wt%	$\lg C_S$
	(CaO)	(SiO_2)	(Al_2O_3)	(MgO)	(FeO)			
11	42.7	37.3	12.0	6.0	2.0	0.001379	0.0513	–4.15
12	38.7	37.3	12.0	10.0	2.0		0.0469	–4.19
13	36.7	37.3	12.0	12.0	2.0		0.0412	–4.25
14	33.7	37.3	12.0	15.0	2.0		0.0284	–4.41
15	28.7	37.3	12.0	20.0	2.0		0.0242	–4.48
21	44.4	35.6	12.0	6.0	2.0	0.001379	0.0525	–4.14
22	40.4	35.6	12.0	10.0	2.0		0.0498	–4.16
23	38.4	35.6	12.0	12.0	2.0		0.0455	–4.20
24	35.4	35.6	12.0	15.0	2.0		0.0300	–4.38
31	40.8	37.0	12.0	10.0	0.2	0.001379	0.0193	–4.57
32	40.3	36.7	12.0	10.0	1.0		0.023	–4.50
33	38.7	35.3	12.0	10.0	4.0		0.0233	–4.49
34	37.7	34.3	12.0	10.0	6.0		0.0284	–4.41
35	35.7	32.3	12.0	10.0	10.0		0.0307	–4.37
36	34.7	31.3	12.0	10.0	13.0		0.0347	–4.32
41	41.7	34.3	12.0	10.0	2.0		0.0620	–4.07
42	44.3	31.7	12.0	10.0	2.0		0.0576	–4.05

3.2. Experimental apparatus and procedure

Fig. 1 shows the experimental apparatus used in this study. All experiments were carried out in the $MoSi_2$ furnace. Two sets of Pt-30%Rh/Pt-6%Rh thermocouples were used to control the experimental temperature at 1773 K within ±3 K. One was installed between the heating elements and the reaction tube and was connected to a temperature controller, whereas the other was set just behind the crucibles to measure the experimental temperature.

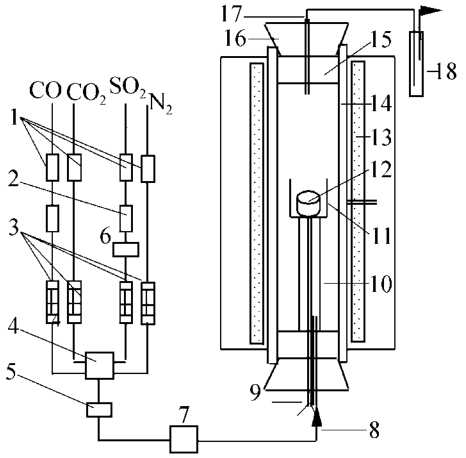

Fig. 1. Schematic diagram of experimental apparatus. 1—decontaminating columns; 2—ascarite columns; 3—flow meters; 4—gas mixture; 5—gas bubblers; 6—copper getter furnace; 7—gas container; 8—gas inlet; 9—thermocouple; 10—center supporting; 11—alumina crucible; 12—Pt crucible; 13—heating element; 14—alumina tube; 15—refractory brick; 16—silicon rubber; 17—gas outlet; 18—scrubber solution.

A gas mixture of CO-CO_2-SO_2-N_2 was used to provide a controlled furnace atmosphere. The residual oxygen in the nitrogen was removed by passing it through a copper getter furnace at 723 K. Any carbon dioxide in the N_2 and CO streams was removed by passing these gases through an ascarite column. Flow rates were controlled by conventional capillary flow meters. The gas mixture was introduced into the equilibration zone of the furnace by an alumina tube, and the gas leaving the reaction tube passed through a packed column containing aqueous sodium hydroxide saturated solution to remove acid gas, and the tail gas was burnt in a burner to remove CO.

A slag sample weighing about 3 g was held in a Pt crucible (10 mm in diameter and 10 mm in height), which was held in an alumina holder. To prevent the slag melt from creeping out of the Pt crucible, the edges of the crucible were carefully bent inwards. The sample was heated up to the experimental temperature under the flow of N_2 and then exposed to a gas mixture of CO-CO$_2$-SO$_2$-N$_2$ (the volume ratio of CO:CO$_2$:SO$_2$:N$_2$ =100:100:10:190), with a constant flow of 400 mL/min for 6 h. This duration was found to be sufficient for the slag to reach equilibrium with the gas according to the pre-experiment. The partial pressures of oxygen and sulphur in the gas, which were computed using the data listed in Table 2 provided by Seo and Kim [7] and Wang [8], were fixed as 5.44×10^{-3} Pa and 2.86 kPa, respectively. After equilibrium, the sample was quenched by pulling the crucible to the cold end of the furnace. The sulfur content of the slag was determined by the combustion analysis method.

Table 2. Free energy change of gas reaction of CO-CO$_2$-SO$_2$-N$_2$ mixture

Reaction	ΔG^Θ / J
$1/2S_{2(g)}+O_{2\,(g)}=SO_{2\,(g)}$	$-86410+17.34T$
$1/2S_{2(g)}+3/2O_{2(g)}=SO_{3\,(g)}$	$-109350+39.09T$
$1/2S_{2(g)}+CO_{\,(g)}=COS_{\,(g)}$	$-20300+18.07T$
$1/2O_{2(g)}+CO_{\,(g)}=CO_{2\,(g)}$	$-66950+20.20T$
$1/2S_{2(g)}+1/2O_{2(g)}=SO_{\,(g)}$	$-13810+1.19T$
$2O_{(g)}=O_{2\,(g)}$	$-121800+31.85T$
$2S_{(g)}=S_{2\,(g)}$	$-86500+29.20T$

4. Results and discussion

A series of experiments were carried out to measure the sulphide capacity of the CaO-SiO$_2$-Al$_2$O$_3$-MgO-Fe$_t$O slags. The experimental results, including the composition of the slags, the sulphur content of the slags after equilibrium, and the value of lgC_S, are listed in Table 1.

4.1. Effect of MgO content

To estimate the effect of MgO content on the desulphurizing capacity of slags, the variation of the sulphide capacity of the CaO-SiO$_2$-Al$_2$O$_3$-MgO-Fe$_t$O slag system is plotted as a function of MgO content in Fig. 2.

As shown in Fig. 2, for the slags of the constant {(%CaO)+(%MgO)}/(%SiO$_2$) ratio, (%Fe$_t$O)=2, (%Al$_2$O$_3$)=12, the sulphide capacities decrease with increasing MgO content. The relative contribution of CaO and MgO to the sulphide capacity can be discussed thermodynamically by examining the equilibrium constants of MeO/MeS reaction (Me=Ca, Mg) [9], which are listed as follows,

$$CaO_{(S)}+1/2S_2=CaS_{(S)}+1/2O_2 \qquad (4)$$

$K_4=2.67\times10^{-3}$;

$$MgO_{(S)}+1/2S_2=MgS_{(S)}+1/2O_2 \qquad (5)$$

$K_5=0.0162\times10^{-3}$.

The equilibrium constant for the MgO/MgS equilibrium, K_5, is substantially lesser than that for the CaO/CaS equilibrium, K_4. Considering Eq. (3), it can be mentioned that the substitution of MgO for CaO shows a strong influence on the ratio of $a_{O^{2-}}$ to $f_{S^{2-}}$. It is also shown in Fig. 2 that the sulphide capacities increase with the increase of slag basicity at the identical MgO content.

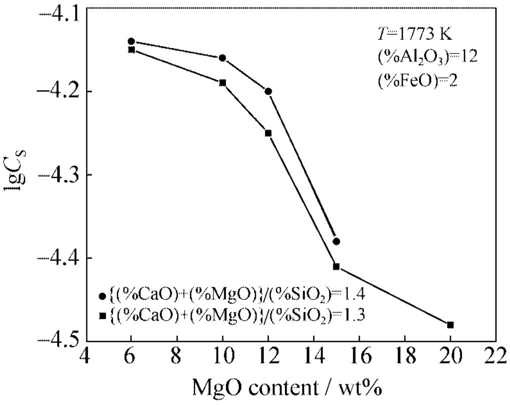

Fig. 2. Relationship between lgC_S and MgO content.

4.2. Effect of Fe$_t$O content

Fig. 3 shows the variation of the sulphide capacity as a function of Fe$_t$O content, added to the slags at a fixed (%CaO)/(%SiO$_2$) ratio, MgO, and Al$_2$O$_3$ content.

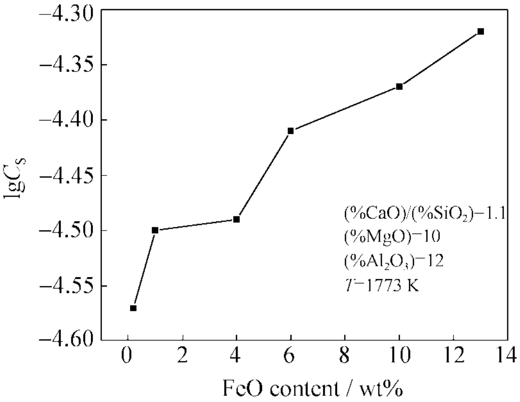

Fig. 3. Relationship between lgC_S and Fe$_t$O content.

It is shown in Fig. 3 that the sulphide capacity increases significantly with increasing Fe$_t$O content under the fixed (%CaO)/(%SiO$_2$) ratio. Lee *et al.* [10] investigated the influence of CaO/Fe$_t$O ratio on the density and structure of the CaO-Fe$_t$O-SiO$_2$ slag system and reported that the partial molar volume of iron silicate decreases, whereas that of calcium silicate increases when Fe$_t$O is substituted for CaO. For the interpretation of the structure variation, they postulated that depolymerization occurs in the various silicate anion atmospheres such as $Si_9O_{21}^{6-}$ and $Si_6O_{15}^{6-}$ around Fe^{2+}, whereas polymerization proceeds in the anion atmospheres around Ca^{2+}. The Fe$_t$O role silicate network breaker is much more meaningful in the slag composition of the slags with relatively low (%CaO)/(%SiO_2) ratio, such as the COREX slag. However, the degrees of depolymerization in the anion atmospheres around Fe^{2+} and Ca^{2+} are nearly equivalent in the highly basic slag systems. Shim *et al.* [11] also studied the equilibria of sulphur between liquid iron and Fe_tO-SiO_2-CaO-MgO slags saturated with MgO. The data in their study showed that the (%S) to [%S] ratio increases with the increase of Fe_tO, which results in the increase of sulphur capacity.

4.3. Effect of basicity

The relationship between the sulphide capacity and basicity is shown in Fig. 4. The basicity was herein defined as (%CaO)/(%SiO_2). For the slags of constant MgO, Fe_tO, and Al_2O_3 content, the sulphide capacity increases when the basicity increases from 1.0 to 1.4. Shim *et al.* have concluded that CaO is the strongest basic oxide to dusulfurization compared to Fe_tO and MgO in the slags. According to Eq. (3), it can be mentioned that the increase of the basicity shows a strong influence on the ratio of $a_{O^{2-}}$ to $f_{S^{2-}}$. In other words, an increase in the basicity, which corresponds to an increase in CaO content, results in a significant increase in the free oxygen ion activity, assuming that the variation of $f_{S^{2-}}$ is insignificant because of the dilute solution behavior of sulphur in slags.

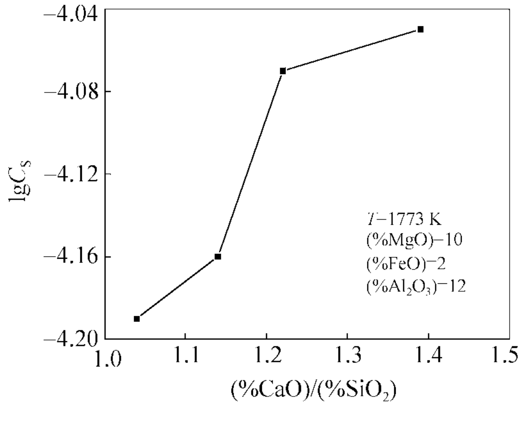

Fig. 4. Relationship between lgC_S and (%CaO)/(%SiO_2).

The increasing basicity of slags means that the CaO content is rising and the SiO_2 content is falling. Pierre *et al.* [12] have also studied the sulfur equilibrium between gases and slags containing Fe_tO at 1723 K and 1823 K. In their measurements, Fe_tO slags with the addition of CaO, SiO_2 and MgO, were equilibrated with the atmospheres of SO_2 containing the additions of CO and O_2. They analyzed the effect of silica additions on the sulfide content and concluded that lgC_S is plotted against the molar percentage of SiO_2. The relationship between the sulphide capacity and SiO_2 mole percent of the present study is also shown in Fig. 5.

As shown in Fig.5, the replacement of silicon by calcium at constant iron content results in a decrease in the value of lgC_S. The influential trend of SiO_2 additions in the slags on the sulfide capacity is similar to that of Pierre and Chipman. But the data of lgC_S in Fig.5 were little than those mentioned by Pierre and Chipman. The reason for the difference is that the data of Pierre and Chipman were obtained from high Fe_tO slags in equilibrium with gases, whereas in Fig.5 the value of Fe_tO in slags is far less than that cited by Pierre and Chipman.

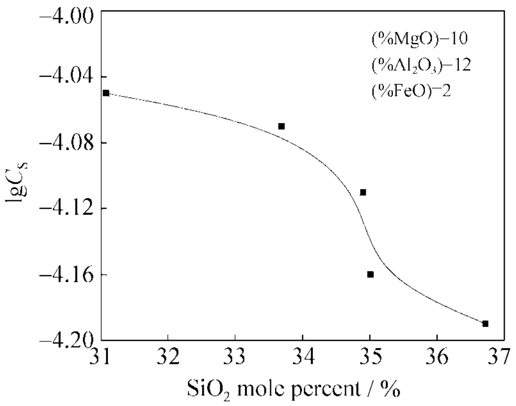

Fig. 5. Relationship between lgC_S and SiO_2 mole percent.

The distribution equilibrium between liquid iron and the slags of Fe_tO-MgO, Fe_tO-SiO_2-MgO and Fe_tO-SiO_2-CaO-MgO systems: Saturated MgO was carried in magnesia crucibles in the temperature range from 1823 K to 1923 K, by J.D. Shim and S. Ban-ya [11]. The distribution ratio, S-O ration and the sulphide capacity of the slags were determined as the function of the slag composition in their paper, but the sulphide capacity data were all larger than those of the present study. It may be explained that reactants could contact more adequately in two liquid phases than those in the phase of liquid and gas.

5. Conclusions

The sulphide capacity of CaO-SiO_2-Al_2O_3-MgO-Fe_tO slags was investigated at 1773 K by equilibrating the slags with a mixture of gases, namely, CO, CO_2, SO_2, and N_2. The results are summarized as follows:

(1) For the slags at fixed {(%CaO)+(%MgO)}/(%SiO_2) ratio, Fe_tO and Al_2O_3 contents, the sulphide capacity decreases with the increase of MgO content.

(2) For the slags of constant (%CaO)/(%SiO_2) ratio and constant MgO and Al_2O_3 contents, increasing Fe_tO content results in a significant increase in the sulphide capacity.

(3) For the slags of constant MgO, Fe_tO and Al_2O_3

contents, the sulphide capacity increases when the ratio of (%CaO)/(%SiO_2) increases from 1.0 to 1.4.

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