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Effect of components on desulfurization of an Al_2O_3-CaO base pre-molten slag containing SrO

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Abstract: The desulfurization experiment of an Al_2O_3-CaO base pre-molten refining slag containing SrO was carried out. Experimental samples were made from industrial materials. In order to predict the slag's desulfurization ability, sulphur capacity was calculated by means of optical basicity, and there is consistency between calculated results and experimental data. A mathematical model between components and sulphur partition ratio was established with the experimental data. Based on the regression equation, the effects of single and interactive components on sulphur partition ratio were discussed. The results show that the sulphur capacity and distribution ratio decrease with the increment of Al_2O_3/CaO. SrO and MgO can increase the sulphur partition ratio. The best content of SrO in the slag should not be more than 10%, and the MgO content should be about 8%. The effect of CaF_2 on sulphur partition ratio is not obvious, therefore the addition should be limited for environmental protection.

Key words: Al_2O_3-CaO base; refining slag; desulfurization; SrO

1 Introduction

With the development of metallurgical industry and the requirement of high quality of steel, refining processes become more and more important. To some refining equipment such as a ladle furnace (LF), selecting proper refining slags can improve the efficiency of buried arc, increase the heating efficiency apparently, reduce the duration of heating, and decrease the consumption of power, electrode and refractory. An Al_2O_3-CaO base pre-molten refining slag has many merits such as homogeneous composition, a lower melting temperature, a higher melting speed and containing low or without fluorine. The physical and chemical properties of the refining slag, for example melting temperature and viscosity, will influence the desulfurization speed of molten steel and sulfide removal from molten steel into the slag. It is inevitable for the best refining purpose to study and analyze the effect of components on the metallurgical properties of the refining slag.

2 Research method

A refining slag system was composed of Al_2O_3, CaO, MgO, CaF_2, SrO and SiO_2. The composition (mass fraction) is determined according to the updated reference: CaF_2, 3%-9%; MgO, 4%-10%; SrO, 0-10%; Al_2O_3/CaO, 0.8-1.2. The codes, which stand for different components, are shown as follows:

C_1=(MgO%−7%)/3%, C_2=(Al_2O_3/CaO−1.0)/0.2,
C_3=(CaF_2%−6%)/3%, C_4=(SrO%−5%)/5%.

When the content of MgO in the slags is 4%, 7%, and 10% respectively, C_1 would be −1, 0, 1; when Al_2O_3/CaO is 0.8, 1.0, 1.2 respectively, C_2 would be −1, 0, 1; when CaF_2 is 3%, 6%, 9% respectively, C_3 would be −1, 0, 1; when SrO is 0%, 5%, 10% respectively, C_4 would be −1, 0, 1. 17 groups were designed with the 1/2 orthogonal regression method (4 factors, 3 levels) [1]. The code of factor level is shown in **table 1**.

The materials selected in this study came from industrial materials containing CaO, MgO, CaF_2 and SiO_2. It is unavoidable that SiO_2 was introduced into slag samples as gangue, the composition of SiO_2 in samples was arranged as 8%, and MgO is also considered as a important factor as well. SrO used to substitute for some of CaO not only benefits for melting but also increases the sulphur capacity of the refining slag, so SrO was introduced into samples. A little of CaF_2 was added in order to study its effect on desulfurization properties of the slag. Dolomite and limestone were triturated to the size less than 40 mesh, homogeneously mixed with all the raw materials, melted in the graphite crucible in induction electric furnace, finally the pre-molten refining slags were also triturated

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in 200 mesh. Desulfurization experiments were carried out in an $MoSi_2$ furnace protected by N_2 at 1600°C. There was no gas stirring in molten steel, all experiments were in static diffusion state. The composition of a steel samples is shown in **table 2**. The slag mass is 5% of steel sample. Samples were took out from the furnace when refining time reached to 25min, then treated and analyzed the sulphur contents in the steel and slag respectively.

Table 1 Code of factor level

Factor	Composition (wt%)			
	MgO	Al_2O_3/CaO	CaF_2	SrO
0	7	1.0	6	5
Δ	3	0.2	3	5
1	10	1.2	9	10
−1	4	0.8	3	0
1.353	11.0	1.27	10.1	8.7
−1.353	3.0	0.73	1.9	1.3

Table 2 Composition of steel sample (wt%)

C	Si	Mn	P	S
0.65	0.30	0.55	0.023	0.051

3 Calculations of optical basicity and sulphur capacity

According to the theoretical optical basicity of each oxide listed in **table 3**, the following expression was used to calculate the optical basicity (Λ) of samples [2]:

$$\Lambda = \frac{\sum (w_i \Lambda_i O_i / M_i)}{\sum (w_i O_i / M_i)} \tag{1}$$

where w_i, Λ_i, O_i / M_i are the mass fraction, the theoretic optical basicity and the oxide number coefficient of component i respectively.

Table 3 Optical basicity and oxide number coefficient

Oxide	Optical basicity	Oxide number coefficient
SiO_2	0.46	0.0666
Al_2O_3	0.60	0.0588
CaO	1.00	0.0357
MgO	0.78	0.0496
CaF_2	0.43	0.0512
SrO	1.10	0.0294

By means of large-quantity experimental data, Sommerville obtained the following expression [3]:

$$\lg C_s = \left(\frac{22690 - 54640\Lambda}{T}\right) + 43.6\Lambda - 25.2 \tag{2}$$

where C_s is the sulphur capacity, T is the temperature (K). The above expression is only suitable for calculating the samples with low sulphur capacity. Because there is no simple linear relationship between optical basicity and $\lg C_s$, equation (2) is modified with Λ^2 and oxides' mass fraction by the multivariant regression method [4], then two expressions were acquired:

$$\lg C_s = -13.193 + 42.84\Lambda - 23.82\Lambda^2 - (11710/T) - 0.02223 SiO_2\% - 0.02275 Al_2O_3\% \quad \Lambda < 0.8 \tag{3}$$

$$\lg C_s = -0.6261 + 0.4808\Lambda + 0.7197\Lambda^2 + (1697/T) - (2587\Lambda/T) + 0.0005144 FeO\% \quad \Lambda \geq 0.8 \tag{4}$$

Calculated results reveal that the Λ of each group sample is less than 0.8, so equation (3) is used to calculate the sulphur capacity (C_s) of the refining slags, and the calculated data are shown in **table 4**. Consequently, we have previous knowledge to evaluate the desulfurization ability of each group slag.

Table 4 Calculated data of optical basicity and sulphur capacity

No.	Optical bassicity	Sulphur capacity / 10^4	No.	Optical bassicity	Sulphur apacity / 10^4	No.	Optical bassicity	Sulphur capacity / 10^4
1	0.743	16.23	7	0.722	8.92	13	0.725	9.01
2	0.705	7.40	8	0.685	3.86	14	0.698	6.39
3	0.698	3.62	9	0.708	6.42	15	0.700	5.21
4	0.697	5.28	10	0.714	9.17	16	0.723	11.21
5	0.729	12.37	11	0.731	15.12	17	0.711	7.64
6	0.725	15.81	12	0.697	4.51			

4 Data processing

4.1 Orthogonal regression analysis

The chemical analysis data of sulphur content in slags and metals were shown in **table 5**.

According to the data listed in the above table, the desulphurization ratio and the sulphur partition ratio were calculated, and the regression equation, which expresses the relationship between sulphur partition ratio (L_S) and component code, was described as fellow:

$$L_S = 58.55 + 3.38C_1 - 22.77C_2 - 5.81C_3 + 13.27C_4 + 1.33C_1C_2 + 1.60C_1C_3 - 2.13C_1C_4 + 2.13C_2C_3 - 1.60C_2C_4 - 1.33C_3C_4 + 3.14C_1^2 + 3.99C_2^2 + 1.03C_3^2 + 0.89C_4^2 \quad (5)$$

Regression coefficient significance was tested by the expression:

$$F_j = \frac{U_j}{S_e / f_e} \quad (6)$$

where F_j is a statistic, U_j is the partial regression square sum of a variable, S_e is the sum of residual square, and f_e is the degree of residual freedom, here it is 4. The results were shown in **table 6**. The insignificant coefficients (C_{13} and C_{14}) were removed according to the test results, then the significance of remained coefficients was increased. The general regression equation excluded C_{13} and C_{14} is tested by F function:

$$F = \frac{S_r/f_r}{S_e/f_e} \quad (7)$$

where S_r is the sum of regression square, f_r is the degree of regression freedom. Variant test results are shown in **table 7**, S_t and f_t are the total sum of square and the total degree of freedom, respectively, and they are significant at the level α=0.01, which means the quadric regression model conforms with the experiment data.

Table 5 Experimental results and data processing

No.	Sulphur content in steel/ %	Sulphur content in slag/ %	Desulfurization ratio	Sulphur partition ratio	No.	Sulphur content in steel /%	Sulphur content in slag/ %	Desulfurization ratio	Sulphur partition ratio
1	0.010	1.017	81.37	107.06	10	0.014	0.907	72.55	64.79
2	0.015	0.922	70.59	61.47	11	0.011	0.986	78.43	89.64
3	0.028	0.671	45.10	23.96	12	0.022	0.762	56.86	34.64
4	0.019	0.823	62.75	43.32	13	0.014	0.932	72.55	66.57
5	0.012	0.966	76.47	80.50	14	0.018	0.837	64.71	46.50
6	0.01	0.977	80.39	97.70	15	0.020	0.816	60.78	40.80
7	0.015	0.887	70.59	59.13	16	0.013	0.933	74.51	71.77
8	0.025	0.694	50.98	27.76	17	0.017	0.864	66.67	50.82
9	0.016	0.901	68.63	56.31					

Table 6 Significance test of regression coefficient

Item	F_j value	Significance	Item	F_j value	Significance
C_1	F_j=17.03>$F_{0.01}$(1,14)=8.86	*	C_8	F_j=4.62>$F_{0.05}$(1,14)=4.60	*
C_2	F_j=772.14>$F_{0.01}$(1,14)=8.86	* *	C_9	F_j=2.62>$F_{0.25}$(1,14)=1.44	*
C_3	F_j=50.22>$F_{0.01}$(1,14)=8.86	*	C_{10}	F_j=1.80>$F_{0.25}$(1,14)=1.44	*
C_4	F_j=262.40>$F_{0.01}$(1,14)=8.86	* *	C_{11}	F_j=8.42>$F_{0.05}$(1,14)=4.60	*
C_5	F_j=1.80>$F_{0.25}$(1,14)=1.44	*	C_{12}	F_j=13.63>$F_{0.01}$(1,14)=8.86	*
C_6	F_j=2.62>$F_{0.25}$(1,14)=1.44	*	C_{13}	0.79	\
C_7	F_j=4.62>$F_{0.05}$(1,14)=4.60	*	C_{14}	0.58	\

Note: * means significance; * * means great significance; \ means insignificance.

Table 7 Significance test of regression equation

Index	Sum of squares	Degree of freedom	Significance
	S_t=8967.70	f_t=16	
L_S	S_r=8941.24	f_r=12	F=112.64>$F_{0.01}$(12,4)=14.4
	S_e=26.46	f_e=4	

The following expression was obtained from equation (5) excluded insignificant coefficients (C_{13} and C_{14}), and code values are replaced by components mass fraction:

$$L_S = 308.36 - 633.11x_1 - 342.17x_2 - 628.78x_3 + 578x_4 + 221.67x_1x_2 + 1777.78x_1x_3 - 1420x_1x_4 + 355x_2x_3 - 160x_2x_4 - 886.67x_3x_4 + 3488.89x_1^2 + 99.75x_2^2 \quad (8)$$

where x_1, x_3, x_4 are the mass fractions of MgO, CaF_2 and SrO respectively, x_2 is the mass ratio of Al_2O_3/CaO.

4.2 Effect of single component on sulphur partition ratio

(1) Effect of MgO on sulphur partition ratio.

When the code values of C_2, C_3 and C_4 all are 0, that is to say, Al_2O_3/CaO is 1.0, CaF_2 is 6%, SrO is 5%, the regression equation, which expresses the relation of MgO and sulphur partition ratio, is expressed as:

$$L_S = 70.49 - 375.78x_1 + 3488.89x_1^2 \quad (9)$$

The effect of MgO on sulphur partition ratio is shown in **figure 1**. When the mass fraction of MgO is more than 6%, L_S would increase with the increasing of the mass fraction of MgO. MgO is an alkalinous component, which has strong ability to combine with sulphur, but a little weaker than that of CaO. The main effect of MgO is to decrease the activity of SiO_2 and increase the activity of CaO in the slags, the result is to improve the sulphur partition ratio between slags and metals. Another function of MgO is to decrease the viscosity of slag, which results in the easier removing of S^{2-} from the boundary layer between metals and slags into the bulk of slags, and improving the desulfurization ability of slags. A previous study indicated that the diffusion of S^{2-} would be difficult and the desulfurization kinetics condition would be worsen if MgO content was relative high, because indissoluble materials, such as periclasite, would result in the increasing of the melting temperature and viscosity of slags [5]. Comprehensivly considering physical and metallurgical properties, the mass fraction of MgO in refining slags should not be more than 10%, and 8% is suitable.

Calculated results show that the mass fraction of MgO of about 5% is the demarcation value on the sulphur partition ratio. When the mass fraction of MgO is less than 5%, the effect of MgO on L_S is gentle; when the mass fraction of MgO is more than 5%, L_S is rapidly increased with the increasing mass fraction of MgO.

(2) Effect of Al_2O_3/CaO on sulphur partition ratio.

When C_1, C_3 and C_4 is 0, that is to say, MgO is 7%, CaF_2 is 6%, SrO is 5%, the regression equation is expressed as:

$$L_S = 274.89 - 313.35x_2 + 99.75x_2^2 \quad (10)$$

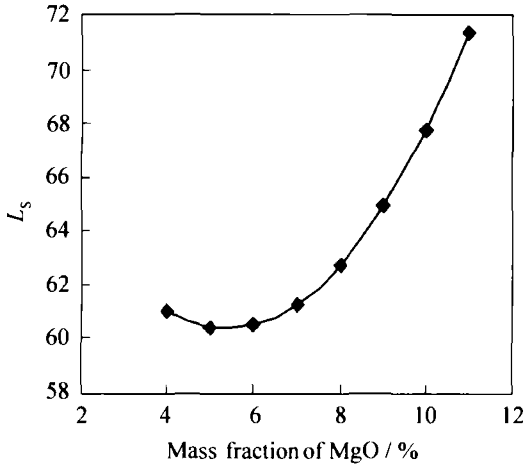

Figure 1 Effect of the mass fraction of MgO on sulphur partition ratio.

According to this expression, we can calculate the minimum value of L_S through the partial differential method, which is 28.80, when Al_2O_3/CaO is 1.57. The effect of Al_2O_3/CaO on sulphur partition ratio is shown in **figure 2**. The sulphur partition ratio decreases with the increment of Al_2O_3/CaO. This can be explained as the following. Firstly, the increase of Al_2O_3/CaO would result in the decreasing of sulphur capacity of refining slags [6]. From the following expression:

$$\lg L_S = -\frac{935}{T} + 1.375 + \lg C_S + \lg f_S - \lg a_O \quad (11)$$

where f_S is the activity coefficient of sulphur in metal phase, and a_O is the activity of oxygen, we know that a decrease in sulphur capacity brings sulphur partition ratio drop directly. Secondly, the increment of Al_2O_3/CaO will introduce overmuch Al_2O_3 in slags, which results in the increasing of the oxygen activity of slags, and the sulphur partition ratio would be decreased with the activity of oxygen increasing [7].

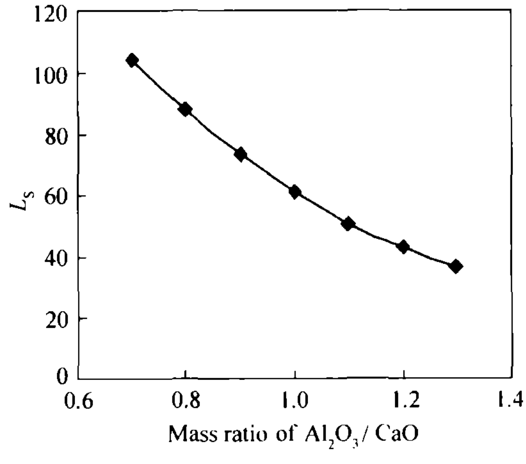

Figure 2 Effect of Al_2O_3/CaO on sulphur partition ratio.

4.3 Effects of interactive composition on sulphur partition ratio

(1) Effect of Al_2O_3/CaO and CaF_2 on sulphur partition ratio.

The effect of Al_2O_3/CaO and CaF_2 on sulphur partition ratio was described as:

$$L_S = 307.22 - 548.67x_3 - 334.65x_2 + 355x_2x_3 + 99.75x_2^2 \quad (12)$$

The effect of Al_2O_3/CaO and CaF_2 on sulphur partition ratio is shown in **figure 3**. When the Al_2O_3/CaO ratio is fixed, L_S decreases with the increase of CaF_2, but its change is less remarkable than L_S decrease with the increment of the ratio of Al_2O_3/CaO.

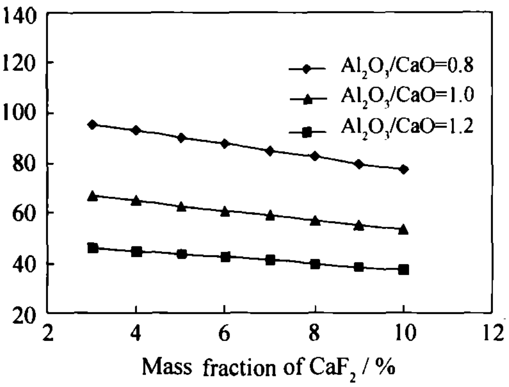

Figure 3 Effect of Al_2O_3/CaO and CaF_2 on sulphur partition ratio.

Based on the metallurgical theory, CaF_2 addition benefits for the desulfurization ability of slags when basicity components are kept as constant. The main action of CaF_2 is to reduce the melting temperature, improve the liquidity of slags and increase the diffusion of desulfurated products [8]. The author's study reveals that the effect of CaF_2 on melting temperature and the viscosity is not obvious in the Al_2O_3-CaO base pre-molten refining slag because the whole slag system has low melting temperature, so reducing the CaF_2 content in slag will not bring any negative effect on metallurgical properties of this kind of refining slags [9]. S. Simeonov believed that CaF_2 increase would reduce the O^{2-} content in slag [10], this theory is consistent with experimental results, the sulphur partition ratio has a little drop when CaF_2 content increases. According to the interface balance reaction between slags and metals:

$$[S] + (O^{2-}) = (S^{2-}) + [O] \quad (13)$$

A less dissolved oxygen and a higher O^{2-} content will make the reaction move to right. This is advantage to desulfurization. If the basicity of slags is higher, the O^{2-} content is more, sulphur is easy removal from molten steel into slags. The content of O^{2-} depends on that of SiO_2, Al_2O_3, CaO and MgO.

(2) Effect of Al_2O_3/CaO and MgO on sulphur partition ratio.

The expressed relationship among Al_2O_3/CaO, MgO and sulphur partition ratio is expressed as:

$$L_S = 296.88 - 597.44x_1 - 328.87x_2 + 221.67x_1x_2 + 3488.89x_1^2 + 99.75x_2^2 \quad (14)$$

The contours of MgO, Al_2O_3/CaO and sulphur partition ratio are shown in **figure 4**. The sulphur partition ratio reduces with the ratio of Al_2O_3/CaO increasing. The effect of MgO on L_S is much less obvious than that of Al_2O_3/CaO.

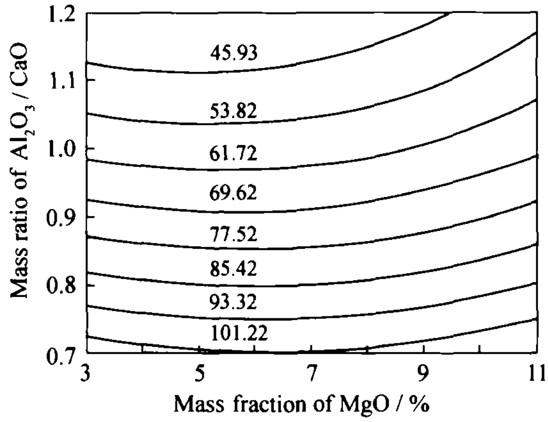

Figure 4 Contours of MgO, Al_2O_3/CaO and sulphur partition ratio.

According to the ionic theory of molten slag, alkalinous oxides will be dissociated as positive ion and negative ion. Acid oxides form compound negative ions by absorbing oxygen ions. The viscosity increases with the increment of the radius of compound negative ions, because the radius of compound negative ions is bigger than that of simple ions, the interior frictional force will increase in molten slags, which cause the viscosity increase. Al_2O_3 is an amphoteric oxide, its acidity is predominant in the environment of basic slags. Aluminum ions characterize small radius and high charge, and the static electric potential is enough high, so a compound negative ions $(Al_XO_Y)^{Z-}$ is composed of aluminum ions and oxygen ions. At the meantime, aluminum ions can replace Si^{4-} in $(Si_XO_Y)^{Z-}$ partly, and then Si-Al-O compound negative ion is formed, which would result in the increasing of the viscosity of slags. When the Al_2O_3 content reaches a certain content, MgO will form series of low melting temperature compounds with Al_2O_3, SiO_2 and silicate. At the same time, MgO can make compound negative ions disintegrate, then cause the viscosity of slags decrease. If the Al_2O_3 content increases continuously, the effect of MgO will be weaken, the desulfurization ability will be weaken gradually [11].

(3) Effect of SrO and MgO on sulphur partition ratio.

The following equation expresses the relation among SrO, MgO and sulphur partition ratio:

$$L_S = 52.26 - 304.78x_1 + 364.80x_4 - 1420x_1x_4 + 3488.89x_1^2 \quad (15)$$

The contours of MgO, SrO and sulphur partition ratio are shown in **figure 5**. The sulphur partition ratio increases with the increment of MgO and SrO. The effect of SrO is stronger than that of MgO, because SrO has a higher ability of providing O^{2-}. When the other three components, code values are fixed as zero level, the relation of SrO with sulphur partition ratio can be expressed as:

$$L_S = 50.17 + 265.40x_4 \quad (16)$$

Equation (16) indicates that the relationship between SrO and L_S is linear. But the suitable content of SrO in slags should be less than 10%, because the molecular mass of SrO (104) is much more than that of CaO (55). When the addition amount of SrO is excessive, the composition of molten slags would be non-uniform, and the melting processing would be non-homogeneous. At the same time, the lattice energy of SrO is smaller than CaO, it is easier to compose high melting temperature compounds, which would worsen the physical properties of slags.

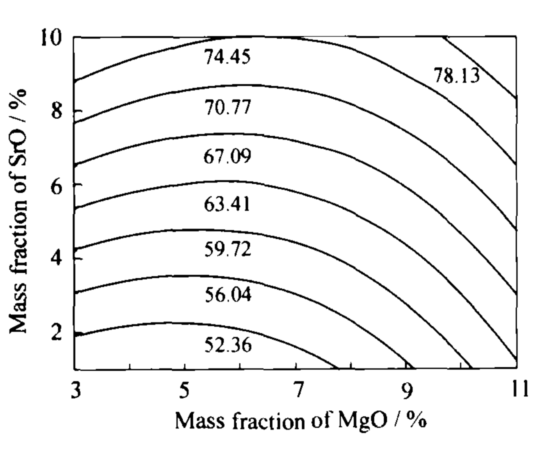

Figure 5 Contours of MgO, SrO and sulphur partition ratio.

5 Conclusions

(1) The established mathematical model could be used to describe the sulphur partition ratio of an Al_2O_3-CaO-SrO pre-molten refining slag.

(2) The sulphur capacity and sulphur partition ratio decrease with the increment of Al_2O_3/CaO.

(3) The increasing of SrO and MgO content in slags could increase the sulphur partition ratio of slags. Comprehensivly considering every factor, the SrO content in slags should be less than 10%, and 8% is suitable.

(4) The effect of CaF_2 on sulphur partition ratio is not obvious, so the addition should be limited for environmental purpose.

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