Improving the Desulfurization in COREX-3000 Process by the Optimization of Chemical Compositions of Slag

Shengli WU, Laixin WANG,* Yanan LU and Kai GU

School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, 30 Xueyuan Road, Haidian District, Beijing, 100083 P. R. China.

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To improve the desulfurization in the COREX-3000 process, several aspects are studied and practiced. The work documented in the present paper focuses on the effects of chemical compositions of slag, such as CaO/SiO₂, MgO, MgO/Al₂O₃ and MnO, on desulfurization. Theoretical calculations of sulfide capacity and viscosity of slag and diffusion coefficient of S²⁻ in the slag are given to study the effects of slag chemical compositions on the thermodynamics and dynamics of desulfurization. After that, experiments are carried out to verify the theoretical analyses and give the appropriate ranges of these four parameters. The suggested suitable ranges of CaO/SiO₂, MgO content, MgO/Al₂O₃ and MnO content for COREX-3000 are 1.20–1.30, 10 wt%–12 wt%, 0.80–0.90 and 0.4 wt%–0.7 wt%, respectively.

KEY WORDS: sulfide capacity; sulfur distribution ratio; viscosity; diffusion coefficient; polymerization degree; desulfurization efficiency.

1. Introduction

Extensive efforts have been undertaken due to environmental pressures and the increasing scarcity of good quality coking coal to develop alternative processes for iron-making to the conventional blast furnace route. So far, COREX, a smelting reduction process, has emerged as one of the most promising alternatives. It is the first commercially established and industrially proven smelting reduction process based mainly on non-coking coal, which capable of meeting the economical and environmental requirements.^{1–3)} However, the COREX-3000, designed productivity of which is 1.5 million tons per year, still has some disadvantages. For example, the sulfur content of COREX hot metal (HM) is higher on average and has more severe fluctuations than that of the blast furnace (BF). The detailed description of the problem in COREX hot metal and transfer process of sulfur were listed in the authors' previous paper.⁴⁾

Sulphur is a problematic impurity in the steelmaking industry that contributes to the embrittlement of steel on account of the formation of continuous intergranular liquid films in the solidified steel. This promotes intergranular weakness and solidification cracking of the metal.⁵⁾ Accordingly, the desulfurization of hot metal is a vital part of the steelmaking process since sulfur in many steel products is detrimental. In general, desulfurization of hot metal is more economical than desulfurization of steel, and about 90 pct of the hot metal produced in blast furnace is desulfurized before it is sent to be processed in a steelmaking furnace.⁶⁾

So far, many research works in desulfurization have been carried out in the context of BF slags and ladle slags.^{7–10)} However, it should be stressed that the composition of slag in COREX process was different from those of BF and ladle slags. So it's worthwhile to study the desulfurization in COREX process and method of adjusting chemical compositions of hot metal has been expounded in the former paper.¹¹⁾

In this paper, theoretical analysis has been carried out firstly to study the influence of chemical compositions of COREX slag, such as binary basicity, MgO and MnO, on the sulfide capacity and viscosity. After that, experiments were carried out to verify the influence of chemical compositions of slag on the desulfurization efficiency and give the suitable compositions of slag for COREX-3000.

2. Theoretical Background

2.1. Calculation of C_S and L_S

The concept of sulfide capacity (C_S) is clearly of great importance in relation to the desulfurization of pyrometallurgical process, which is the main parameter in the following theoretical analysis. The sulfide capacity is a property of the slag, which is dependent only on the temperature and the slag composition. It describes the potential ability of an arbitrary homogeneous molten slag to remove sulfur, and it could be used to compare the desulfurization characteristics of different slags.¹²⁾ The sulfide capacity was defined by Fincham and Richardson, which is shown in Eq. (3).¹³⁾

$$C_S = (pct S) \left(\frac{p_{O_2}}{p_{S_2}} \right)^{1/2} \dots\dots\dots (1)$$

* Corresponding author: E-mail: wanglaixinustb@163.com
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where p_{O_2} and p_{S_2} are the partial pressures of $O_2(g)$ and $S_2(g)$, respectively. (pct S) is the sulfur content of slag in wt pct.

Effect of oxides on the sulfide capacity are determined not only the concentration of free oxygen that is bond with metal cation M only but also the stability of the formed sulfide MS. High concentration of free oxygen and higher stability of the sulfides can increase the sulfide capacity. For example, the order of free oxygen concentration in binary MO–SiO₂ slags with the same contents of SiO₂ is FeO–SiO₂>MnO–SiO₂>MgO–SiO₂>CaO–SiO₂, while order of the sulfide stability is CaS>MnS>FeS>MgS. Both factors contribute to the order of sulfide capacity for binary MO–SiO₂ systems with same content of MO at the same temperature follows the order MnO–SiO₂>FeO–SiO₂>CaO–SiO₂>MgO–SiO₂.^{14,15)} Therefore, Zhang's model (Eq. (2)) was adopted to calculate the sulfide capacity in this article as it is easier for calculation and has wider scope of application and higher accuracy.

$$\log C_S = -6.08 + 4.49 / \Lambda + (15\,893 - 15\,864 / \Lambda) / T \quad \dots (2)$$

where Λ is the optical basicity, which is calculated by Eq. (3),¹⁶⁾ and T is the temperature, K.

$$\Lambda = \frac{\sum N_i X_i \Lambda_i}{\sum N_i X_i} \quad \dots (3)$$

where N_i is the number of oxygen in component i ; X_i is the mole fraction of component i ; Λ_i is the optical basicity of component i (Listed in **Table 1**), respectively.

Relationship between sulfur distribution ratio (L_S) with C_S has been deduced and expounded in the former paper¹¹⁾ and it is shown as Eq. (4).

$$\lg L_S = \lg C_S + \lg(f_S f_C [\text{pct C}]) + \frac{100.366}{T} + 2.895 \quad \dots (4)$$

Where f_S and f_C are activity coefficients of respective sulfur and carbon in hot metal relative to the 1 wt pct standard state, [pct C] is the carbon content in hot metal.

The activity coefficient is calculated using Wagner's equation:¹⁶⁾

$$\log f_j = \sum (e_j^i [\%i]) \quad \dots (5)$$

where f_j is the activity coefficient for element j in the hot iron, i represents the dissolved elements in the hot iron, and e_j^i is the interaction parameter for element j . The interaction parameters in the present case were taken from a publication

Table 1. Optical basicity of different oxides.¹⁴⁾

Oxides	CaO	MgO	Al ₂ O ₃	SiO ₂	FeO	MnO
Optical basicity	1	0.78	0.61	0.48	1.24	1.43

Table 2. Interaction parameters among different elements in hot metal.¹⁹⁾

i	j			
	Si	Mn	C	S
S	0.063	−0.026	0.110	−0.028
C	0.080	−0.012	0.140	0.046

by Liang and Che¹⁷⁾ and listed in **Table 2**.

2.2. Calculation of Viscosity and Diffusion Coefficient of Sulfur in the Slag

The rate-controlling step of desulfurization reaction between hot metal and slag is the diffusion process of sulfur in the slag, which has been analyzed in the former paper.¹¹⁾ The diffusion coefficient of sulfur in the slag can be calculated as shown in Eq. (6).

$$D = \frac{RT}{N_0} \cdot \frac{1}{6\pi r \cdot \eta} \quad \dots (6)$$

where D is the diffusion coefficient of sulfur in the slag, R is the molar gas constant, N_0 is the Avogadro constant, r is the radius of S^{2-} , η is the viscosity of slag, and T is the temperature, K.

In the present paper, adjustments of chemical compositions of COREX slag would have an effect on the viscosity of slag and so influence the diffusion coefficient of sulfur in the slag. The influence of chemical composition of COREX slag on the kinetic conditions of desulfurization reaction will be discussed in Part 3.

The viscosity of silicate slag plays significant roles in ironmaking and steelmaking processes, which are not only closely related to the practical operation but also are intimately associated with the diffusion controlled kinetics. Therefore, considerable attentions should be paid on viscosity of slag for its great importance in understanding the desulfurization reaction kinetics in COREX process.

The rheological properties of liquid suspensions have been studied since many years ago, by Einstein (Eq. (7)).¹⁸⁾ Many years later, Brinkman modified and generalized the Einstein formula to determine the effective viscosity of the slag, Eq. (8).^{19–21)}

$$\eta = \eta_0 (1 + 2.5\varphi) \quad \dots (7)$$

$$\eta = \eta_0 (1 - \varphi)^{-2.5} \quad \dots (8)$$

where η and η_0 are the viscosity of the solid-containing and the solid-free slag, respectively; φ is the volume fraction of solid particles in the slag. In this paper, η_0 and φ of different slags were calculated by FactSage 6.4 and the viscosity of slag will be calculated by Eq. (8) based on the results of FactSage.

3. Theoretical Calculations and Analyses

3.1. Theoretical Calculations of C_S and L_S (Thermodynamics)

It's necessary to have a theoretical cognition of the effects of slag chemical compositions on desulfurization in thermodynamics and dynamics. Firstly, theoretical calculations of thermodynamics are discussed based on Eqs. (2) and (4).

3.1.1. Effect of Binary Basicity (R_2)

The calculated C_S and L_S at 1 773 K (1 500°C) are plotted against binary basicity and shown in **Fig. 1**. In Fig. 1, the temperature, compositions of hot metal and all the other oxides contents are maintained, while only the CaO/SiO₂ in the slag is allowed to vary. As seen in the figure, C_S and L_S increase with increase of R_2 . In the slag, at lower oxygen

Fig. 1. Theoretical C_S and L_S as function of R_2 in the slag at 1773 K (1500°C).

Fig. 2. Theoretical C_S and L_S as function of MgO content in the slag at 1773 K (1500°C).

partial pressures, sulfur will dissolve by replacing free oxygen ions. So the trend in the figure can thus be explained by the increase of free oxygen ions when the slag becomes more basic. At the lower basicity, the CaO content in the slag is less, so that only a few free oxygen ions exist and this results in low C_S and low L_S of slags. As R_2 increases, the SiO_2 networks are broken into smaller anion groups and the proportion of free oxygen ions starts to increase. Therefore, the C_S and L_S of slags increase.

3.1.2. Effect of MgO

Figure 2, in which the variations of MgO content are realized by adjusting CaO and SiO_2 contents while R_2 is constant, shows the effects of MgO content in slag on the theoretical C_S and L_S of slags at 1773 K (1500°C). It can also be seen that MgO increases C_S and L_S because it is also basic oxide like CaO and increases the available free oxygen ions. In addition, the effect of MgO on C_S is somewhat less profound compared to CaO when replacing SiO_2 because of calcium's much higher affinity to sulfur.⁷⁾ As a result, C_S of the slag increases from 2.49×10^{-4} to 3.17×10^{-4} when the MgO content in the slag increases from 5% to 18%. However, C_S increases from 1.65×10^{-4} to 3.73×10^{-4} when the CaO content in the slag increases from 38.03% to 45.63% in Fig. 1. And that is, effect of MgO on C_S is much weaker than that of R_2 .

3.1.3. Effect of $\text{MgO}/\text{Al}_2\text{O}_3$

Figure 3 illustrates the effects of $\text{MgO}/\text{Al}_2\text{O}_3$ in slags on C_S and L_S of the slags. The increase of $\text{MgO}/\text{Al}_2\text{O}_3$ is achieved by the simultaneous increase of MgO and Al_2O_3 mass percent. MgO content increases from 2.4% to 19.95% and Al_2O_3 content increases from 6% to 19%. MgO is known as basic oxide and hence increase the C_S and L_S of the slag, which has been displayed in Fig. 2. According to the ionic potential (Z/r^2) and structural behavior of Al_2O_3 , it behaves as an amphoteric oxide in the ternary CaO– SiO_2 – Al_2O_3 melts, as identified by Banya.²²⁾ However, considering the CaO/ SiO_2 ratio in the present slags, Al^{3+} is typically in a tetrahedral configuration with oxygen. In this case, part of free oxygen ions will be consumed by added Al_2O_3 . It can be seen in Fig. 3 that the C_S and L_S of slag decrease firstly and then increase with the increase of $\text{MgO}/\text{Al}_2\text{O}_3$ in the slag.

Fig. 3. Theoretical C_S and L_S as function of $\text{MgO}/\text{Al}_2\text{O}_3$ ratio in the slag at 1773 K (1500°C).

The quaternary basicity ($R_4 = (\text{CaO} + \text{MgO})/(\text{SiO}_2 + \text{Al}_2\text{O}_3)$) is used to explain this phenomenon and it almost has the same variation with C_S and L_S of slag. C_S and L_S keep almost constant during interval of $\text{MgO}/\text{Al}_2\text{O}_3$ in 0.5–0.7. In the low $\text{MgO}/\text{Al}_2\text{O}_3$ range, negative effect of Al_2O_3 on desulfurization, especially free oxygen ions, is stronger than positive effect of MgO. Then positive effect of MgO on desulfurization becomes stronger gradually and lowers the negative effect of Al_2O_3 in the high $\text{MgO}/\text{Al}_2\text{O}_3$ range. So, MgO in slag helps to reduce the bad role of Al_2O_3 in desulfurization when the binary basicity of slag is constant.

3.1.4. Effect of MnO

Effect of MnO content on C_S and L_S is shown in **Fig. 4**. It shows that C_S and L_S increase with the increases of MnO content as MnO is a basic oxide, which provides free oxygen ions and Mn^{2+} itself combines with S^{2-} . After comparing calculated results of MgO, CaO and MnO on C_S , effects of CaO and MnO are almost the same but much more profound than MgO. The sulfide capacity increases by increasing the MnO/CaO ratio at a fixed silica content which is greater than about 30 wt%, whereas it decreases by increasing the MnO/CaO ratio at silica content lower than about 30 wt%.^{23,24)} The critical SiO_2 content is about 30 wt% based on the competitive dissolution mechanism of

Fig. 4. Theoretical C_s and L_s as function of MnO content in the slag at 1 773 K (1 500°C).

sulfur in Ca–Mn–silicate melts. The used SiO_2 content in the calculation is 33 wt% and so the effects of MnO and CaO are similar in the present slag system.

3.2. Theoretical Calculations of Viscosity and Diffusion Coefficient (Dynamics)

Viscosity of slags is the most important parameter in the desulfurization dynamics, which determines the extent of desulfurization reactions. Variation of chemical compositions of slag has a great effect on the viscosity besides the sulfide capacity discussed previously. Slag-forming cations, such as Si, Ca, Mg, and Al, are all linked with oxygen by different bondings. There are three kinds of oxygen existing in the molten slag: the bridging oxygen (O^0) connecting elements with two oxygen bonds, non-bridging oxygen (O^-) connecting elements with one oxygen bond, and free oxygen (O^{2-}) without oxygen bond. Usually, Si–O tetrahedral is combined by the bridging oxygen. When the basic oxides such as CaO or MgO are added into the silicate melt, reticular complex compounds will be fractured by the non-bridging oxygen ion and the free oxygen, and viscosity will be decreased.^{25,26)} Effects of variation of chemical compositions on viscosity of slag at 1 773 K (1 500°C) are given below. Results are calculated by Factsage 6.4 based on Eq. (8). Diffusion coefficients are calculated according to Eq. (6).

3.2.1. Effect of Binary Basicity (R_2)

Relationship between binary basicity CaO/SiO_2 and the viscosity and diffusion coefficient in slag is shown in Fig. 5. It can be seen that the viscosity of slag decreases with the increase of R_2 but weakens gradually. As we all know, CaO/SiO_2 has a significant effect on the viscosity of slag, because the availability of free oxygen ions increases due to the CaO dissociation for a higher basicity. In the molten slag, the free oxygen ions can react with the bridged oxygen in the viscous units network structures to form the non-bridging oxygen. The polymerization degree of complex viscous units in the slag can be reduced and the complex viscous units are broken down into the smaller units. Therefore, the viscosity decreases, and the fluidity of slags is improved.²⁷⁾ However, more addition of CaO exerts a limited effect when depolymerisation of the slag complex

Fig. 5. Calculated viscosities and diffusion coefficient in slag based on different R_2 at 1 773 K (1 500°C).

network structures has already occurred markedly because the viscosity is fairly low.^{25,28)} Diffusion coefficients, which represents the dynamics of desulfurization reaction, have opposite changes with viscosity, and so it will not be repeated here and after.

3.2.2. Effect of MgO

Variations of viscosity and diffusion coefficient with MgO content in the slag are shown in Fig. 6, Al_2O_3 , MnO, FeO contents and CaO/SiO_2 are constant. It can be seen that the viscosity decreases with increases of MgO content when the MgO content less than 14 wt%. This is because that MgO is also a basic oxide and can provides free oxygen ions to break the complex network structure into simple polymer units, such as monomers and dimmers. Furthermore, the polarizing power of Mg^{2+} is stronger than that of Ca^{2+} and Mg^{2+} exhibits a stronger electrostatic interaction with oxygen ions.²⁹⁾ Therefore, the ability of MgO to offer free oxygen (FO) ions is considered to be relatively weaker than that of CaO and so the network breaking ability of MgO is not as high as that of CaO.³⁰⁾ Consequently, the ability of decreasing degree of polymerization and viscosity of MgO is weaker than that of CaO.

Besides, results show that the viscosity of slag increases with increase of MgO when the MgO content greater than 14 wt% (Inflection point in the present slag system). This may be caused by the sharply increased liquidus temperature, which is also shown in Fig. 6, and so viscosity of present slag at 1 773 K is increased by the increasing solid phase fraction after the inflection point.³¹⁾

3.2.3. Effect of $\text{MgO}/\text{Al}_2\text{O}_3$

Calculation results about the effect of $\text{MgO}/\text{Al}_2\text{O}_3$ on the viscosity and diffusion coefficient in slag are shown in Fig. 7. MgO content, Al_2O_3 content and $\text{MgO}/\text{Al}_2\text{O}_3$ are all increase, other compositions are constant. Results show that viscosity of slag decreases with the increase of $\text{MgO}/\text{Al}_2\text{O}_3$ in slag and then effect diminishes gradually and followed by increases with the increasing $\text{MgO}/\text{Al}_2\text{O}_3$. This can be explained by two aspects, i.e., effect of MgO and effect of Al_2O_3 . The effect of MgO content in slag on viscosity has been discussed in detail in the former section.

Effect of Al_2O_3 content on the viscosity of slag is attrib-

Fig. 6. Calculated viscosities, liquidus temperature of slag and diffusion coefficient based on different MgO contents at 1 773 K (1 500°C).

Fig. 8. Calculated viscosities and diffusion coefficient in slag based on varying MnO contents at 1 773 K (1 500°C).

Fig. 7. Calculated viscosities and diffusion coefficient in slag based on varying MgO/Al₂O₃ ratio at 1 773 K (1 500°C).

uted to the amphoteric behavior of Al₂O₃ in the aluminosilicate melts.³²⁾ It is either a basic oxide for a network modifier or an acidic oxide for a network former depending on the slag compositions. When Al₂O₃ behaves as a network former, it can absorb the free oxygen ions to form the complex viscous units [AlO₄]⁵⁻ network, and Al³⁺ substitutes for Si⁴⁺ in [Si_xO_y]²⁻ complex viscous units to form the Si–Al–O composite anionic group network.³³⁾ As a result, the polymerization degree of viscous units in the slags increases, and the slag structure becomes more complicated, leading to the increase in viscosity. However, the Al³⁺ ions would form the [AlO₆]-octahedra for the network modifying role.^{27,34)}

Both effects of MgO and Al₂O₃ on viscosity result in the relationship between MgO/Al₂O₃ in slag and viscosity of slag. It can be concluded that the MgO/Al₂O₃ of the slag can not to be too high or too low, and the proper range of the MgO/Al₂O₃ can obviously decrease the viscosity and improve the fluidity of the slag.

3.2.4. Effect of MnO

Effects of MnO content on the viscosity and diffusion coefficient in slag are shown in Fig. 8, in which, CaO/SiO₂, MgO, Al₂O₃ and FeO contents are constant. Results show that the viscosity of slag decreases with the increase of MnO content. The viscosity just decreases from 0.204 Pa·s

to 0.198 Pa·s because of the small change of MnO content. As the role of CaO and MgO, MnO is also a basic oxide and provides free oxygen to break the complex structure of slag. And so increase of MnO content helps to decrease the viscosity and improve the fluidity of slag.

4. Experimental Results and Discussions

All the theoretical calculations are only shown to indicate the qualitative effects of these compositions. And effects on thermodynamics and dynamics are discussed respectively. Therefore, desulfurization experiments are obviously needed to confirm the suitable chemical compositions of slag considering both thermodynamics and dynamics of desulfurization reaction.

Desulfurization efficiency (η_s), which is calculated as Eq. (9), is defined to evaluate the desulfurization experimental results of interaction between slag and iron.

$$\eta_s = \frac{[\text{pct } S]_0 - [\text{pct } S]_1}{[\text{pct } S]_0} \dots\dots\dots (9)$$

where [pct S]₀ and [pct S]₁ are the initial and the final sulfur contents in iron sample, respectively. Time for all the desulfurization experiments in this paper is 60 minutes and the reason has been explained in the former paper.¹¹⁾

Detailed experimental methods have been illustrated in authors' former paper.¹¹⁾ Experimental parameters and base slag compositions are decided based on actual production of COREX-3000 in Bayi Steel of China. All experiments are carried out according to the chemical compositions of slag in Table 3. Experimental results are discussed as follows.

4.1. Experimental Effect of CaO/SiO₂ on Desulfurization Efficiency

Figure 9 shows that desulfurization efficiency (η_s) and sulfur distribution ratio (L_s) increase with the increase of CaO/SiO₂ at 1 773 K (1 500°C). This is the combined effects of CaO/SiO₂ on sulfide capacity and fluidity of slag, which has been discussed detailedly in Part 3. It can be seen that the η_s and L_s increase slowly when the CaO/SiO₂ exceeds 1.3, which may results from the subdued improvement of CaO/SiO₂ on the fluidity of slag. According to Fig.

Table 3. Chemical compositions of all slags (mass percent).

Compositions	CaO	MgO	SiO ₂	Al ₂ O ₃	FeO	MnO	R ₂	MgO/Al ₂ O ₃
Base Slag	42.72	9.83	33.33	13.02	0.98	0.12	1.28	0.75
	38.95	9.83	37.10	13.02	0.98	0.12	1.05	0.75
R ₂	40.68	9.83	35.37	13.02	0.98	0.12	1.15	0.75
	43.69	9.83	32.36	13.02	0.98	0.12	1.35	0.75
	45.01	9.83	31.04	13.02	0.98	0.12	1.45	0.75
	44.84	6.00	35.04	13.02	0.98	0.12	1.28	0.46
MgO	43.72	8.00	34.16	13.02	0.98	0.12	1.28	0.61
	41.48	12.00	32.40	13.02	0.98	0.12	1.28	0.92
	40.35	14.00	31.53	13.02	0.98	0.12	1.28	1.08
MgO/Al ₂ O ₃	47.69	4.95	37.26	9.00	0.98	0.12	1.28	0.55
	45.33	7.15	35.42	11.00	0.98	0.12	1.28	0.65
	39.94	12.75	31.21	15.00	0.98	0.12	1.28	0.85
	36.91	16.15	28.84	17.00	0.98	0.12	1.28	0.95
MnO	42.59	9.83	33.28	13.02	0.98	0.30	1.28	0.75
	42.48	9.83	33.19	13.02	0.98	0.50	1.28	0.75
	42.37	9.83	33.10	13.02	0.98	0.70	1.28	0.75
	42.26	9.83	33.01	13.02	0.98	0.90	1.28	0.75

Fig. 9. Experimental results on the relationship between η_s , L_S and R_2 in the slag at 1 773 K (1 500°C).

9, it is suggested that the CaO/SiO₂ of slag in Bayi Steel should be controlled in the range of 1.20–1.30.

4.2. Experimental Effect of MgO content on Desulfurization Efficiency

Figure 10 illustrates the variation of the η_s and L_S with the MgO content in the slag sample at 1 773 K (1 500°C). It can be seen that the η_s and L_S increase gently with the increase of MgO content of slag. On the one hand, MgO is a basic oxide and it has favorable effects on sulfide capacity and fluidity of slag, and so improves the desulfurization efficiency of slag. On the other hand, MgO has weaker effects on desulfurization, compared with that of CaO, because of its weaker ability of offering free oxygen ions. Furthermore, effect of MgO should be associated with that of Al₂O₃. Based on these, the MgO content of slag in Bayi Steel should be controlled in the range of 10 wt% to 12 wt%.

Fig. 10. Experimental results on the relationship between η_s , L_S and MgO content in the slag at 1 773 K (1 500°C).

Fig. 11. Experimental results on the relationship between η_s , L_S and MgO/Al₂O₃ in the slag at 1 773 K (1 500°C).

4.3. Experimental Effect of MgO/Al₂O₃ on Desulfurization Efficiency

Experimental results about the effect of MgO/Al₂O₃ ratio on desulfurization efficiency and sulfur distribution ratio are shown in Fig. 11. Both the effects of MgO/Al₂O₃ on sulfide capacity and viscosity have opposite tendency before and after the inflection points. Considering these two aspects and experimental results show that inflection point is still exists in the η_s and L_S –MgO/Al₂O₃ curves, and the inflection point appears when the MgO/Al₂O₃ equals to 0.85. In addition, the desulfurization efficiency and sulfur distribution ratio increase gently when the MgO/Al₂O₃ increases from 0.55 to 0.75, and it may be caused by the little change in sulfide capacity, which is shown in Fig. 3. η_s and L_S increase sharply when the MgO/Al₂O₃ increase from 0.75 to 0.85 because of the increased sulfide capacity and decreased viscosity. And then η_s and L_S decrease when the MgO/Al₂O₃ exceeds 0.85 on account of the sharply increased viscosity, which is shown in Fig. 7. Consequently, the applicable MgO/Al₂O₃ for the present slag system ranges from 0.80 to 0.90.

4.4. Experimental Effect of MnO on Desulfurization Efficiency

Figure 12 shows the experimental results about the effect

Fig. 12. Experimental results on the relationship between η_s , L_s and MnO content in the slag at 1 773 K (1 500°C).

of MnO content on desulfurization efficiency. It can be seen that η_s and L_s increase sharply with the increase of MnO content in the slag. It seems that the experimental results of the effect of MnO content are more prominent than the theoretical calculation results. This may be explained by the coupled reactions among $(\text{MnO})-(\text{SiO}_2)-[\text{Mn}]-[\text{Si}]$, coupled reactions promote the desulfurization reaction between slag and hot metal.¹¹⁾ Based on these, the appropriate MnO content of slag may be controlled in the range of 0.4 wt% to 0.7 wt%.

5. Conclusions

Theoretical calculations of sulfide capacity and viscosity of different slag are carried out to study the effects of chemical compositions on desulfurization. And then experiments are conducted to determine the optimal chemical composition ranges of slag in the COREX-3000 process. The following conclusions are drawn:

(1) The theoretical calculation results of sulfide capacity show that the increase of CaO/SiO_2 , MgO content and MnO content are all benefit for the improvement of sulfide capacity of slag. And for the relationship between $\text{MgO}/\text{Al}_2\text{O}_3$ and C_s , inflection point is exist and effects are opposite before and after the inflection point.

(2) The theoretical calculation results of viscosity show that the viscosity decreases with the increase of CaO/SiO_2 and MnO content in the slag. But for MgO content and $\text{MgO}/\text{Al}_2\text{O}_3$ in the slag, inflection points are both exist and viscosity decreases with the increase of MgO content and $\text{MgO}/\text{Al}_2\text{O}_3$ before the inflection points and then increase.

(3) Experimental results, which combine both sulfide capacity and viscosity of slag, verify the effects of slag compositions in theoretical calculations and suggested

ranges for each parameter are given for the production in the COREX-3000 process.

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