Estimation of Sulfide Capacities of Multicomponent Slags using Optical Basicity

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An empirical model has been developed based on optical basicity to calculate the sulfide capacity of metallurgical molten slag. The model estimated sulfide capacities agree well with the experimental data for CaO–MgO–FeO–MnO–TiO₂–Al₂O₃–SiO₂–CaF₂ multicomponent slags. It is found that the abilities of increasing sulfide capacity in MO–SiO₂ (M=Ca, Mg, Fe and Mn) melts follow the order: MnO>FeO>CaO>MgO. Also, substitution of CaO for CaF₂ decreases the sulfide capacity and substitution of TiO₂ for SiO₂ increases the sulfide capacity.

KEY WORDS: sulfide capacity; optical basicity; free oxygen; slag.

1. Introduction

Metallurgical slag plays a significant role in removing the sulfur (undesirable element) in the metal during pyrometallurgical processes. The dissolution behavior of sulfur in molten slag was first quantitatively defined by Fincham and Richardson¹⁾ as “sulfide capacity”. In order to accurately control the sulfur content in metal, knowledge of sulfide capacity of slag is required. To date, numerous experimental^{1–44)} and theoretical studies^{45–49)} have been carried out. Theoretical models can make up for the shortage of available experimental data and extend our ability for prediction. Thermodynamic models were proposed by Reddy and Blander,⁴⁵⁾ Moretti and Ottonello,⁴⁶⁾ Kang and Pelton.⁴⁷⁾ These models calculate the sulfide capacity solely from the knowledge of thermodynamic activity calculated by different slag polymer models. The precisions of sulfide capacities are determined by the precisions of activity calculations. However, these models are inconvenient to be used for their complexity and/or commercial use. Furthermore, these models cannot calculate the sulfide capacity of slags containing CaF₂. KTH model³⁶⁾ considers all the complex polymeric ions as dissociated simple species. Good agreement is obtained when estimating the sulfide capacity of CaO–MgO–FeO–MnO–Al₂O₃–SiO₂ slag by the KTH model. However, too many parameters need to be optimized in this model.

The optical basicity, a measure of basicity or the capacity of the oxides to donate electrons was first proposed by Duffy and Ingram,⁵⁰⁾ and used to relate slag composition to viscosity,⁵¹⁾ electrical conductivity,⁵²⁾ activity⁵³⁾ and phosphide capacity of the slag.⁴⁸⁾ Sosinsky and Sommerville⁴⁸⁾ first proposed a simple sulfide capacity prediction model

using optical basicity. Young *et al.*⁴⁹⁾ found Sosinsky and Sommerville’s relationship is not sufficiently accurate particularly in the high basicity region. Thereby, a new sulfide capacity model was proposed.⁴⁹⁾ However, its accuracy is also very low. Therefore, in the present study, a new optical basicity model is proposed to improve the calculation accuracy of sulfide capacity.

2. Model

The dissolution behavior of sulfur in oxide slags is usually described by the following sulfur-oxygen exchange chemical reaction,¹⁾

$$C_s = (\text{wt pct S}) \left(\frac{P_{\text{O}_2}}{P_{\text{S}_2}} \right)^{\frac{1}{2}} \quad \dots\dots\dots (2)$$

$$K = \frac{a_{\text{S}^{2-}}}{a_{\text{O}^{2-}}} \left(\frac{P_{\text{O}_2}}{P_{\text{S}_2}} \right)^{\frac{1}{2}} = \frac{f_{\text{S}^{2-}}}{a_{\text{O}^{2-}}} \frac{\bar{M}}{100M_s} (\text{wt pct S}) \left(\frac{P_{\text{O}_2}}{P_{\text{S}_2}} \right)^{\frac{1}{2}} = \frac{f_{\text{S}^{2-}}}{a_{\text{O}^{2-}}} \frac{\bar{M}}{100M_s} C_s \quad \dots\dots\dots (3)$$

where P_{O_2} and P_{S_2} are the partial pressures of O₂ and S₂; $\bar{M}$ and M_s are the molar mass of slag and sulfur; $f_{\text{S}^{2-}}$ is the activity coefficient of sulfur ion; $a_{\text{O}^{2-}}$ is the activity of free oxygen ion; C_s is the sulfide capacity; (wt pct S) is the equilibrium sulfur content in the slag; K is the equilibrium constant for reaction (1), which can be calculated by the following equation.

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus = -RT \ln K \quad \dots\dots\dots (4)$$

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where $\Delta G^\ominus$, $\Delta H^\ominus$, and $\Delta S^\ominus$ are the changes for Gibbs free energy, enthalpy and entropy. According to Eqs. (3) and (4),

$$\text{Log}C_s = \frac{2.303\Delta H^\ominus}{-RT} + \frac{2.303\Delta S^\ominus}{R} + \text{Log}\frac{100M_s}{M} + \text{Log}\frac{a_{\text{O}^{2-}}}{f_{\text{S}^{2-}}} \dots\dots\dots (5)$$

If the sum of the second, the third and the fourth terms of the right hand side of Eq. (5) is temperature independent, the temperature dependence of sulfide capacity will obey the van't Hoff Eq. (6). Experimental data^{21,22,25,34,48)} also indi-

cated that the logarithm of sulfide capacity is the line function of the reciprocal of temperature. However, generally, activity and activity coefficient are correlated with temperature. So, the fourth term seems to be temperature dependent. The reason for this discrepancy may be that the temperature coefficients of $a_{\text{O}^{2-}}$ and $f_{\text{S}^{2-}}$ may be similar to each other which leads to the ratio of them temperature independent, or the logarithm of their ratio is the linear function of the reciprocal of temperature.

$$\text{Log}C_s = \frac{E}{T} + A \dots\dots\dots (6)$$

where the activation energy term E is related to the enthalpy change for reaction (1), while the pre-exponent factor term A is related to the entropy change for reaction (1) as well as activity of free oxygen ion and activity coefficient of sulfur ion. Both A and E should be composition dependent. Sosinsky and Sommerville model⁴⁸⁾ assumed that both E and A are linear functions of optical basicity, while Young *et al.*⁴⁹⁾ pointed out that the simple linear relationship was unreasonable. The strategy Young *et al.* adopted was to consider the quadratic term of optical basicity and include slag composition, as follows:

$$\begin{aligned} \Lambda < 0.8 : \text{Log}C_s = & -13.913 + 42.84\Lambda - 23.82\Lambda^2 \\ & -11710/T - 0.02223X_{\text{SiO}_2} - 0.02275X_{\text{Al}_2\text{O}_3} \\ \Lambda \geq 0.8 : \text{Log}C_s = & -0.6261 + 0.4808\Lambda + 0.7197\Lambda^2 \\ & + 1697/T - 2587\Lambda/T + 0.0005144X_{\text{FeO}} \dots\dots\dots (7) \end{aligned}$$

where C_s is sulfide capacity; T is temperature, K; X is mole fraction; Λ is optical basicity which is calculated as:

$$\Lambda = \frac{\sum N_i X_i \Lambda_i}{\sum N_i X_i} \dots\dots\dots (8)$$

where N_i is the number of oxygen in component i ; Λ_i is the optical basicity of component i , respectively. The available sulfide capacity data for the molten slag system CaO–MgO–FeO–MnO–TiO₂–Al₂O₃–SiO₂–CaF₂ is referenced in **Table 1**. Comparisons of about 1 600 groups of calculated sulfide capacities by Young *et al.* model with the measured values are shown in **Fig. 1**, from which it can be seen that Young

Table 1. References for Sulfide Capacity Data.

	Systems	References
Group I	CaO–SiO ₂	[1],[2],[3],[4],[5],[6]
	MgO–SiO ₂	[1],[7],[8]
	CaO–Al ₂ O ₃	[1],[9],[10],[11],[12],[13]
	CaO–MgO–SiO ₂	[7],[14]
	CaO–Al ₂ O ₃ –SiO ₂	[1],[4],[10],[13],[14],[15], [16],[17],[18]
	MgO–Al ₂ O ₃ –SiO ₂	[8],[19]
	CaO–MgO–Al ₂ O ₃	[17],[19]
	CaO–MgO–Al ₂ O ₃ –SiO ₂	[20],[14],[16],[21],[22],[23], [24],[25],[26],[27],[28]
Group II	MnO–SiO ₂	[2],[5],[6],[8]
	MnO–Al ₂ O ₃	[8]
	CaO–MnO–SiO ₂	[2],[5],[6],[29]
	MgO–MnO–SiO ₂	[8],[30]
	MnO–Al ₂ O ₃ –SiO ₂	[8],[19]
	CaO–MgO–MnO–SiO ₂	[30]
	CaO–MgO–MnO–Al ₂ O ₃	[24]
	CaO–MnO–Al ₂ O ₃ –SiO ₂	[24],[25]
Group III	CaO–MgO–MnO–Al ₂ O ₃ –SiO ₂	[24],[25],[31]
	FeO	[32],[33]
	FeO–SiO ₂	[1],[34]
	CaO–FeO–SiO ₂	[35],[36]
	MgO–FeO–SiO ₂	[36]
	FeO–MnO–SiO ₂	[36]
	CaO–MgO–FeO–Al ₂ O ₃ –SiO ₂	[23],[27],[37]
	CaO–MgO–FeO–MnO–Al ₂ O ₃ –SiO ₂	[36]
Group IV	FeO–TiO ₂	[32]
	MnO–TiO ₂	[38]
	CaO–MgO–TiO ₂	[39]
	CaO–FeO–TiO ₂	[40]
	CaO–SiO ₂ –TiO ₂	[39]
	FeO–SiO ₂ –TiO ₂	[40]
	CaO–MgO–SiO ₂ –TiO ₂	[39]
	CaO–FeO–SiO ₂ –TiO ₂	[40]
Group V	CaO–Al ₂ O ₃ –SiO ₂ –TiO ₂	[39]
	CaO–MgO–Al ₂ O ₃ –SiO ₂ –TiO ₂	[21],[26],[27]
	CaO–MgO–FeO–Al ₂ O ₃ –SiO ₂ –TiO ₂	[27]
	CaO–SiO ₂ –CaF ₂	[41],[42],[43],[44]
	CaO–Al ₂ O ₃ –CaF ₂	[16],[43]
	CaO–MgO–SiO ₂ –CaF ₂	[42]
	CaO–MnO–SiO ₂ –CaF ₂	[42]
	CaO–Al ₂ O ₃ –SiO ₂ –CaF ₂	[16],[42]

Fig. 1. Comparisons between calculated and measured sulfide capacity values for CaO–MgO–FeO–MnO–TiO₂–Al₂O₃–SiO₂–CaF₂ slag.

Table 2. Optical Basicity of Different Components.

CaO	MgO	Al ₂ O ₃	SiO ₂	FeO*	MnO*	TiO ₂ *	CaF ₂ *
1.00	0.78	0.61	0.48	1.24	1.43	0.61	0.88

* Optical basicity is optimized from the sulfide capacity.

et al. model could not give a good accurate estimation.

The strict theoretical relations between composition and terms E and A in Eq. (6) are hard to deduced. Therefore, an empirical treatment will be adopted to represent the experimental data of sulfide capacity. In order to express the non-linear relation between the logarithm of sulfide capacity and optical basicity, the present model assumes that the activation energy term E is the linear function of the reciprocal of optical basicity (the estimation results show that this treatment works well). Mills *et al.*⁵¹⁾ also used the reciprocal of optical basicity to describe the activation energy of viscosity. The temperature compensation effect⁵⁴⁾ is also considered, which is widely used to relate activation energy with pre-exponent factor (using a linear relationship) in the van't Hoff or Arrhenius type equation. Therefore, in the present model, both E and A in Eq. (6) will be the linear functions of the reciprocal of optical basicity.

$$\text{Log}C_s = m_0 + m_1/\Lambda + (n_0 + n_1/\Lambda)/T \dots\dots\dots (9)$$

where m and n are parameters. When calculating the optical basicity in Eq. (9) using Eq. (8), the optical basicity of CaO, MgO, Al₂O₃, SiO₂ is taken from the work of Duffy and Ingram⁵⁰⁾ (shown in Table 2), while the optical basicity of transition metal oxide are optimized from the sulfide capacity data because these oxides are opaque to UV light which prevents the direct measurement of optical basicity.⁴⁹⁾ Therefore, there are totally eight parameters need to be optimized: m_0 , m_1 , n_0 and n_1 and the optical basicity values of FeO, MnO, TiO₂ and CaF₂. The first step during the optimization is to regress the values of m_0 , m_1 , n_0 and n_1 by using the experimental sulfide capacities of CaO–MgO–Al₂O₃–SiO₂ system. Therefore, Eq. (9) becomes

$$\text{Log}C_s = -6.08 + 4.49/\Lambda + (15\,893 - 15\,864/\Lambda)/T \dots\dots\dots (10)$$

After obtaining values of m and n , the apparent optical basicity values of transition metal oxides MnO, FeO and TiO₂ are optimized in turn with the measured sulfide capacity data of Groups II, III and IV shown in Table 1, respectively. Apparent optical basicity of CaF₂ is determined by fitting the experimental data of Group V in Table 1. It should be pointed out that when calculating optical basicity of slag containing CaF₂ by Eq. (8), N_i for CaF₂ is 1 since two fluorine ions can be considered equivalent to one oxygen ion. Table 2 shows the optical basicity of different components, and by using them the sulfide capacity of CaO–MgO–FeO–MnO–TiO₂–Al₂O₃–SiO₂–CaF₂ system can be calculated according to Eq. (10).

3. Comparison of Calculated and Experimental Sulfide Capacity

Comparisons of calculated and measured sulfide capacities for slag systems in Groups I, II, III, IV and V are shown in Figs. 2–6, respectively. The model calculated sulfide capacities agree well with the measured values. In the fol-

Fig. 2. Comparisons between calculated and measured sulfide capacity values for CaO–MgO–Al₂O₃–SiO₂ slag.

Fig. 3. Comparisons between calculated and measured sulfide capacity values for slag containing MnO.

Fig. 4. Comparisons between calculated and measured sulfide capacity values for slag containing FeO.

lowing sections, variation of sulfide capacity with composition for some binary and ternary systems will be given to show how the sulfide capacity varies with composition.

3.1. Binary Systems

The sulfide capacity variations of MO–SiO₂ (M=Ca, Mg, Fe and Mn) systems with the mole fractions of MO at 1 773 K and 1 923 K are shown in Fig. 7, in which the experimen-

Fig. 5. Comparisons between calculated and measured sulfide capacity values for slag containing TiO_2 .

Fig. 6. Comparisons between calculated and measured sulfide capacity values for slag containing CaF_2 .

Fig. 7. Comparisons between calculated and measured sulfide capacity values for MO-SiO_2 ($\text{M}=\text{Ca}, \text{Mg}, \text{Fe}, \text{Mn}$) slag.

tal data are also included for comparison. It can be seen that calculated sulfide capacities agree well with the measured values. Furthermore, the sulfide capacity of different MO-SiO_2 binary systems with same content of MO at the same temperature follows the order: $\text{MnO-SiO}_2 > \text{FeO-SiO}_2 > \text{CaO-SiO}_2 > \text{MgO-SiO}_2$. The reason for this order is that sulfide capacity is determined by both the concentration of free oxygen that is bond with metal cation M only and the stability of the sulfide MS .⁵⁵⁾ High concentration of free oxygen and higher stability of the sulfides can increase the sul-

Fig. 8. Comparisons between calculated and measured sulfide capacity values for MO-TiO_2 ($\text{M}=\text{Fe}, \text{Mn}$) slag.

Fig. 9. The iso- $\text{Log}(C_S)$ curves of CaO-MgO-SiO_2 slag at 1773 K. (■) Ref. 14; (—) iso- $\text{Log}(C_S)$ curves calculated by the present model.

fide capacity. The order of free oxygen concentrations in binary MO-SiO_2 slags with the same contents of SiO_2 is $\text{FeO-SiO}_2 > \text{MnO-SiO}_2 > \text{MgO-SiO}_2 > \text{CaO-SiO}_2$, while order of the sulfide stability is: $\text{CaS} > \text{MnS} > \text{FeS} > \text{MgS}$. Both factors contribute to the order of sulfide capacity for binary MO-SiO_2 system.

Influence of MO ($\text{M}=\text{Fe}, \text{Mn}$) content on sulfide capacity of MO-TiO_2 system at 1773 K is shown in Fig. 8. Increasing MO content can lead to the increase of sulfide capacity of MO-TiO_2 system. It also can be concluded from Fig. 8 that Mn has a stronger ability of increasing sulfide capacity than FeO.

3.2. Ternary Systems

The iso- $\text{log}(C_S)$ curves at 1773 K for CaO-MgO-SiO_2 system is plotted using the present model in Fig. 9, and the experimental data are also included for comparison. It can be seen that the substitution of CaO by MgO can decrease the sulfide capacity. The iso- $\text{Log}(C_S)$ curves at 1923 K for CaO-MnO-SiO_2 and MgO-MnO-SiO_2 systems are plotted in Figs. 10 and 11, respectively. For a given (constant) SiO_2 content, C_S in both melts will increase as increasing MnO content.

From the iso- $\text{Log}(C_S)$ curves of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ melt at

Fig. 10. The iso-Log(C_s) curves of CaO–MnO–SiO₂ slag at 1923 K. (■) Ref. 5; (—) iso-Log(C_s) curves calculated by the present model.

Fig. 11. The iso-Log(C_s) curves of MgO–MnO–SiO₂ slag at 1923 K. (■) Ref. 8; (—) iso-Log(C_s) curves calculated by the present model.

Fig. 12. The iso-Log(C_s) curves of CaO–Al₂O₃–SiO₂ slag at 1773 K. (■) Ref. 14; (□) Ref. 15; (—) iso-Log(C_s) curves calculated by the present model.

Fig. 13. The iso-Log(C_s) curves of CaO–CaF₂–SiO₂ slag at 1776 K and 1473 K. (■) Ref. 44; (○) Ref. 41; (—) iso-Log(C_s) curves calculated by the present model.

1773 K shown in **Fig. 12**, it can be seen that in the region of low basicity, substitution of Al₂O₃ for SiO₂ can increase the sulfide capacity greatly, while in the region of high basicity the substitution can only slightly increase sulfide capacity. The reason for this may be that Al₂O₃ is an amphoteric oxide which can behave as a basic oxide under the condition of low basicity, and as an acidic oxide under the condition of high basicity. Increasing the content of the basic oxide could increase the concentration of free oxygen which is very important for increasing the dissolution of sulfur in slag (increases the sulfide capacity). The present model uses the reciprocal of optical basicity in Eq. (9), so in the range of high optical basicity, the sulfide capacity increment at same increment of optical basicity will decrease. Therefore, though the model does not consider the amphoteric behavior information of Al₂O₃, it can still embody this variation phenomenon.

During the pyrometallurgical processes, CaF₂ is always added to enhance the fluidity and desulfurization ability of the slag. So, it is significant to understand its influence on the sulfide capacity. The iso-Log(C_s) curves of CaO–CaF₂–

SiO₂ melt at 1776 K and 1473 K are shown in **Fig. 13**. At a given (constant) SiO₂ content, the sulfide capacity of CaO–CaF₂–SiO₂ melt decreases when increasing the content of CaF₂. Therefore, CaF₂ has a weaker ability to increase the sulfide capacity compared to CaO. However, it can be seen from Fig. 13 that when adding CaF₂ to CaO–SiO₂ melt while keeping the ratio of CaO to SiO₂ constant, there will be an increase in sulfide capacity.

From the iso-Log(C_s) curves of CaO–TiO₂–SiO₂ melt at 1773 K shown in **Fig. 14**, it can be concluded that sulfide capacity of CaO–TiO₂–SiO₂ system increases when SiO₂ is replaced by TiO₂ for a given (constant) CaO content. It is known to all that Ti is a multivalence element, which has the valences of 2+, 3+ and 4+. The proportions of different TiO_x oxides are determined by oxygen fugacity, temperature and basicity.⁵⁶⁾ So, the coexistences of several TiO_x oxides in melt are also the reason for model discrepancy from the measured values. It was pointed out that at ambient pressure the reduced valences are favored by high temperature, but the proportions of them in air become significant only above

Fig. 14. The iso- $\text{Log}(C_s)$ curves of CaO–TiO₂–SiO₂ slag at 1773 K. (■) Ref. 39; (—) iso- $\text{Log}(C_s)$ curves calculated by the present model.

2273 K.⁵⁶⁾ So, it is assumed that all the Ti present as TiO₂ because all the sulfide capacity data for TiO_x containing slags used in this study are measured below 1873 K. Mysen⁵⁶⁾ reviewed the spectroscopic data on titania bearing glasses and found that more than one structural position of Ti⁴⁺ might be possible. Or, TiO₂ may act either as a network modifier or a network former. If it behaves as a network modifier, it can obviously increase sulfide capacity relative to SiO₂ because it can decrease the degree of polymerization and help increase the free oxygen content. Even if TiO₂ acts as a network former like SiO₂, because the Ti⁴⁺ ion is larger than the Si⁴⁺ cation, the Ti–O–Ti bond is expected to be weaker than Si–O–Si bond. Thus, substitution of TiO₂ for SiO₂ will decrease the degree of polymerization, and thereby increase sulfide capacity. Accordingly, replacement of SiO₂ by TiO₂ for a given (constant) CaO content will increase sulfide capacity regardless of the acid or base behavior of TiO₂.

4. Discussion

(1) With about sixty optimized parameters, KTH model can give a good estimation results for CaO–MgO–FeO–MnO–Al₂O₃–SiO₂ systems. The calculated sulfide capacities by KTH model and our model of Groups I, II and III in Table 1 are compared with the measured values as shown in Fig. 15. It is indicated that with only eight adjustable parameters, our model can still obtain good results.

(2) The apparent optical basicity of FeO is optimized to be 1.00 in the work of Young *et al.*⁴⁹⁾ Obviously, this value is unreasonable because if the optical basicity of FeO is the same as that of CaO, the sulfide capacity of CaO–FeO–SiO₂ melt should not change when FeO is substituted for CaO at constant SiO₂ content. However, according to the experimental results this is not true. It is found that when CaO is replaced by FeO for a given (constant) SiO₂ content in CaO–FeO–SiO₂ melt, the sulfide capacity increases.³⁶⁾ Hence, the optimized optical basicity value of 1.24 for FeO is more reasonable and is able to rationalize the observation.

(3) In the definition formula of sulfide capacity (Eq. (3)),

Fig. 15. Comparisons between calculated and measured sulfide capacity values for CaO–MgO–FeO–MnO–Al₂O₃–SiO₂ slag.

both the influences of activity coefficient of sulfur ion and activity of free oxygen ion are included. Generally, the optical basicity could reflect the activity of free oxygen ion, while in the present model both the two terms are expressed by the sulfide capacity. Therefore, the optimized apparent optical basicity values of FeO, MnO, TiO₂ and CaF₂ are also incorporated the influence of sulfur ion. So, the presently derived optical basicity values for these components may be applicable only to the sulfide capacity estimation, not to other ones such as the phosphate capacity.

5. Conclusions

The concept of optical basicity is used to model the sulfide capacity of CaO–MgO–FeO–MnO–TiO₂–Al₂O₃–SiO₂–CaF₂ melt, and good estimation results are obtained. The model assumed a linear relationship between the logarithm of sulfide capacity and the reciprocal of optical basicity of the slag. Apparent optical basicity of FeO, MnO, TiO₂ and CaF₂ are optimized in this study. The order of sulfide capacity for MO–SiO₂ binary systems for a given (constant) SiO₂ content and temperature is MnO–SiO₂>FeO–SiO₂>CaO–SiO₂>MgO–SiO₂; substitution of CaO by CaF₂ decreases the sulfide capacity and substitution of SiO₂ by TiO₂ increases the sulfide capacity.

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