

Application of the generalised central atom model to sulphur containing oxide slags

Ling ZHANG^{1)*} and Jean LEHMANN²⁾

1) CSIRO Process Science & Engineering, Box 312, Clayton South, Vic. 3169, Australia

2) ArcelorMittal Global R&D Maizières BP 30320 57 283 Maizières les, Metz Cedex, France

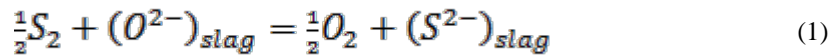
Abstract: Through a collaborative research project between CSIRO and ArcelorMittal, the capability of the Generalised Central Atom (GCA) model in describing complex oxide slags has been assessed. A slag model database for the Na₂O-K₂O-CaO-MgO-MnO-FeOx-Al₂O₃-P₂O₅-SiO₂ and its sub-systems has been developed. Recently the applicability of the GCA model has been further assessed for sulphur containing oxide slags. The published experimental data on sulphur behaviour in various metallurgical systems has been critically reviewed and analysed. Systematic approach was taken to first model sulphur solubility and sulphide capacity in the binary oxide systems. The sulphide capacity in ternary and high order systems was then predicted by the model using binary parameters. The results of the application of the GCA model to sulphide containing metallurgical slag systems of the CaO-MgO-MnO-Al₂O₃-SiO₂ and its sub-systems will be discussed in the present paper.

Keywords: The GCA model, oxide slags, sulphide capacity

1. Introduction

The study of behavior of sulphur in molten slags has been one of the important topics in the thermodynamic properties of high temperature melts. This is mainly due to practical interests in steelmaking processes. The measured sulphide capacity data up to 1995 were compiled in Slag Atlas by Gaye and Lehmann [1]. The recent paper by Kang and Pelton [2] on modelling sulphide dissolution in oxide slags has also provided comprehensive review of the published data.

Sulphur in slag under reducing conditions can be considered as sulphur exchange between a slag and a gas phase and presented by the following expression [1]



Accordingly, Fincham and Richardson [3] defined the sulphide capacity C_S , as a measure of the capacity of a slag to hold sulphur. It was defined as:

$$C_S = (P_{O_2}/P_{S_2})^{1/2} \cdot (\text{wt}\% S), \quad (2)$$

Where P_{O_2} and P_{S_2} are partial pressure of oxygen and sulphur respectively. Their experimental results on the CaO-Al₂O₃-SiO₂ melts showed that for a given slag composition and over an appropriate range of P_{O_2} , the C_S was constant at a given temperature and S content up to 1 wt%.

Understanding of the behavior of sulphur in molten slags is greatly aided by well developed liquid oxide or slag models. The researchers at the ArcelorMittal Maizières, Research and Development (AMMRD), formerly IRSID have modeled sulphide capacity in the slag $\text{CaO-MgO-MnO-FeO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ system using the cell model approaches [4,5]. More recently Kang and Pelton have reported their modelling work on the sulphide dissolution in oxide slags $\text{CaO-MgO-MnO-FeO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Ti}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2$ system in the framework of the modified quasichemical model [2]. There have been models by Reddy and Blander [6], and Nilsson et al [7]. Attempts were also made to correlate sulphide solubility with optical basicity [8].

AMMRD have further developed the so called generalised central atoms (GCA) model for modelling both liquid slag and liquid steel phases. Application of the GCA model to the liquid steel has shown significant improvement in the model descriptions [9,10]. In recent years there has been a collaborated research effort between CSIRO and AMMRD in evaluation of the applicability and database development of the GCA model to molten slags. The improvement by the GCA model over the cell model for the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system has been reported at the last conference MOLTEN2009 [11]. Since then a slag model database for the $\text{Na}_2\text{O-K}_2\text{O-CaO-MgO-MnO-FeO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-SiO}_2$ and its sub-systems has been developed. More recently the applicability of the GCA model has been further assessed for sulphur containing oxide slags of the $\text{Na}_2\text{O-K}_2\text{O-CaO-MgO-MnO-FeO-Al}_2\text{O}_3\text{-SiO}_2$ system. In that work, the published experimental data on sulphur behaviour in various metallurgical systems were critically reviewed and analysed. Systematic approach was taken to first model sulphur solubility and sulphide capacity in the binary oxide systems. The sulphide capacity in ternary and high order systems was then predicted by the model using binary parameters. Due to the restriction on the length of the paper only the results of the $\text{CaO-MgO-MnO-Al}_2\text{O}_3\text{-SiO}_2$ and its sub-systems will be presented and discussed in the present paper.

2. The GCA Model

The generalised central atoms (GCA) model developed by Lehmann and co-workers [9] was based on the central atoms model, originally proposed by Lupis and Elliott [12]. In this approach the cell model for the slag phase (oxides and oxo-sulphides) and the central atom model for liquid metallic phase were unified to the GCA model. The main advantage of the GCA model is its ability to treat the short range order in the liquid phase more precisely than the Cell model. Instead of pair interactions between cations around a given anion as in the cell model the GCA model considers interactions around a central atom between its neighbouring atoms, cations and anions.

In the GCA model the structure of liquids is described in terms of cells composed of a central atom and its shell of nearest neighbours. In a system with m components, t cations and $(m-t)$ anions, the cell will be denoted as

$i_1, i_2, \dots, i_k, \dots, i_t$	Atoms on cationic shell
J	Central atom
$j_{t+1}, \dots, j_r, \dots, j_m$	Atoms on anionic shell

In such a cell, around the central atom **J**, either a cation or an anion, there are i_1 cations # 1, i_2 cations # 2... on the

cation shell and j_{t+1} anions # t+1, j_{t+2} anions # t+2... on the anion shell. Similar to the cell model, there are two kinds of parameters in the GCA model, namely the formation and the interaction energy. The formation energy of the cell is **错误!** **未定义书签**. $\varphi_{\{i\},\{j\}}^J$ where J represents the central atom and {i} and {j} are the whole set of cations and anions respectively present on J-neighbouring shells. For the sake of simplicity, this formation energy term is assumed as the sum of the contributions of the two shells:

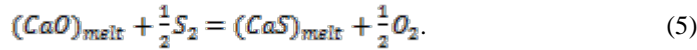
$$\varphi_{\{i\},\{j\}}^J = \varphi_{\{i\}}^J + \varphi_{\{j\}}^J \quad (3)$$

To reduce the number of parameters, different assumptions can be formulated to describe the energy variation for the central atom according to the composition of the chemical neighbourhood. To be compatible with the expression of the cell model the following form was chosen for the GCA model for the contribution of the cationic shell [13]

$$\varphi_{\{i\}}^J = \sum_{k=1}^t i_k \varphi_{kk}^J + \frac{1}{2} \sum_{\substack{k,l=1 \\ k \neq l}}^t i_k i_l \varphi_{kl}^J. \quad (4)$$

Equation (4) applies to both cations and anions as central atoms and the equivalent equation can be derived for the anionic shell. In addition to these parameters, interaction parameters are also considered. Details of the formalism of the GCA model have been given by Lehmann et al [9,10].

In S containing oxide system, for example in CaO containing melts, the reaction was considered as [3],



The Gibbs free energy of the reaction can be expressed as $\Delta G_{(1)} = 1/2G_{\text{O}_2} + G_{\text{CaS}}(\text{l}) - 1/2G_{\text{S}_2} - G_{\text{CaO}}(\text{l})$, where G_{O_2} , $G_{\text{CaS}}(\text{l})$, G_{S_2} and $G_{\text{CaO}}(\text{l})$ are Gibbs free energy of formation of O_2 , liquid CaO, S_2 and liquid CaS. In the GCA model the oxide-sulphide exchange formation parameter was defined as $\varphi_{\text{S}}^{\text{Ca}} = G_{\text{CaS}}(\text{l}) - G_{\text{CaO}}(\text{l})$. In the current work the values of $G_{\text{MS}}(\text{l})$, M represents cations of Si, Al, Ca, Mg, Mn, were obtained by using the published data [14-16]. In a two cation systems, such as CaO-SiO₂-S, there are formation energy parameters for anions O and S, $\varphi_{\text{O-S}}^{\text{M}}$, for both Ca and Si. The formation energy parameters for sulphides, $\varphi_{\text{Ca-Si}}^{\text{S}}$, are also available as well as interaction energy parameters. The model parameters were obtained via optimization by using a special version of the PARROT program in the Thermo-Calc Software [17]. A systematic approach has been taken by modelling the sulphide capacities in the binary systems and parameters obtained were further refined if it was required to fit data of ternary and high order systems.

3. Results and Discussion

The sulphide capacity in the slag phase were calculated by the GCA model and using Eq.(2) under gas and slag equilibrium. In most cases the partial pressure of oxygen was set to $P_{O_2}=10^{-7}$ atm and the partial pressure of sulphur, $P_{S_2}=10^{-3}$ atm in the equilibrium calculations. This choice was based on the study by Fincham and Richardson [3] on the effect of oxygen partial pressure on sulphide capacity, in which it was found that sulphide capacity was independent of oxygen partial pressure when $P_{O_2}<10^{-7}$ atm in the CaO-Al₂O₃-SiO₂ melts at 1500°C. Some recent measurements for various slag systems were carried out at KTH under the same order of P_{O_2} and P_{S_2} values [18,19]. A number of test runs have been carried out at lower P_{O_2} values, such as $P_{O_2}=10^{-9}$ atm in the CaO-Al₂O₃, and CaO-Al₂O₃-SiO₂ systems, and it was found that the calculated sulphide capacity were almost identical as those under $P_{O_2}=10^{-7}$ atm. In the present work the modelling results were presented as sulphide capacity variations with temperature and slag compositions in comparison with the published data.

3.1 Binary systems

The sulphide capacity data in the binary oxide systems of concern of the current study were available in the Al₂O₃-SiO₂ system at 1650°C and alumina mole fraction $X_{Al_2O_3}< 0.3$ [20], CaO-Al₂O₃ in a temperature range of 1500 to 1650°C [3,18,21-24], CaO-SiO₂ in 1500 to 1650°C [3,25-27], MgO-SiO₂ in 1580 to 1650°C [3,20,26,28], MnO-Al₂O₃ in 1500 to 1650°C [19,20] and MnO-SiO₂ in 1300 to 1650°C [20,29-32]. The published data for these binary oxides are shown in Figures 1 to 6. The calculated sulphide capacity values by the GCA model are also shown in these Figures for comparison.

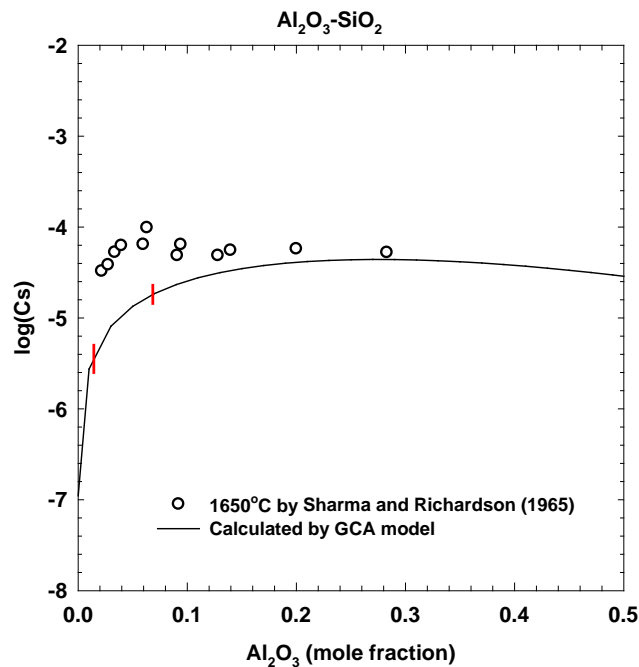


Fig. 1 Comparison between the calculated sulphide capacity $\text{Log}_{10}(C_s)$ at $P_{O_2}=10^{-7}$ and $P_{S_2}=10^{-3}$ atm and the experimental data [20] at 1650°C in the Al₂O₃-SiO₂ system (vertical bars show the calculated oxide solid/liquid boundaries).

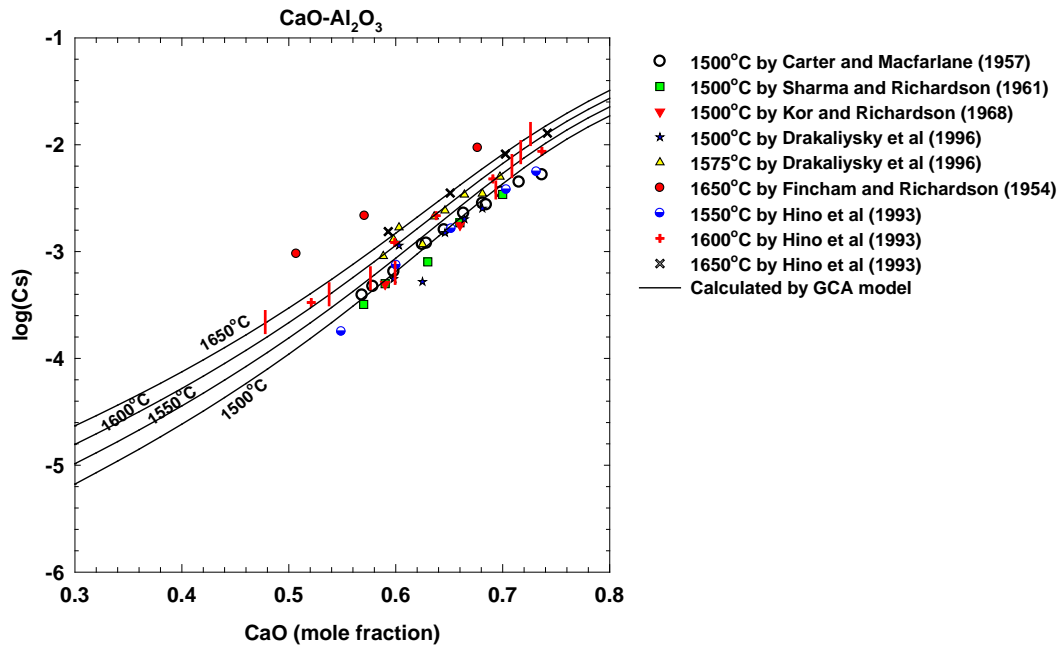


Fig. 2 Comparison between the calculated sulphide capacity $\text{Log}_{10}(C_S)$ at $P_{O_2}=10^{-7}$ and $P_{S_2}=10^{-3}$ atm and the experimental data [3,18,21-24] in the temperature range of 1500 to 1650°C in the CaO-Al₂O₃ system (vertical bars show the calculated oxide solid/liquid boundaries).

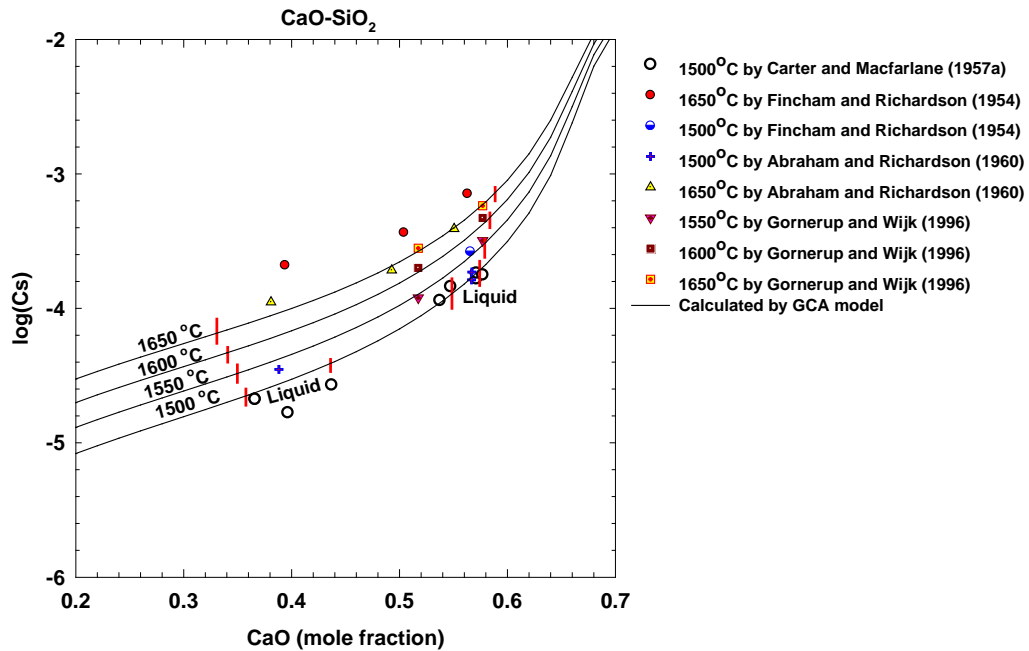


Fig. 3 Comparison between the calculated sulphide capacity $\text{Log}_{10}(C_S)$ at $P_{O_2}=10^{-7}$ and $P_{S_2}=10^{-3}$ atm and the experimental data [3,25-27] in the temperature range of 1500 to 1650°C in the CaO-SiO₂ system (vertical bars show the calculated oxide solid/liquid boundaries).

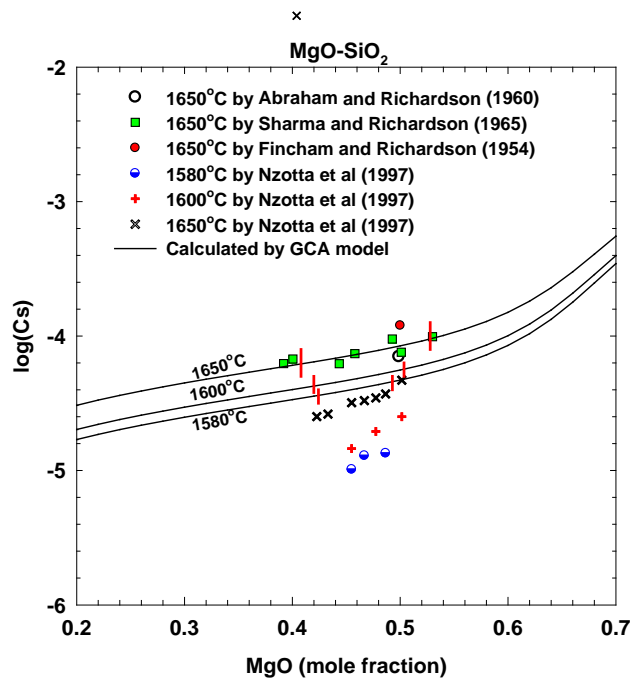


Fig. 4 Comparison between the calculated sulphide capacity $\text{Log}_{10}(C_S)$ at $P_{O_2}=10^{-7}$ and $P_{S_2}=10^{-3}$ atm and the experimental data [3,20,26,28] at 1580 to 1650°C in the MgO-SiO₂ system (vertical bars show the calculated oxide solid/liquid boundaries).

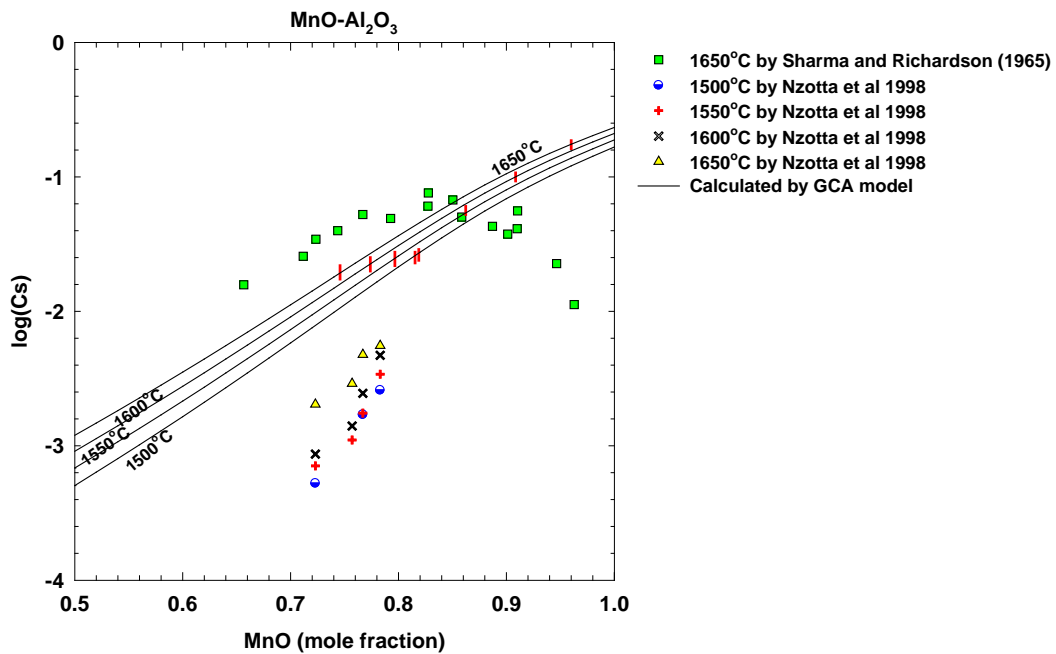


Fig. 5 Comparison between the calculated sulphide capacity $\text{Log}_{10}(C_S)$ at $P_{O_2}=10^{-8}$ and $P_{S_2}=10^{-5}$ atm and the experimental data [19,20] at 1500 to 1650°C in the MnO-Al₂O₃ system (vertical bars show the calculated oxide solid/liquid boundaries).

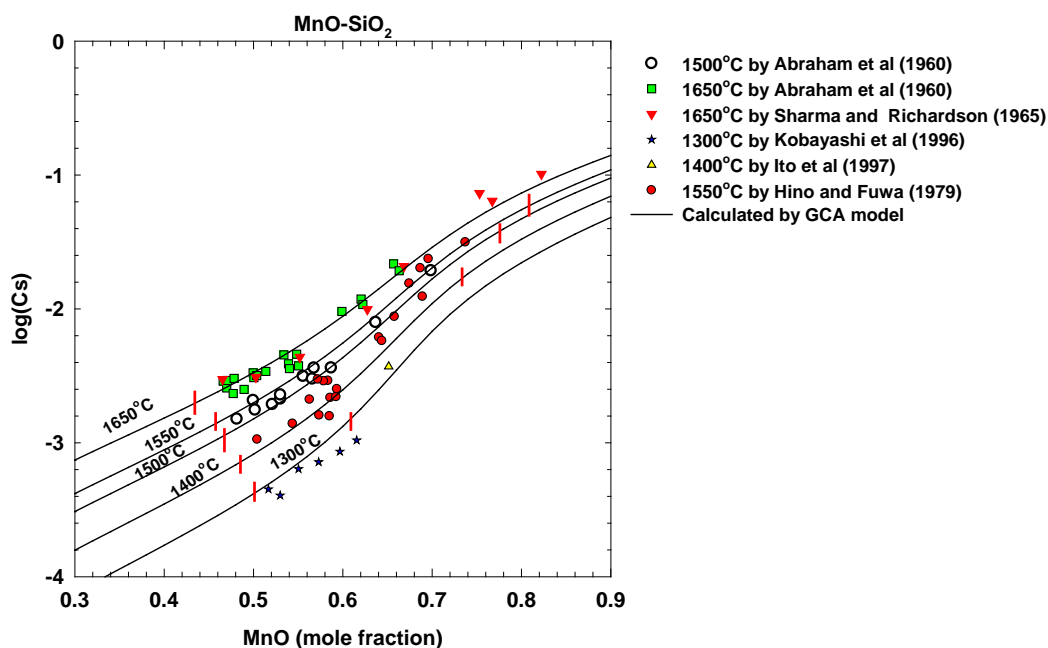


Fig. 6 Comparison between the calculated sulphide capacity $\text{Log}_{10}(C_s)$ at $P_{O_2}=10^{-8}$ and $P_{S_2}=10^{-5}$ atm and the experimental data [20,29-32] at 1300 to 1650°C in the MnO-SiO₂ system (vertical bars show the calculated oxide solid/liquid boundaries).

In the Al₂O₃-SiO₂ system at 1650°C the experimental data shows that sulphide capacity C_s increases with increasing alumina content in the liquid region ($0.014 < X_{Al_2O_3} < 0.069$) and reaches a plateau [20]. It can be seen that the model was able to reproduce such a trend though the calculated values were lower than the data. The model parameters were determined by compromising the accuracy of the binary Al₂O₃-SiO₂ system in order to fit data in higher order systems, such as the CaO-Al₂O₃-SiO₂ system.

In other binary systems the general trend of the behavior sulphide capacity was that C_s increased with increasing temperature and metal oxide (Ca,Mg,Mn)O content. The scatters and discrepancy of the data were significantly large in some systems, such as in MnO-SiO₂ and MnO-Al₂O₃. The model parameters for the MnO-Al₂O₃ (data with large uncertainties) and MgO-Al₂O₃ (no data were available) systems were determined mainly based on ternary information. In general it can be seen that the fit of the model to the data was satisfactory in most binary systems.

3.2 Ternary systems

In the ternary systems the sulphide capacity data were found in the CaO-Al₂O₃-SiO₂ at 1500, 1550, 1600 and 1650°C [3,24,27,33,34,35], MgO-Al₂O₃-SiO₂ [20] and MnO-Al₂O₃-SiO₂ at 1650°C [20], CaO-MgO-SiO₂ at 1550, 1550, 1600 and 1650°C [28,29,35,36], CaO-MnO-SiO₂ in a range of 1500 to 1650°C [29,30,37,38], MnO-MgO-SiO₂ in 1550 to 1650°C [20,30,39], CaO-MgO-Al₂O₃ at 1550, 1600 and 1650°C [24], MnO-MgO-Al₂O₃ at 1600 and 1650°C for 6 MnO rich composition points [19]. The published data in the form of iso-sulphide capacity curves in the ternary oxides are shown in Figures 7a to g and Table 1. Due to the page restriction for the current paper only one temperature 1600°C

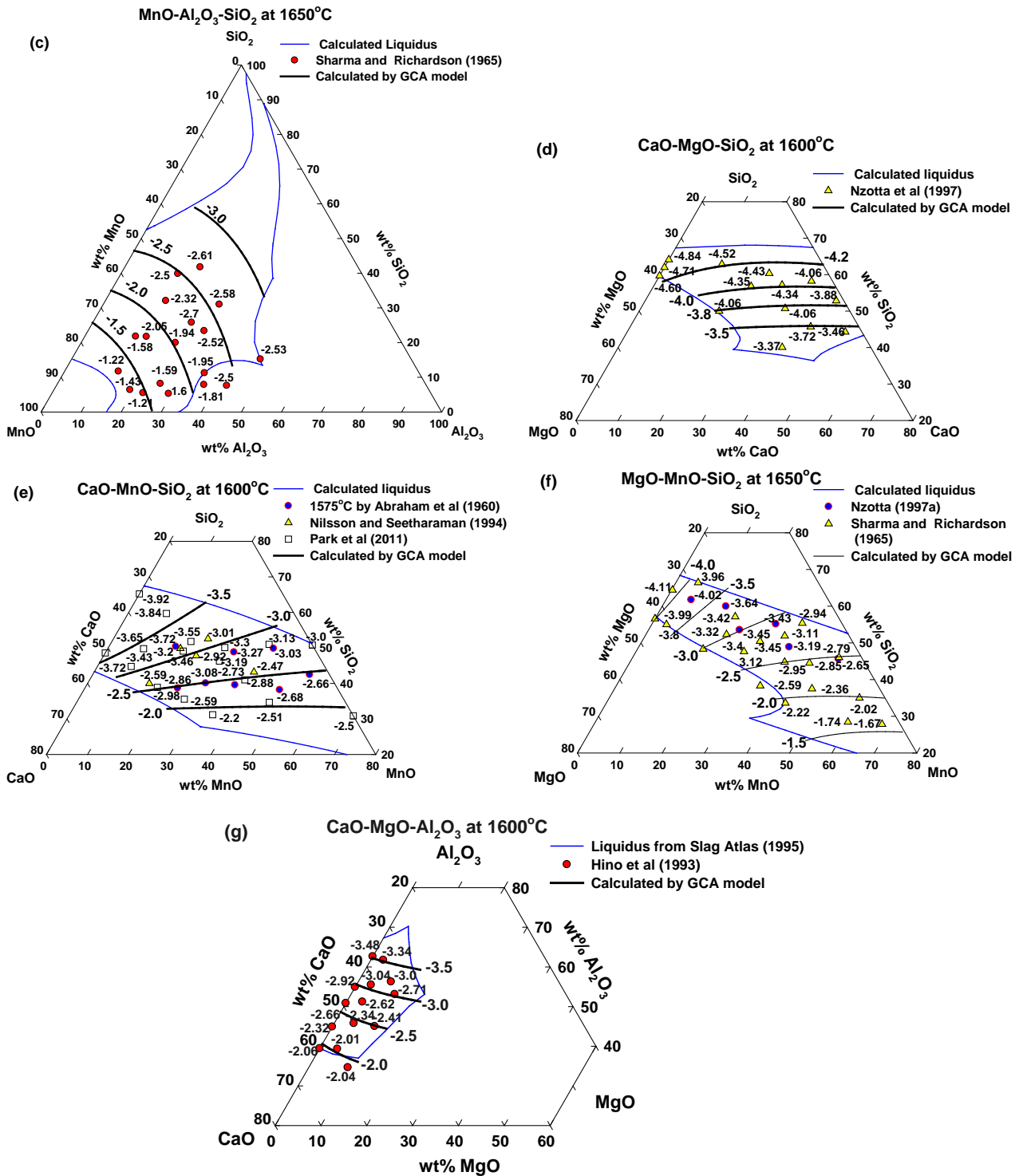


Fig. 7 Comparison between the calculated sulphide capacity $\text{Log}_{10}(C_S)$ at $P_{O_2}=10^{-7}$ and $P_{S_2}=10^{-3}$ atm and the experimental data in (a) CaO-Al₂O₃-SiO₂ at 1600°C [24,27,34], (b) MgO-Al₂O₃-SiO₂ at 1650°C [20], (c) MnO-Al₂O₃-SiO₂ ($P_{O_2}=10^{-8}$ and $P_{S_2}=10^{-5}$ atm) at 1650°C [20], (d) CaO-MgO-SiO₂ at 1600°C [28], (e) CaO-MnO-SiO₂ at 1600°C [29,37,38], (f) MnO-MgO-SiO₂ at 1650°C [20,39] and (g) CaO-MgO-Al₂O₃ at 1600°C [24].

Table 1. Comparison between the calculated sulphide capacity $\text{Log}_{10}(C_s)$ at $P_{O_2}=10^{-8}$ and $P_{S_2}=10^{-5}$ atm and compiled experimental data [19] in the MnO-MgO- Al_2O_3 system

Temperature °C	Composition (mole fraction)			$\text{Log}_{10}(C_s)$	
	Al_2O_3	MgO	MnO	Exp. data	Calculated
1650	0.235	0.113	0.652	-1.92	-1.71
	0.207	0.148	0.645	-1.89	-1.60
	0.193	0.159	0.648	-1.81	-1.54
1600	0.161	0.253	0.586	-1.73	-1.48
	0.235	0.113	0.652	-2.09	-1.79
	0.161	0.253	0.586	-1.81	-1.55

3.3 Multi-component systems

Owing to its practical importance, the sulphide capacity of the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ system has been studied extensively from 1960's till very recent in 2009 [19,26,35,40- 46]. The published data are available in a temperature range of 1400 to 1650°C and silica contents of 7 to 67 wt pct. Figure 8 showed the comparison between the model predicted values and ten sets of data. It can be seen that the model was able to fit reasonably close to most sets of data. The sulphide capacity data were also available in the quaternary $\text{CaO-MnO-Al}_2\text{O}_3\text{-SiO}_2$ [19,43], CaO-MgO-MnO-SiO_2 [39] and $\text{CaO-MgO-MnO-Al}_2\text{O}_3$ systems [19]. Comparison between the calculated sulphide capacity and the data was shown in Figure 9. Apart from the data by Nzotta et al in $\text{CaO-MnO-Al}_2\text{O}_3\text{-SiO}_2$ [19], close agreement between the model and the data was obtained.

The sulphide capacity in the $\text{CaO-MgO-MnO-Al}_2\text{O}_3\text{-SiO}_2$ system has been reported by Nzotta et al in a temperature range of 1500 to 1650°C for MgO and SiO_2 rich slags [19] and Taniguchi et al at 1400 to 1500°C for CaO and Al_2O_3 rich slags [43]. Comparison between the calculated sulphide capacity and the experimental data are shown in Figure 10. It can be seen that the fit by the model to the data by Taniguchi et al [43] was closer than that to the data by Nzotta et al [19]. Close examinations found that the model reproduce the same trend as the measurements.

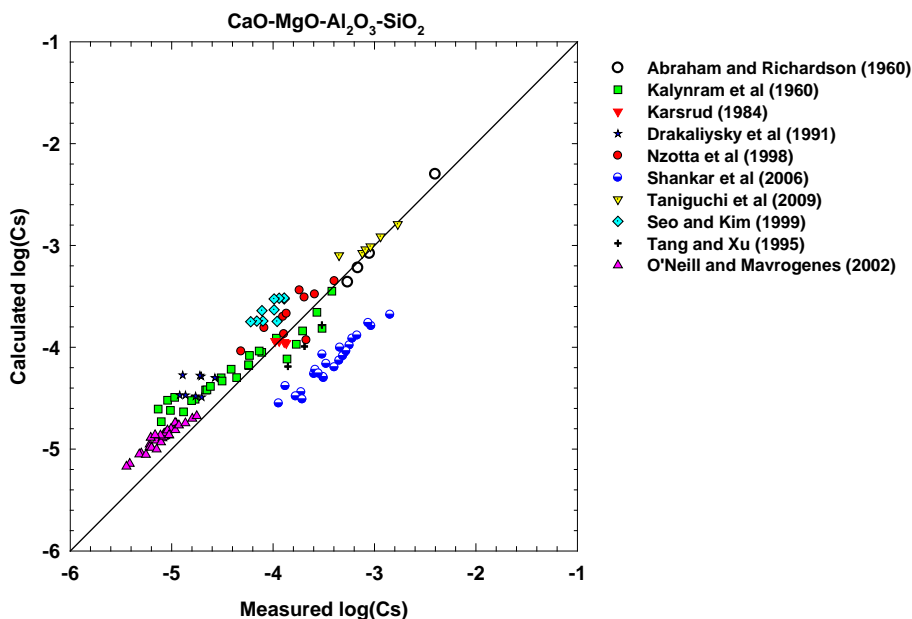


Fig. 8 Comparison between the calculated sulphide capacity $\text{Log}_{10}(C_S)$ at $P_{O_2}=10^{-7}$ and $P_{S_2}=10^{-3}$ atm and all compiled experimental data [19,26,35,40-46] in the temperature range of 1400 to 1650°C in the CaO-MgO-Al₂O₃-SiO₂ system.

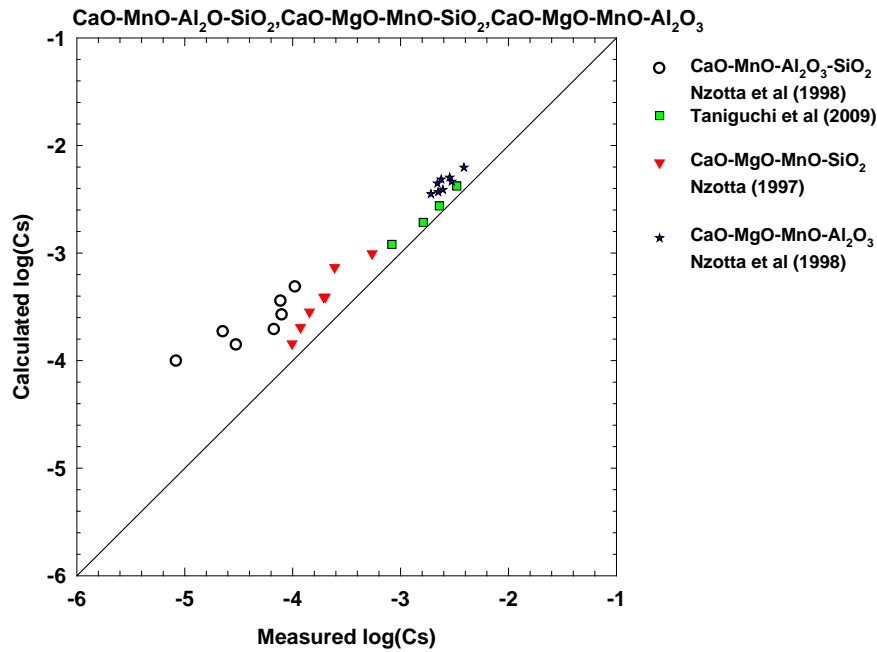


Fig. 9 Comparison between the calculated sulphide capacity $\text{Log}_{10}(C_S)$ at $P_{O_2}=10^{-7}$ and $P_{S_2}=10^{-3}$ atm and the experimental data in the CaO-MnO-Al₂O₃-SiO₂ [19,43], CaO-MgO-MnO-SiO₂ [39] and CaO-MgO-MnO-Al₂O₃ systems [19].

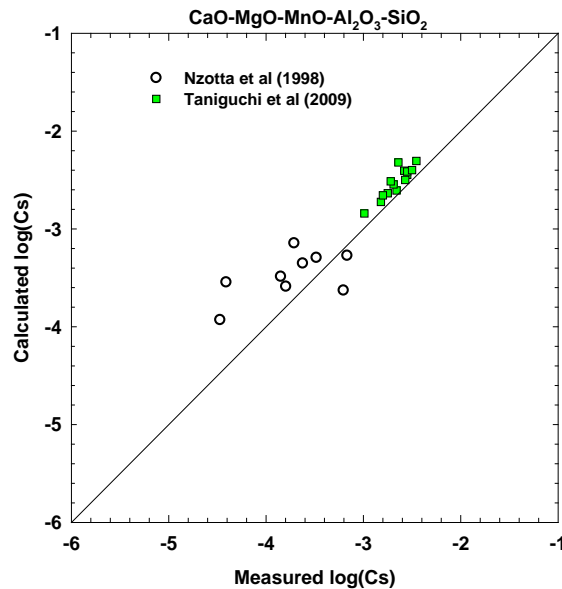


Fig. 10 Comparison between the calculated sulphide capacity $\text{Log}_{10}(C_S)$ at $P_{O_2}=10^{-7}$ and $P_{S_2}=10^{-3}$ atm and the experimental data in the CaO-MgO-MnO-Al₂O₃-SiO₂ [19,43],

4. Conclusions

The published sulphide capacity data in the CaO-MgO-MnO-Al₂O₃-SiO₂ slags and sub-systems have been reviewed. The behavior of sulphide capacity in terms of variation with melt compositions were analyzed to provide guidance in the modeling when data were lacking or the scatters of the available data were significant. The GCA model parameters were mostly obtained by fitting the binary data or referred to ternary data when lack of data for some binaries. The modeling results showed that the GCA model was able to describing the behavior of sulphur in oxide slags by reproducing the trends found by the experiments on variation of sulphide capacity with slag compositions and temperatures. Good representations of the binary sulphide capacity data were obtained in most cases. The model predicted sulphide capacities for ternary and high order systems were in general close agreement with the published data. The model was able to account for the effects of different oxides on the sulphide capacity of slags.

Acknowledgement

The authors wish to acknowledge the financial support by CSIRO Minerals Down Under Flagship and ArcelorMittal Maizières, Research and Development. The authors also wish to acknowledge Dr Qing Chen from the Thermo-Calc Software AB for compilation of a special version of the TC-GCA package. Useful discussions with Drs S. Jahanshahi and S. Sun of CSIRO are highly appreciated.

References

- [1] Slag Atlas, 2nd Edition, (1995), Ed: Verein Deutscher Eisenhüttenleute. Verlag Stahleisen GmbH, D-Dusseldorf, Germany.
- [2] Y-B. Kang and A.D. Pelton, "Thermodynamic model and database for sulphides dissolved in molten oxide slags", *Metall. Mater. Trans. B*, 2009, 40B, p 979-994.
- [3] C.J.B. Fincham and F.D. Richardson, "The behaviour of sulphur in silicate and aluminate melts", *Proc. Roy. Soc.*, 1954, .223A, p 40-62.
- [4] J. Lehmann, H. Gaye, "Modeling of thermodynamic properties of sulphur bearing metallurgical slags" *Rev. Int. Hautes Tempér. Réfract., Fr.*, 1992-1993, 28, p 81-90
- [5] H. Gaye, J. Lehmann, T. Matsumiya and W. Yamada, (1992). "A Statistical Thermodynamics Model of Slags: Applications to Systems Containing S, F, P₂O₅ and Cr Oxides" in 4th International Conference on Molten Slags and Fluxes, The Iron and Steel Institute of Japan, Tokyo, 1992, pp.103-108.
- [6] R.G. Reddy and M. Blander, *Metall. Trans. B*, 1987, 18B, p 591-596.
- [7] R. Nilsson, Du Sichen and S. Seetharaman, "Estimation of sulphide capacities of multi-component silicate melts", *Scan. J. Metall.*, 1996, 25, p128-134.
- [8] D.J. Sosinsky and I.D. Sommerville, *Metall. Trans. B*, 1986, 17B, p 331-337.
- [9] J. Lehmann, F. Bonnet and M. Bobadilla, "Thermodynamic Description of Liquid Steel and Metallurgical Slags by the "Generalized Central Atoms" Model", 2006, *AIST Transactions*, 3(6), p 114-123.
- [10] J. Lehmann, " Application of ArcelorMittal Maizières Thermodynamic Models to Liquid Steel Elaboration", in Physical Chemistry of Steel Refining - 28th International ATS Steelmaking Days, December 13-14, 2007, Paris, p 89-104.

- [11] L. Zhang and J. Lehmann “Application of the Generalised Central Atom Model to Oxide Slags” MOLTEEN2009, Eds., M. Sanchez, R. Parra , G. Riveros and C. Diaz, Proceedings of the VIII International Conference on Molten Slags, Fluxes and Salts, 18-21 January 2009, Satiago, Chile CD-ROM, p 403-411.
- [12] C.H.P. Lupis and J.F. Elliott, (1967). “Prediction of Enthalpy and Entropy Interaction Coefficients by the “Central Atoms” Theory”, 1967, *Acta Met.* 15, p 265-276.
- [13] J. Lehmann, F. Bonnet, M. Bobadilla and H. Gaye, “General Thermodynamic Description of Liquid Steel by the “Central Atoms” Model”, in *Proc. of the Metal Separation Technology III Conference*, Colorado, June 20-24, 2004. P 52-57.
- [14] Barin, I. (1989), *Thermochemical Data of Pure Substances*, VCH, Weiheim, Germany.
- [15] M.W. Chase, Jr., C.A. Davies, J.R. Downey, Jr., D.J. Frurip, R.A. McDonald and A.N. Syverud, “JANAF thermochemical tables third edition”, *J. Phys. Chem. Ref. Data*, 1985, 14, supp.1.
- [16] SGTE Substances Database v3, <http://www.thermocalc.com>.
- [17] B. Sundman, User Aspects of Phase Diagrams, ed. Hayes, F.H., Inst. Metals, London, 1991, p 130.
- [18] E. Drakaliysky, R. Nilsson, Du, Sichen and S. Seetharaman, “Sulphide capacity of CaO-Al₂O₃ slags in the temperature range 1173-1848 K”, *High Temp. Mater. Processes.*, 1996, 15, p 263-272.
- [19] M.M. Nzotta, Du, Sichen and S. Seetharaman, “Sulphide capacity in some multi component slag systems”, *ISIJ Int.*, 1998, 38, p 1170-79.
- [20] R.A. Sharma and F.D. Richardson, “Activities of manganese oxide, sulphide capacity, and activity coefficient in aluminate-silicate melts”, *Trans. Met. Soc. AIME*, 1965, 233, p 1586-92.
- [21] P.T. Carter and T.G. Macfarlane, “Thermodynamics of slag systems part 1 the thermodynamic properties of CaO-Al₂O₃ slags”, *J. Iron Steel Inst.*, 1957, 185, p 54-62.
- [22] R.A. Sharma and F.D. Richardson, “Activities in lime-alumina melts”, *J. Iron Steel Inst.*, 1961, 198, p 386-90.
- [23] G.J.W. Kor and F.D. Richardson, “Sulphur in lime-alumina mixtures”, *J. Iron Steel Inst.*, 1968, 206, p 700-704.
- [24] M. Hino, S. Kitagawa and S. Ban-Ya, “Sulphide capacity of CaO-Al₂O₃-MgO and CaO-Al₂O₃-SiO₂ slags”, *ISIJ Int.*, 1993, 33, p 36-42.
- [25] P.T. Carter and T.G. Macfarlane, “Thermodynamics of slag systems part 2 the thermodynamic properties of CaO-SiO₂ slags”, *J. Iron Steel Inst.*, 1957, 185, p 62-66.
- [26] K.P. Abraham and F.D. Richardson, “Sulphide capacity of silicate melts part II”, *J. Iron Steel Inst.*, 1960, 196, p 313-317.
- [27] M. Gornerup and O. Wijk, “Sulphide capacity of CaO-Al₂O₃-SiO₂ slags at 1550, 1600, 1650°C”, *Scan.J. Metall.*, 1996, 25, p 103-107.
- [28] M.M. Nzotta, R. Nilsson, Du, Sichen and S. Seetharaman, “Sulphide capacity in MgO-SiO₂ and CaO-MgO-SiO₂ slags”, *Ironmaking and Steelmaking*, 1997, 24(4), p 300-5.
- [29] K.P. Abraham, M.W. Davies and F.D. Richardson, “Sulphide capacity of silicate melts part I”, *J. Iron Steel Inst.*, 1960, 196, p 309-312.
- [30] M. Hino and T. Fuwa, “Sulphide capacity of liquid manganese silicate”, Proc. 3rd Int. Iron and Steel Congress, ASM International, Materials Park, OH, 1979, p 321-326.
- [31] T. Kobayashi, K. Morita and N. Sona, “Thermodynamics of sulphur in the BaO-MnO-SiO₂ flux system”, *Metall. Mater. Trans. B*, 1996, 27B, p 652-657.
- [32] M. Ito, K. Morita and N. Sona, “Thermodynamics of the MnO-SiO₂-TiO₂ system at 1673 K”, *ISIJ Int.*, 1997, 37, p 839-843.

- [33] J. Cameron, T.B.Gibbons and J. Taylor, "Calcium sulphide solubilities and lime activities in the lime-alumina-silica system", *J. Iron Steel Inst.*, 1966, 204, p 1223-28.
- [34] E. Drakaliysky, Du, Sichen and S. Seetharaman, "An experimental study of the sulphide capacity in the system $\text{Al}_2\text{O}_3\text{-CaO-SiO}_2$ ", *Can. Metall. Q.*, 1997, 36, p 115-20.
- [35] M.R. Kalyanram, T.G. Macfarlane and H.B. Bell, "The activity of calcium oxide in slags in the systems CaO-MgO-SiO_2 , $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ and $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ at 1500°C ", *J. Iron Steel Inst.*, 1960, 195, p 58-64.
- [36] A. Bronson and G. St.Pierre, "The sulphide capacity of CaO-SiO_2 melts containing MgO , FeO , TiO_2 and Al_2O_3 ", *Metall. Mater. Trans. B*, 1981, 12B, p 729-731.
- [37] R. Nilsson and S. Seetharaman, "Experimental determination of the sulphide capacity of CaO-MnO-SiO_2 ternary slags", *Scan. J. Metall.*, 1994, 23, p 81-86.
- [38] G-H Park, Y-B Kang and J-H Park, "Sulfide capacity of the $\text{CaO-SiO}_2\text{-MnO}$ slag at 1873 K", *ISIJ Int.*, 2011, 51(9), p 1375-1382.
- [39] M.M. Nzotta, "Experimental studies of the sulphide capacity of MgO-MnO-SiO_2 and MgO-MnO-CaO-SiO_2 slags", *High Temp. Mater. Processes.*, 1997, 16, p 261-271.
- [40] K. Karsrud "Sulphide capacity of synthetic blast furnace slags at 1500°C ", *Scan.J. Metall.*, 1984, 13, p 144-150.
- [41] E. Drakaliysky, N.S. Srinivasan and L.I. Staffansson, "Sulphide capacity of $\text{CaO-MgO-SiO}_2\text{-Al}_2\text{O}_3$ slags with small amount of Cr_2O_3 ", *Scan. J. Metall.*, 1991, 20, p 251-255.
- [42] A. Shankar, M. Gornerup, A.K., Lahiri and S. Seetharaman , "Sulphide capacity of high alumina blast furnace slags", *Metall. Mater. Trans. B*, 2006, 37B, p 941-947.
- [43] Y. Taniguchi, N. Sano and S. Seetharaman, "Sulphide capacity of $\text{CaO -SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-MnO}$ slags in the temperature range of 1673-1773K", *ISIJ Int.*, 2009, 49, p 156-163.
- [44] J-D. Seo and S-H. Kim, "The sulphide capacity of $\text{CaO -SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-(FeO)}$ smelting reduction Slags, *Steel Res.*, 1999, 70(6), p 203-208.
- [45] Tang Xin and Xu Chushao, *ISIJ Int.*, 1995, 35, p 367-371.
- [46] H.St.C. O'Neill and J.A. Mavrogenes, *J. Petrol.*, 2002, 43, p 1049-87.