Determination of the sulphide capacities of multicomponent slag systems by gas/slag equilibration method

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ABSTRACT

The present work consists of experimental measurements of the sulphide capacities of three quaternary silicate slags, viz. Al_2O_3-CaO-MgO-SiO_2, Al_2O_3-CaO-MnO-SiO_2 and CaO-MgO-MnO-SiO_2. The experimental values are compared with those calculated using the model for sulphide capacities developed at the Division of Theoretical Metallurgy, from the relevant binary and ternary systems. It is shown that the model gives reasonable predictions of the quaternary sulphide capacities. As a next step, the model parameters up to ternary interactions, which were obtained based on the experimental data for corresponding binary and ternary systems were employed to evaluate the sulphide capacities of the quinary system, Al_2O_3-CaO-MgO-MnO-SiO_2. Parallelly, the sulphide capacities in this system were also experimentally measured and the results obtained are compared with the model predictions. The agreement between the two is satisfactory confirming the usefulness of the predictive ability of the present model in estimating the sulphide capacities of complex slags from lower order systems.

1. INTRODUCTION

The concept of sulphide capacity, since its inception by Fincham and Richardson[1], has widely been used by steelmakers in connection with the desulphurization of steel. According to these authors, the sulphide capacity of a slag can be expressed as:

$$C_S = \exp(-\Delta G/RT)\cdot\frac{a_{O^{2-}}}{f_{S^{2-}}} \qquad (1)$$

where $a_{O^{2-}}$ is the activity of oxygen ions in the slag, $f_{S^{2-}}$ is the activity coefficient of sulphide ions in the slag, R is the gas constant, T is the temperature in K and ΔG is the standard Gibbs energy change for the reaction:

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

In terms of measurable quantities, the sulphide capacity can be expressed as

$$C_S = (Wt\text{-}\%S)(p_{O_2}/p_{S_2})^{1/2} \qquad (3)$$

While the exponential factor on the right side of equation (1) is independent of the system, the ratio, $a_{O^{2-}}/f_{S^{2-}}$ is characterized by the system studied. Fincham and Richardson[1] assumed the constancy of the above ratio for a given slag. While Richardson's justification of $a_{O^{2-}}$ being constant due to polymerization/ depolymerization reactions in silicate melts is acceptable, the term $f_{S^{2-}}$ need not be constant. The activity coefficient of sulphide ions in the case of CaO-SiO_2 and Al_2O_3-MnO-SiO_2 slags, available in literature[2] are shown in Figures 1 and 2. Any modelling of the sulphide capacities for complex slags must take into account this variation and thus the sulphide capacities are difficult to predict purely on the basis of the thermodynamics of the silicate melts alone,

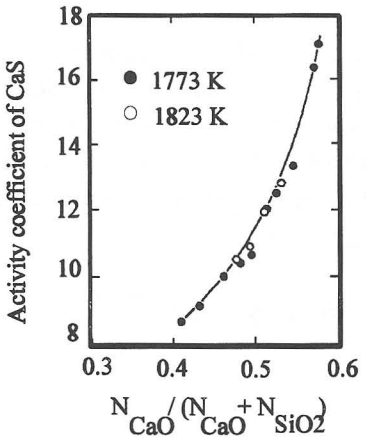

Figure 1. Activity coefficient of CaS at saturation in $CaO-SiO_2-CaS$ melts.

unless the activity coefficient of the sulphide ion is taken into the consideration. Modelling of the sulphide capacities thus poses a serious theoretical problem.

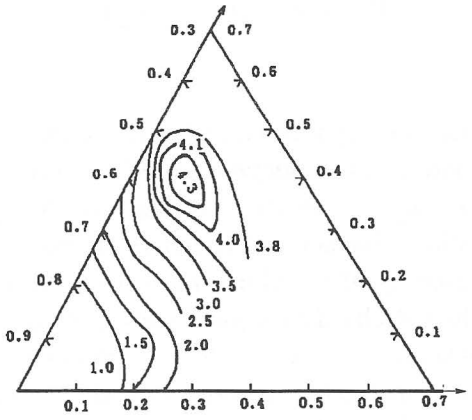

Figure 2. Activity coefficient of MnS in $Al_2O_3-MnO-SiO_2-MnS$ melts at 1923 K.

The optical basicity concept, proposed originally by Sosinsky and Sommerville[3] and modified later by Young et al[4] has been shown to be a useful method of sulphide capacity prediction even though, the approach is entirely empirical. Gaye et al[5] has made a polyanionic extension to their oxide slag model in order to introduce sulphur in their slag model. Reddy and Blander[6] have proposed a method of calculating the sulphide capacities based on the Flory model for polymeric silica chains. Calculations for some binary systems showed good agreement with available experimental data. The model was extended to higher order systems containing up to five components ($Al_2O_3-CaO-FeO-MgO-SiO_2$) by Pelton et al[7]. When fully developed for complex melts, this approach could be of immense use to the steelmakers. Parallelly, a mathematical approach to the estimation of sulphide capacities of complex slags from the lower order systems was attempted in the Division of Theoretical Metallurgy[8]. This model was later slightly modified[9] to take into account the drastic variation of the sulphide capacities between two pure components like CaO and Al_2O_3. The model was used to predict the sulphide capacities of a number of ternary systems and even the quaternary $CaO-FeO-Fe_2O_3-SiO_2$ system[10].

The above mentioned model is based on the optimization of the experimental sulphide capacity values using a method analogous to the standard thermodynamic approach. Since the reliability of the model predictions depend, to a great extent, on the accuracy of the input data, it is necessary to carry out parallel experimental studies under well-controlled conditions. A series of such measurements for a number of binary and ternary systems have been carried out at the Division of Theoretical Metallurgy[11-14] and the model parameters for the lower order systems are now well-defined[10].

In order to verify the predictive capacity of the model in the case of higher order systems, it is necessary to make model calculations for

four and five component systems using the lower-order parameters. This is carried out in the present work. The model predictions are also compared with experimental values, both available in literature as well as those measured as part of this work. The systems taken up for the present study are the quaternary silicate melts Al_2O_3-CaO-MgO-SiO_2, Al_2O_3-CaO-MnO-SiO_2 and CaO-MgO-MnO-SiO_2 as well as the quinary system Al_2O_3-CaO-MgO-MnO-SiO_2.

2. EXPERIMENTAL

The experimental method adopted was based on the principle of gas-slag equilibration method developed by Fincham and Richardson[1]. The details of the method have been given in detail in earlier publications[11,12].

2.1 Materials

Aluminium oxide and calcium oxide were supplied by Fisher Scientific, New Jersey, USA. Magnesium oxide and silicon oxide were supplied by E. Merck, Darmstadt, Germany. Spec. pure MnO was supplied by Johnson Matthey, Karlsruhe, Germany. All oxides except MnO were heated to 1273 K in air for 12 h to remove any trace of water, and then rapidly cooled and stored in a desiccator. The gases used for the equilibration studies, viz. CO, CO_2, SO_2 and Ar were supplied by AGA Gas, Stockholm.

2.2 Procedure

The furnace assembly and the gas cleaning system have been described earlier[11]. The experimental slag was prepared *in situ* in the equilibration furnace. Appropriate amounts of the slag components were accurately weighed, mixed thoroughly in an agate mortar and melted in platinum crucibles in argon atmosphere. For purposes of homogenization, the slag was retained in the furnace overnight. The choice of the melting temperature was based on the phase diagram constraints wherever it was available. In all cases, the complete melting of the slags was confirmed after the experiments by microscopic examination of the solidified slag lump.

The equilibration with CO-CO_2-SO_2-Ar gas mixture was carried out for a period of 6 h at the appropriate temperature. The gas flows were controlled by Bronkhorst hi-tec mass flow meters, model F 201C-FA, connected to a four-channel control system, Bronkhorst flow-bus. The partial pressures of S_2 and O_2 in the gas mixtures were computed by using the Gibbs energy minimization program SOL-GAS MIX[15]. During all the experiments, a total gas flow of approximately 400 ml/min was maintained. The measurements were carried out at three different temperatures, viz. 1773, 1848 and 1923 K. After the experiments, the samples were pulled to the cold part of the furnace and allowed to solidify. The sulphur content of the slag samples was determined by the stoichiometric combustion method[16].

3. RESULTS

The composition of the quaternary slags studied in the present work are presented in Table I. The experimental p_{S_2}/p_{O_2} ratio as well as the sulphur content obtained by analysis along with the sulphide capacities calculated using the experimental raw data are presented in Table II-IV. Two quinary slags were studied in the present work, at 1773 and 1848 K. The raw experimental data as well as the sulphide capacities calculated are presented in Tables V and VI respectively. Earlier studies have shown that the experiments were generally reproducible.

Table I: Slag compositions of the quaternary slags

Sample	$X_{Al_2O_3}$	X_{CaO}	X_{MgO}	X_{MnO}	X_{SiO_2}
S1	0.0287	0.313	0.0726	0	0.585
S2	0.0274	0.327	0.221	0	0.425
S3	0.0858	0.353	0.202	0	0.358
S4	0.115	0.156	0.291	0	0.438
S5	0.156	0.341	0.0791	0	0.424
S7	0	0.144	0.150	0.143	0.563
S8	0	0.237	0.200	0.103	0.459
S9	0	0.367	0.100	0.0519	0.481
S10	0.0288	0.314	0	0.0728	0.585
S11	0.0856	0.353	0	0.202	0.359
S12	0.115	0.157	0	0.290	0.438

Table II: Experimental data for sulphide capacity measurements of Al_2O_3-CaO-MgO-SiO_2-slags

Sample	Temp [K]	p_{S_2}/p_{O_2}	Wt-%S	C_S
S1	1848	125.64	0.00484	3.85e-5
S2	1773	221.59	0.0121	5.46e-5
S2	1848	125.64	0.0113	8.98e-5
S2	1923	107.24	0.0183	1.7e-4
S3	1773	221.59	0.0202	9.12e-5
S3	1923	107.24	0.0360	3.36e-4
S4	1848	125.64	0.00513	4.08e-5
S5	1773	221.59	0.0117	5.27e-5
S5	1923	107.24	0.00956	8.92e-5

Table III: Experimental data for sulphide capacity measurements of CaO-MgO-MnO-SiO_2-slags

Sample	Temp [K]	p_{S_2}/p_{O_2}	Wt-%S	C_S
S7	1923	107.24	0.0421	3.93e-4
S8	1773	221.59	0.0186	8.40e-5
S8	1848	125.64	0.0228	1.82e-4
S8	1923	107.24	0.0379	3.53e-4
S9	1773	221.59	0.0169	7.64e-5
S9	1848	125.64	0.0209	1.66e-4
S9	1923	107.24	0.0334	3.12e-4

Table IV: Experimental data for sulphide capacity measurements of Al_2O_3-CaO-MnO-SiO_2-slags

Sample	Temp [K]	p_{S_2}/p_{O_2}	Wt-%S	C_S
S10	1773	221.59	0.00673	3.04e-5
S10	1848	125.64	0.00788	6.27e-5
S10	1923	107.24	0.0225	2.10e-4
S11	1773	221.59	0.147	6.65e-4
S11	1848	125.64	0.117	9.31e-4
S11	1923	107.24	0.212	1.98e-3
S12	1773	221.59	0.0848	3.82e-4
S12	1848	125.64	0.0794	6.32e-4
S12	1923	107.24	0.129	1.20e-3

Table V: Composition of the Al_2O_3-CaO-MgO-MnO-SiO_2 five component slags studied in the present work

Sample	$X_{Al_2O_3}$	X_{CaO}	X_{MgO}	X_{MnO}	X_{SiO_2}
Q1	0.027	0.328	0.120	0.100	0.425
Q2	0.115	0.156	0.141	0.150	0.438

4. THE PRESENT MODEL

The mathematical model developed earlier in the Division of Theoretical Metallurgy has been described in detail in an earlier publication[8]. To give an orientation to the reader, some of the salient features of the model are presented in this section.

Table VI: Experimental data for sulphide capacity measurements of Al_2O_3-CaO-MgO-MnO-SiO_2-slags

Sample	Temp. K	p_{S_2}/p_{O_2}	Wt-%S	C_S
Q1	1773	221.59	0.0457	2.06E-04
Q1	1848	125.64	0.0694	5.53E-04
Q2	1773	221.59	0.0414	1.87E-04
Q2	1848	125.64	0.0335	2.67E-04

From the experimental data for C_S (FeO), the Gibbs energy of reaction (2) in the case of $FeO_{(l)}$ has been calculated to be

$$\Delta G = 118535 - 58.8157 \cdot T \quad [J/mole] \qquad (4)$$

In the modified version of the model[9], which is used in the present work, it was found necessary to represent the ratio, $a_{O^{2-}}/f_{S^{2-}}$ in equation (1) as an exponential function of the form:

$$\left(\frac{a_{O^{2-}}}{f_{S^{2-}}}\right) = \exp\left(-\frac{\xi}{RT}\right) \qquad (5)$$

while, in an earlier version a linear equation was used[8]. In the case of unary systems, ξ in equation (5) can be expressed as a function of temperature.

$$\xi = {}^1L + {}^2L \cdot T \qquad (6)$$

On the other hand, in the case of multi-component systems, ξ is a function of both temperature as well as composition. In the model, ξ in a multi-component system is expressed as

$$\xi = \Sigma X_i \xi_i + \xi_{Mix} \qquad (7)$$

where i stands for component i and X_i is the mole fraction of this component in the multi-component system. While the first term on the right hand side of equation (7) represents the "linear" variation of ξ from the pure components in the absence of the interaction between different species, the second term represents the part due to mutual interaction between different species. In the case of a binary system A-B, these two terms are illustrated in Fig. 3. As it is seen, the experimental values take into account the changes in the activity coefficient of the sulphide ions as a function of composition and thus the errors due to the constancy assumption are elegantly avoided in the present model.

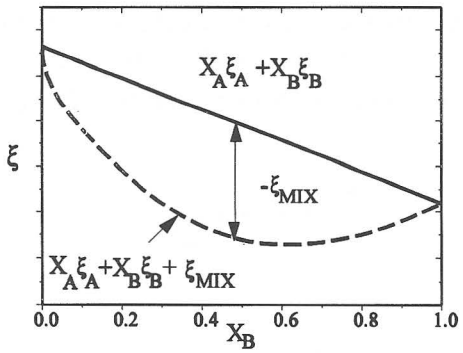

Figure 3. Schematic variation of ξ in a binary system A-B

The composition of the slag is represented in the model by the classical Temkin-Lumsden description wherein, all the complex species are considered to have disintegrated to simple entities. For example, SiO_4^{4-} was assumed to "decompose" into Si^{4+} and O^{2-}. The deviations from the true structure of the slags are mathematically compensated in the model.

ξ_{Mix} in equation (7) represents the variation of ξ due to the interactions between different species. In the case of oxide systems, only oxygen ions occur in the anionic grouping. Hence, ξ_{Mix} is expressed as:

$$\xi_{Mix} = \sum\sum y_{Ci1}\, y_{Ci2}\, L_{Ci1,Ci2(O^{2-})} + \left(\sum\sum\sum y_{Ci1}\, y_{Ci2}\, y_{Ci3}\, L_{Ci1,Ci2,Ci3(O^{2-})} + \left(\sum\sum\sum\sum y_{Ci1}\, y_{Ci2}\, y_{Ci3}\, y_{Ci4}\, L_{Ci1,Ci2,Ci3,Ci4(O^{2-})} + \cdots \right. \qquad (8)$$

The terms in equation (8) represent the binary, ternary and quaternary interactions between different species, respectively. The product in the first two-power summation stands for the interaction of the cations Ci1 and Ci2 when anion O^{2-} is present. Similarly, The products under the three-power and four-power summations represent the three-cation and four-cation interactions when anion O^{2-} is present.

The L parameters are expressed as polynomials. The binary interactions can be expressed as:

$$L_{Ci1,Ci2(O^{2-})} = ({}^0_bL_1 + {}^0_bL_2 \cdot T) + ({}^1_bL_1 + {}^1_bL_2 \cdot T)(y_{Ci1} - y_{Ci2}) + \qquad (9)$$

In the case of ternary interaction,

$$L_{Ci1,Ci2,Ci3(O^{2-})} = ({}^0_tL_1 + {}^0_tL_2 \cdot T) + \sum_{m\,=\,Ci1,Ci2} ({}^m_tL_1 + {}^m_tL_2 \cdot T)\, y_m \qquad (10)$$

The L parameters for four-cation interactions are expressed as:

$$L_{Ci1,Ci2,Ci3,Ci4(O^{2-})} = ({}^0_qL_1 + {}^0_qL_2 \cdot T) + \sum_{m\,=\,Ci1,Ci2,Ci3} ({}^m_qL_1 + {}^m_qL_2 \cdot T)\, y_m \qquad (11)$$

The choice of L parameters and how many of them should be taken into consideration in this model would depend on the system studied. In most cases, two or three parameters are found to be sufficient to describe the sulphide capacities in a given system.

A flow sheet of the computing procedure for the model calculations is shown in Fig. 4. It is seen that the model parameters are currently optimized to calculate the sulphide capacities directly. It is felt that, in future it is more appropriate to use the molar sulphide capacities for optimization as it has a fundamental basis. The normal sulphide capacities could, in turn, be computed from the molar sulphide capacities for industrial purposes.

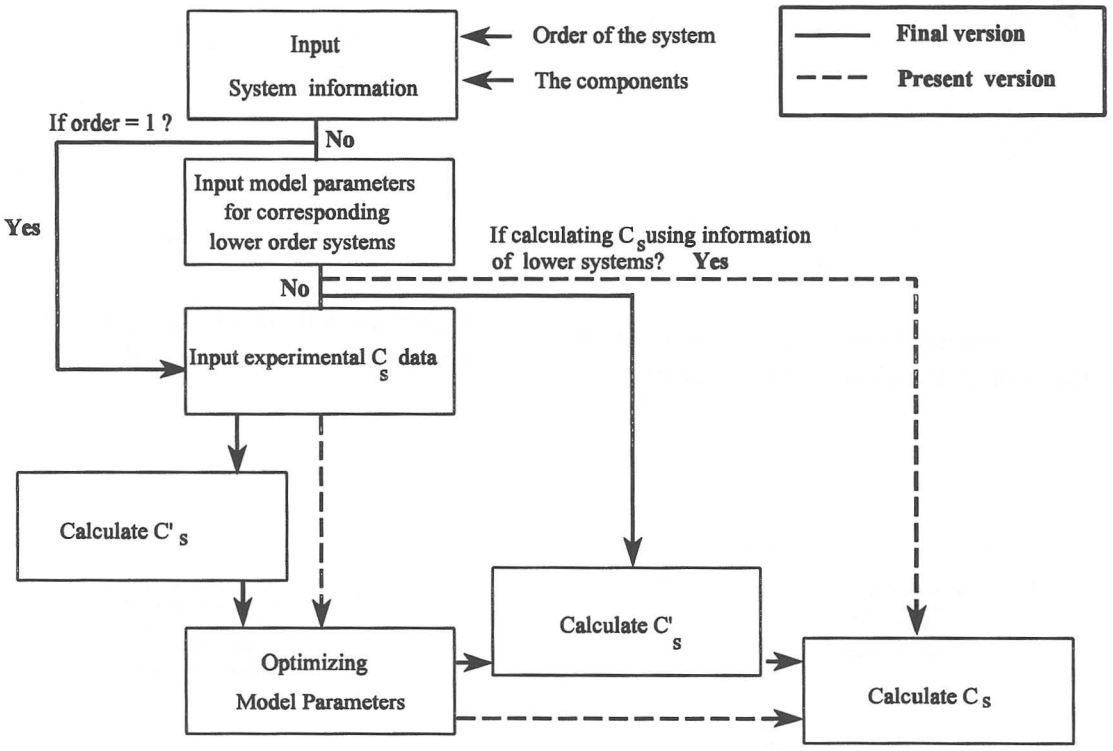

Figure 4. Flow sheet of sulphide capacity model calculations

5. DISCUSSION

The above model has been used to describe the experimental data in the binary systems CaO-Al_2O_3[12], CaO-SiO_2[9], MgO-SiO_2[14], and MnO-SiO_2[9]. It is to be mentioned that in the case of the system CaO-SiO_2 and MnO-SiO_2, the sulphide capacity data available in literature was found to be quite compatible with each other and no further experimental verification was carried out by the author. The sulphide capacities in these binaries are presented in Figures 5a - 5d respectively. The iso-Cs curves of the following ternary systems have been mapped out earlier using the model: CaO-MnO-SiO_2[9], CaO-MgO-SiO_2[14] and Al_2O_3-CaO-SiO_2[9]. These are presented in Figures 6, 7 and 8 respectively. The L parameters corresponding to the various unary, binary and ternary systems are presented in Table VII. It is seen that a minimum number of parameters (1 for unaries, 2-3 for binaries and ternaries) are sufficient to describe these systems.

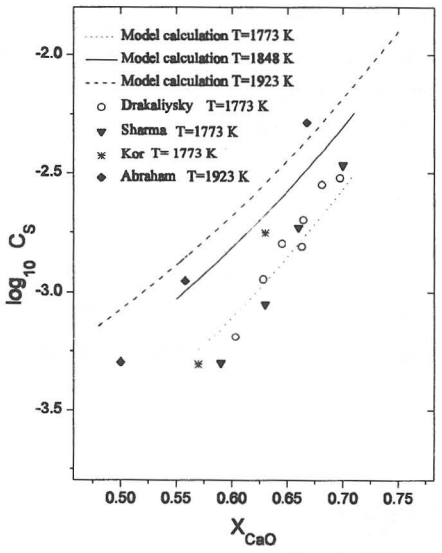

Figure 5a. Sulphide capacities as functions of composition in the $CaO-Al_2O_3$ system[12]

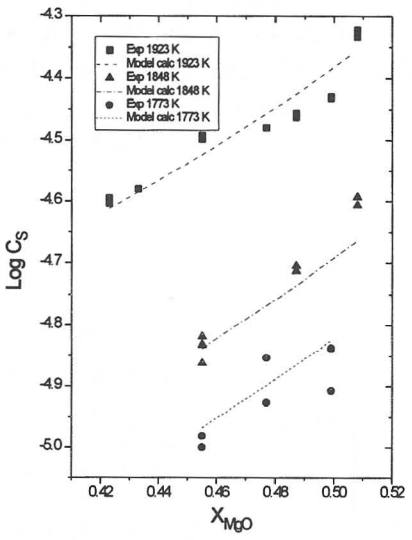

Figure 5c. Sulphide capacities as functions of composition in the $MgO-SiO_2$ system[14]

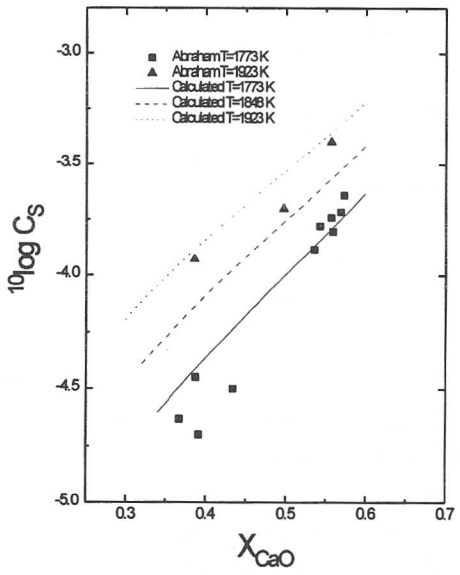

Figure 5b. Sulphide capacities as functions of composition in the $CaO-SiO_2$ system[9]

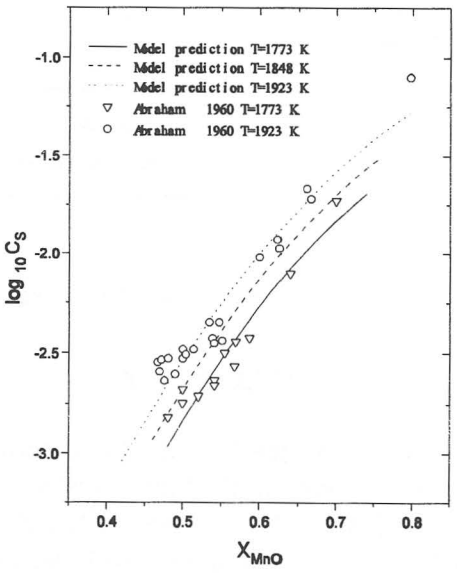

Figure 5d. Sulphide capacities as functions of composition in the $MnO-SiO_2$ system[9]

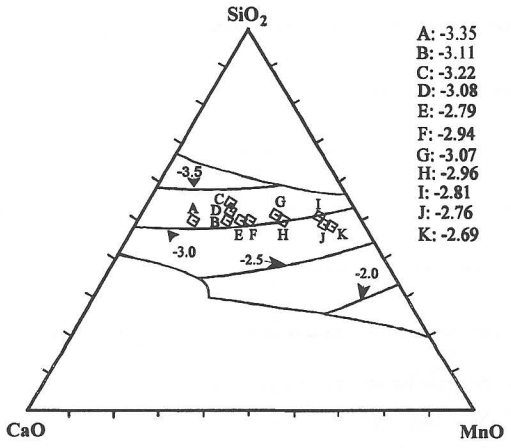

Figure 6. Iso-C_S diagram for the system CaO-MnO-SiO_2 system at 1873 K[9].

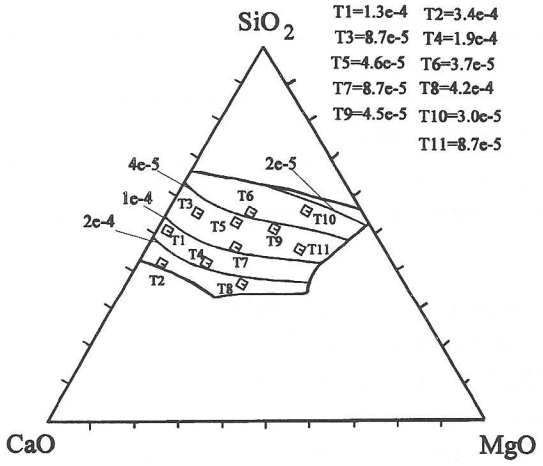

Figure 7. The iso-C_S contours in the system CaO-MgO-SiO_2 system at 1873 K[14].

In order to estimate the sulphide capacities of four and five component systems involving Al_2O_3, CaO, MgO, MnO and SiO_2, it is necessary to have access to the assessed C_S values for a number of other ternary systems. As experimental determination of the sulphide

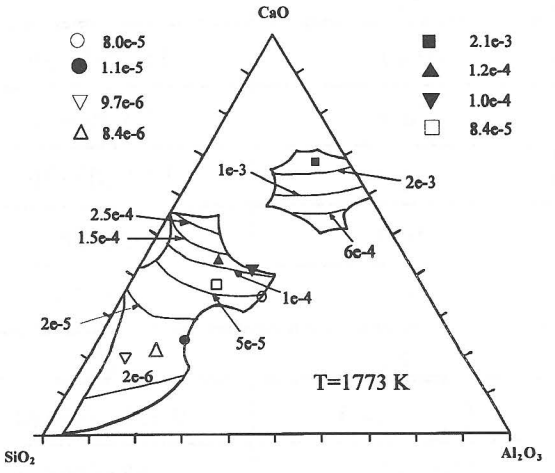

Figure 8. Iso-C_S diagram for the system Al_2O_3-CaO-SiO_2 system at 1773 K[9].

capacities of all these systems would be far beyond the resources available for the present work, attempts were made to evaluate the ternary parameters from the results of the measurements of Sharma and Richardson[17] for the systems Al_2O_3-MgO-SiO_2, Al_2O_3-MnO-SiO_2 as well as MgO-MnO-SiO_2. This is contrary to the established practice of the Division of Theoretical Metallurgy to use input data for models only after proper experimental confirmation. In this case, the policy proved to be correct and the literature values were found to be somewhat incompatible with rest of the data. Hence, the data reported by Sharma and Richardson were not included in the present optimization for obtaining the quaternary parameters. However, further experimental work in these systems is currently being carried out in the division and it is hoped that the data can be sorted out in the very near future.

From the model parameters in table VII, the sulphide capacities were computed corresponding to the various compositions of the four component systems studied and are presented in Tables VIII - X, along with the experimental data. The corresponding sulphide

Table VII: Model parameters previously assessed and used in the present work.

System	^{1}L		
Al_2O_3	157705.276		
CaO	-33099.425		
MgO	9573.07326		
MnO	-36626		
SiO_2	168873		
System	$^{0}_{b}L_1$	$^{0}_{b}L_2$	$^{Mn}_{b}L_1$
Al_2O_3-CaO	9.82827968e4	5.50734094e1	
Al_2O_3-SiO_2	1.86850468e5		
CaO-SiO_2	9.72717695e4	7.28749746e1	
MgO-SiO_2	6.97403222e5	-2.24084556e2	
MnO-SiO_2	-3.22911470e5	2.12029980e2	1.34860658e5
System	$^{0}_{t}L_1$	$^{0}_{t}L_2$	$^{Ca}_{t}L_1$
Al_2O_3-CaO-SiO_2	-2.03579264e6	6.86044695e2	
CaO-MgO-SiO_2	-1.52649771e6	6.25663842e2	
CaO-MnO-SiO_2	-1.17989159e6	6.21243714e2	-1.19111179e5

capacities calculated on the basis of the optical basicities are also presented in these tables. It is to be borne in mind that in these calculations, the experimental values for the four component systems, measured in the present work have not been included in the optimization. The model predictions are quite reasonable and show that the model can advantageously be used to calculate the sulphide capacities of the higher order systems from the lower order values with a certain degree of accuracy. This offers the advantage of minimum experimentation in the case of slags not hither to studied.

In the next step, the present experimental data were included along with those of Kärsrud[18] in the optimization of the L parameters for the four component systems. The L parameters for the three systems studied are presented in Table XI. From these parameters, the iso-C_S contours in these systems can very easily be computed by the model. But, it is important to realize that the phase-diagram information for some of these four component systems is lacking. However, to demonstrate the potentiality of the model calculation, the effect of the replacement of CaO by MgO as well as MnO at constant Al_2O_3 and SiO_2 contents ($x_{Al_2O_3} = 0.05$, $x_{SiO_2} = 0.47$) at 1873 K are presented in Fig. 9. The figure shows an increase of C_S if CaO is replaced with MnO. A similar trend has been observed

Table VIII: Comparison of the experimental C_S values with those predicted by the present model as well as optical basicity - system Al_2O_3-CaO-MgO-SiO_2

Sample	Temp [K]	Expt C_S	Calc C_S		
			Present model	Young et al.	Sosinsky
S1	1848	3.85E-05	3.42E-05	1.61E-05	3.05E-05
S2	1773	5.46E-05	6.84E-05	8.76E-05	7.28E-05
S2	1848	8.98E-05	1.26E-04	1.62E-04	1.42E-04
S2	1923	1.71E-04	2.22E-04	2.87E-04	2.62E-04
S3	1773	9.12E-05	1.63E-04	1.28E-04	1.11E-04
S3	1923	3.36E-04	4.58E-04	4.20E-04	4.30E-04
S4	1848	4.08E-05	5.35E-05	2.29E-05	3.95E-05
S5	1773	5.27E-05	6.41E-05	2.54E-05	4.39E-05
S5	1923	8.92E-05	1.76E-04	8.33E-05	1.44E-04

Table IX: Comparison of the experimental C_S values with those predicted by the present model as well as optical basicity - system CaO-MgO-MnO-SiO_2

Sample	Temp [K]	Expt C_S	Calc C_S		
			Present model	Young et al.	Sosinsky
S7	1923	3.93E-04	2.21E-04	9.95E-05	7.74E-05
S8	1773	8.40E-05	9.98E-05	8.07E-05	5.23E-05
S8	1848	1.82E-04	1.77E-04	1.50E-04	9.86E-05
S8	1923	3.53E-04	3.00E-04	2.64E-04	1.77E-04
S9	1773	7.64E-05	7.66E-05	8.76E-05	6.74E-05
S9	1848	1.66E-04	1.33E-04	1.62E-04	1.30E-04
S9	1923	3.12E-04	2.22E-04	2.87E-04	2.39E-04

Table X: Comparison of the experimental C_S values with those predicted by the present model as well as optical basicity - system Al_2O_3-CaO-MnO-SiO_2

Sample	Temp [K]	Expt C_S	Calc C_S		
			Present model	Young et al.	Sosinsky
S10	1773	3.04E-05	5.08E-05	1.33E-05	2.11E-05
S10	1848	6.27E-05	8.46E-05	2.47E-05	3.64E-05
S10	1923	2.10E-04	1.36E-04	4.36E-05	6.02E-05
S11	1773	6.65E-04	7.20E-04	3.26E-04	1.75E-04
S11	1848	9.31E-04	1.02E-03	6.04E-04	3.72E-04
S11	1923	1.98E-03	1.40E-03	1.07E-03	7.44E-04
S12	1773	3.83E-04	1.76E-04	5.69E-05	4.18E-05
S12	1848	6.32E-04	2.69E-04	1.05E-04	7.70E-05
S12	1923	1.20E-03	3.97E-04	1.86E-04	1.35E-04

Table XI: Model parameters assessed for the four components system studied in the present work.

System	${}^{0}_{q}L_1$	${}^{Al}_{q}L_1$	${}^{Ca}_{q}L_1$
Al_2O_3-CaO-MgO-SiO_2	3.41806552e6	4.90821794e4	
Al_2O_3-CaO-MnO-SiO_2	1.07019481e7	-7.27646198e7	
CaO-MgO-MnO-SiO_2	-1.48326261e6		1.33664894e6

Table XII: A comparison of the experimental results and the model estimations for the sulphide capacities of the five component system Al_2O_3-CaO-MgO-MnO-SiO_2

Sample	Temp [K]	Expt C_S	Calc C_S		
			Present model up to ternary parameters only	Young et al.	Sosinsky
Q1	1773	2.06e-4	1.87e-4	1.47e-4	9.25e-5
Q1	1848	5.53e-4	3.04e-4	2.73e-4	1.84e-4
Q2	1773	1.87e-4	7.43e-5	2.8e-5	3.11e-5
Q2	1848	2.67e-4	1.30e-4	5.19e-5	5.57e-5

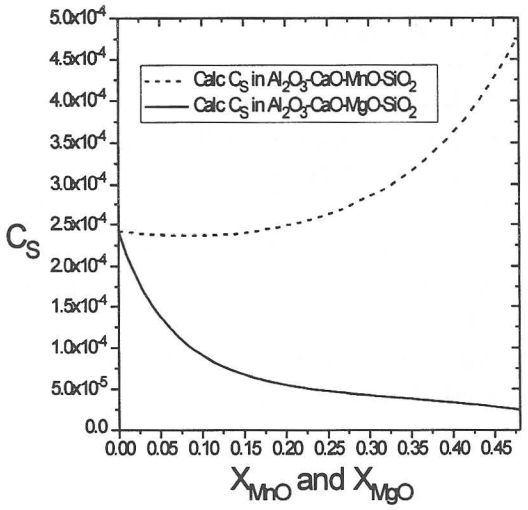

Figure 9. Effect of replacement of CaO by MgO or MnO at constant Al_2O_3 and SiO_2 content in the four component slags as computed by the present model ($x_{Al_2O_3} = 0.05$, $x_{SiO_2} = 0.47$).

previously[11] in the case of the ternary system CaO-MnO-SiO_2. If on the other hand CaO is replaced with MgO, a decrease in the C_S would be expected. Even this has previously been shown by Nzotta et al[14] in the case of the ternary system CaO-MgO-SiO_2.

The sulphide capacities of the five component system Al_2O_3-CaO-MgO-MnO-SiO_2 were evaluated using the model parameters up to the ternary. The calculations were made for those compositions and temperatures corresponding to the experimental points and are compared with the experimental data in Table XII. It is seen that the model predictions are in agreement with the experimental data.

The present model has no limitations with respect to the number of components in the slag. The calculations can easily be extended to six components, which are very important in iron- and steelmaking slags, viz. Al_2O_3-CaO-MgO-MnO-FeO-SiO_2 and infact, take into account the variation of the Fe^{2+} /Fe^{3+} ratio in the slag. This is made possible as the sulphide capacities of the quaternary system CaO-FeO-Fe_2O_3-SiO_2 have earlier been assessed in the Division of Theoretical Metallurgy[10]. However, such calculations need experimental verification which is beyond the scope of the present work. The advantage of the model is also that it can be conveniently used together with simulation models so that the sulphide capacities can be calculated during the continuous variation of the slag composition and temperature during the process. In the present version, the anion subgrouping has only one anion, namely O^{2-}. For slags containing CaF_2, the anion F^- can very easily be added into this subgrouping. Experiments are currently going on in the present laboratory to evaluate and include the model parameters corresponding to Cr^{3+}, Ti^{4+} and similar species that are of importance to steelmaking slags.

6. SUMMARY

In the present work, the sulphide capacities in three four component systems, Al_2O_3-CaO-MgO-SiO_2, Al_2O_3-CaO-MnO-SiO_2 and CaO-MgO-MnO-SiO_2 as well as the quinary system, Al_2O_3-CaO-MgO-MnO-SiO_2 at selected compositions and temperatures were experimentally measured and were compared with those predicted by the mathematical model developed in the Division of Theoretical Metallurgy, using the data from the lower order systems. It was shown that the model could predict the sulphide capacities of the multi-

component systems satisfactorily. The usefulness of the present model for computation of the Cs values of industrial slags is discussed.

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