APPLICATION OF THE GENERALISED CENTRAL ATOM MODEL TO OXIDE SLAGS

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ABSTRACT

The recent development in thermodynamic modelling of metallurgical systems at ArcelorMittal Maizières, Research and Development has resulted in a so-called the generalised central atoms (GCA) model. The model unifies the existing models for alloys and slags, such as the cell model, the oxi-sulphide model and the central atom model proposed by Lupis and Elliot, in the same formalism. The main feature of the GCA model is its ability to provide detailed descriptions of the short range order. Instead of pair interactions in the cell model the GCA treats interactions between the central atom and its neighbouring atoms as interactions among a cluster of atoms within its nearest neighbour shell. It is know that the cell model used for oxide slags encounters difficulties in treating complex behaviour, such as in the CaO-Al_2O_3–SiO_2 *system. This is because the pair wise approach is unable to provide accurate descriptions of impact of a third component, say* Al_2O_3, *on the interactions between CaO and* SiO_2 *in the ternary system.*

CSIRO has developed an extensive database for the cell model. The model and the database have been used in a wide range of ferrous and non-ferrous smelting applications. Through a collaborative research project between CSIRO and ArcelorMittal the capability of the GCA model in describing complex oxide slags has been assessed. The current work has shown that the GCA model is able to overcome some limitations of the cell model for the CaO-Al_2O_3–SiO_2 *system as is discussed in this paper.*

INTRODUCTION

Thermodynamic properties of slags have critical process implications for many metal production processes, such as in the production of clean steels, the interaction of the alloy phase with solid or liquid oxides (non-metallic inclusions for instance). Understanding of the interaction is greatly aided by well developed liquid oxide or slag models. The researchers at the ArcelorMittal Maizières, Research and Development (AMMRD), formerly IRSID have made significant contributions in modelling thermodynamic properties of liquid slag. In 1984 Gaye and Welfringer [1] first demonstrated the successful application of a thermodynamic model, i.e., the cell model, to multi-component liquid slags. Nowadays, slag models are available in most common thermodynamic packages. Some software offers extensive database for oxides, sulphides and halites.

The cell model was proposed by Kapoor and Frohberg [5], initially for binary and ternary silicate melts. Gaye and Welfringer [1] extended the model and applied it to multi-component steel making slags (up to six components) by using only binary parameters. This slag model has been further extended to include second and third anions, i.e., S^{2-} and F^{-}[2], and other common oxide species, such as P_2O_5, Cr_2O_3 [2] and TiO_2 [7, 14] in steel making slags. It is also one the core models in an in-house equilibrium calculation code CEQCSI (Chemical Equilibrium Calculations for Steel Industry) more and more commonly used in ArcelorMittal group [10].

The limitations of the cell model by using only binary parameters in the $CaO\text{-}Al_2O_3\text{–}SiO_2$ system were recognized by Gaye and Welfringer [1]. It was mentioned that in order to fit the data in the practical region for iron and steelmaking, i.e., low silica and low alumina towards $CaO\text{-}SiO_2$ edge well, the fit by the model in the silica rich side of the $Al_2O_3\text{–}SiO_2$ edge was not satisfactory. The deficiency of the approach suggests that using binary parameters only was not able to account for the short-range order exhibited in some complex oxide systems.

The CSIRO group adopted and further developed the cell model far beyond the iron and steel application. The models and the database include a substantial list of oxide species commonly found in both ferrous and non-ferrous metal smelting. The model was incorporated in a computational package, Multi-Phase Equilibrium (MPE) software [19, 20]. Models of transport properties of the slag are also incorporated. The MPE software has been used by researchers and plant metallurgists for the prediction of the multiphase equilibria, and the viscosity and electrical conductivity of the slags.

In developing the cell model database limitations of the cell model were examined closely. It was found that the cell model using only binary parameters gave large errors in calculated silica activity and phase diagrams in the $CaO\text{-}Al_2O_3\text{-}SiO_2$ system in spite of the reasonably accurate descriptions for the binary behaviour. This was due to the inability of the model to account for the complex behaviour in the ternary system by mixing of two binary silicates of $CaO\text{-}SiO_2$ and $Al_2O_3\text{-}SiO_2$ with uneven interactions. In order to overcome the limitations of the cell model an approach was taken to modify the cell model by introducing ternary parameters. The results showed that the modified model provided satisfactory fit to the SiO_2 activity and the liquidus surface [21].

To overcome the limitations of the existing models, 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]. The applicability of the GCA model to molten slags has been the subject of a collaborated research effort between CSIRO and AMMRD. The initial focus has been the $CaO\text{-}Al_2O_3\text{–}SiO_2$ system. This paper presents some of the early findings.

THE SLAG MODELS

The Cell Model

In the cell model oxide melts were treated as a mixture of cells formed among oxygen anions and metal *cations*. For example, the basic structural units considered in a binary MO-SiO_2 system (M=Ca, Mg, Mn, Pb and so forth) are symmetric cells M-O-M and Si-O-Si, and asymmetric cells M-O-Si. The oxygen in a M-O-M cell represents a free oxygen ion (O^{2-}), in a Si-O-Si cell a bridging oxygen (O^0) and in a M-O-Si cell a non-bridging oxygen (O^-). In Gaye and Welfringer's [1] implementation, the model parameters available were the cell formation energy, $W_{M\text{-}Si}$ and the cell interaction energy, $E_{M\text{-}Si}$ for M-O-Si cells. Both $W_{M\text{-}Si}$ and $E_{M\text{-}Si}$ may also include composition dependent terms. In ternary and multi-component systems only the formation and the interaction energy parameters obtained for binary systems were used.

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 [11]. In this approach the cell model for the slag phase (oxides and oxi-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. Instead of pair interactions as in the cell model the GCA model considers interactions between the central atom and its neighbouring atoms as interactions among a cluster of atoms within its nearest neighbour shell.

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:

$i_1, i_2, \ldots i_k, \ldots i_t$	Atoms on cationic shell
J	Central atom
$j_t+1, \ldots j_r, \ldots j_m$	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 of the cell is $\varphi^J_{\{i\},\{j\}}$ where J represents the central atom and {i} and {j} presents the whole set of cations and anions respectively. For the sake of simplicity, this energy term is assumed as the sum of the contributions of the two shells:

$$\varphi^J_{\{i\},\{j\}} = \varphi^J_{\{i\}} + \varphi^J_{\{j\}} \tag{1}$$

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 [8].

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

Equation 2 applies to both cations and anions. Details of the formulism of the GCA model have been given by Lehmann [9, 10].

In the GCA model the number of parameters depends on the type of neighbouring atoms within the nearest neighbour shell for the centre atom. In a M_1O-M_2O-SiO_2 (M_1, M_2, Si as cations) ternary oxide system, the formation energy parameters consist of binary terms, $\varphi_{\text{M1-Si}}$, $\varphi_{\text{M2-Si}}$ and $\varphi_{\text{M1-M2}}$ and ternary terms $\varphi_{\text{M1-M2-Si}}$, $\varphi_{\text{M2-Si-M1}}$ and $\varphi_{\text{Si-M1-M2}}$. A similar set of interaction energy parameters is also available. In addition, both composition and temperature dependent terms can be used if required. In the current work these model parameters were used for the CaO-Al_2O_3–SiO_2 system and were optimised by using a special version of the PARROT program in the Thermo-Calc Software [17].

RESULTS AND DISCUSSION

The modelling results for the CaO-Al_2O_3–SiO_2 system will be presented to show the applicability of the GCA model to oxide slags. It should be mentioned that the current implementation of the GCA model for the liquid oxides embeds the cell model as a special case. As a result the cell model parameters can be transferred directly into the GCA model for systems in which cell model provides satisfactory descriptions. This makes it easy for converting the cell model database to that of the GCA model.

The cell model has been shown to provide satisfactory descriptions for the three sub-binary systems, i.e., CaO-SiO_2, [18] CaO-Al_2O_3 and Al_2O_3–SiO_2 [21] in the CaO-Al_2O_3–SiO_2 system. The cell model parameters for the CaO-Al_2O_3 and Al_2O_3–SiO_2 binaries were used in the GCA model to obtain identical results as in the cell model. In the case of the CaO-SiO_2 binary the GCA model parameters were re-determined and the results are comparable with those of Taylor and Dinsdale [18].

The CaO-Al_2O_3–SiO_2 System

The CaO-Al_2O_3-SiO_2 ternary system has its practical importance as it can be considered as a base system for many metallurgical slags. Some published activity data [3, 4, 6, 12, 13, 22] and phase diagrams [16] are available for this system. The modelling results of the GCA model using binary plus ternary parameters will be shown in comparison with the published data. Comparison to the cell model using only binary parameters will also be presented.

Liquidus

Figure 1 shows a comparison between the calculated (GCA and cell) and the published liquid phase boundary [16] at 1400 and 1600°C in the CaO-Al_2O_3-SiO_2 system. The same values of the Gibbs free energy of formation of the two ternary compounds $Ca_3Si_2O_7$ and $CaAl_2Si_2O_8$ were used for both the GCA model and the cell model. It can be seen that the GCA model reproduces closely the published liquidus at both temperatures. The results of the cell model showed the calculated liquid region at 1400°C hardly visible in the diagram. There was only a very limited area close to the centre of the CaO-Al_2O_3 binary. The calculated liquid regions at 1600°C by the cell model were smaller than the published data. In other words the cell model predicts larger stability regions for solid phases, such as

SiO_2, Ca_2SiO_4, and $Al_6Si_2O_{13}$ than the published data. As a consequence the liquid slag stability region calculated by the cell model is smaller than what it should be. This is due to errors in the calculated component activities as will be discussed below.

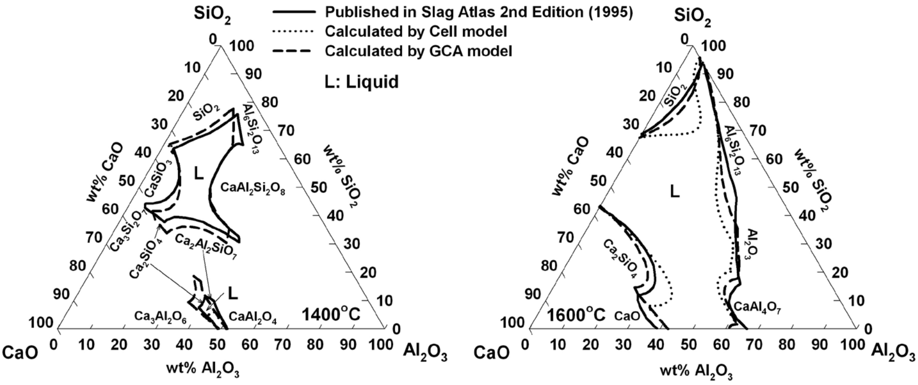

Figure 1: Comparison between the calculated liquid phase boundary and the published data [16] at 1400 and 1600ºC in the CaO-Al_2O_3-SiO_2 system

SiO_2 Activity

The calculated SiO_2 iso-activity (solid SiO_2 as standard state) curves by both the cell model and the GCA model are shown in Figure 2. The published data for 1550˚C [6] and 1600˚C [13] are also shown for comparison. It is apparent that there is a large discrepancy between the published data and the calculated activity using the cell model. The disagreement between the model and the experimental data is greater for high SiO_2 activity values with increasing Al_2O_3 content in the ternary. For example, when the Al_2O_3 content approaches 40 wt %, the calculated iso-activity curve for $a_{SiO_2} = 0.9$ is almost at the same composition as that at which the measured a_{SiO_2} is 0.5. In other words, the model overestimates SiO_2 activity by about 0.4, almost twice the measured values at these compositions. Much improvement, however, can be seen for the GCA model, although the fit to high SiO_2 tends to deteriorate with increasing Al_2O_3.

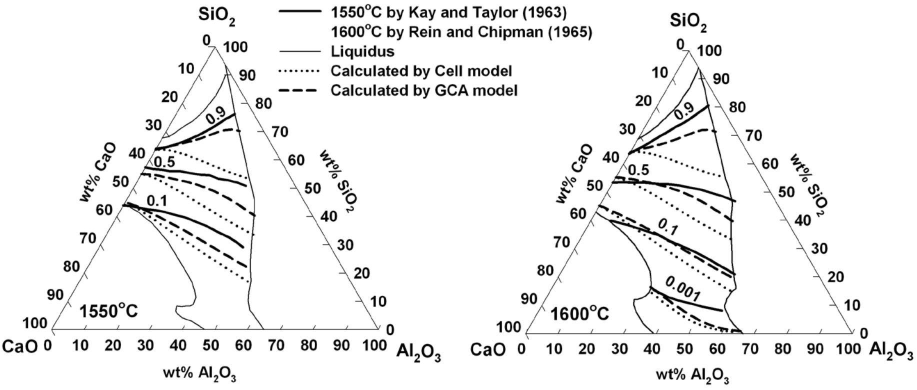

Figure 2: Comparison between the calculated activity of SiO_2 and the published data [6, 13] in slags at 1550 and 1600ºC in the CaO-Al_2O_3-SiO_2 system

The error in the calculated component activities in the $CaO\text{-}Al_2O_3\text{-}SiO_2$ system by the cell model is a major cause of error in the calculated liquid regions. The effects seem to become more prominent towards low temperatures as indicated by the large error in the calculated liquid region at 1400˚C (Figure 1).

CaO Activity

The modelling calculations were also compared with the published CaO activity data (solid CaO as standard state) by Kalyanram *et al.* [3] at 1500˚C and by Zhang *et al.* [22] at 1600˚C in Figure 3. General agreement between the calculated values using both models and the data are observed. The only noticeable discrepancy can be seen for $a_{CaO} = 0.003$ towards the $CaO\text{-}SiO_2$ binary at both 1500 and 1600˚C. There is no significant difference between the GCA model and the cell model in terms of the calculated CaO activity.

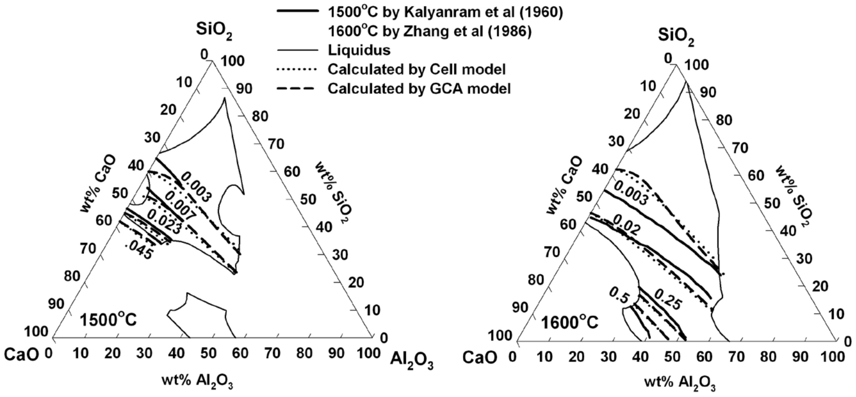

Figure 3: Comparison between the calculated activity of CaO and the published data for 1500ºC [3] and 1600ºC [22] in the $CaO\text{-}Al_2O_3\text{-}SiO_2$ system

Al_2O_3 Activity

The directly measured activity for Al_2O_3 has not been found in the $CaO\text{-}Al_2O_3\text{-}SiO_2$ system. Figure 4 plots the calculated iso-activity curves for Al_2O_3 (solid Al_2O_3 as standard state). There is significant difference between the cell model and the GCA model for $a_{Al_2O_3} = 0.1$ and 0.01 at both 1500 and 1600˚C. The difference is more pronounced along the $CaO/SiO_2 = 1$ to Al_2O_3 join. The fact that the GCA model fits closely to the published liquidus (Figure 1) suggests that the calculated Al_2O_3 activity values by the GCA model are consistent with the activity data for other components and the phase diagrams, and are therefore relatively accurate. The errors in $a_{Al_2O_3}$ predicted by the cell model may be large and may contribute significantly to the errors in the calculated liquidus.

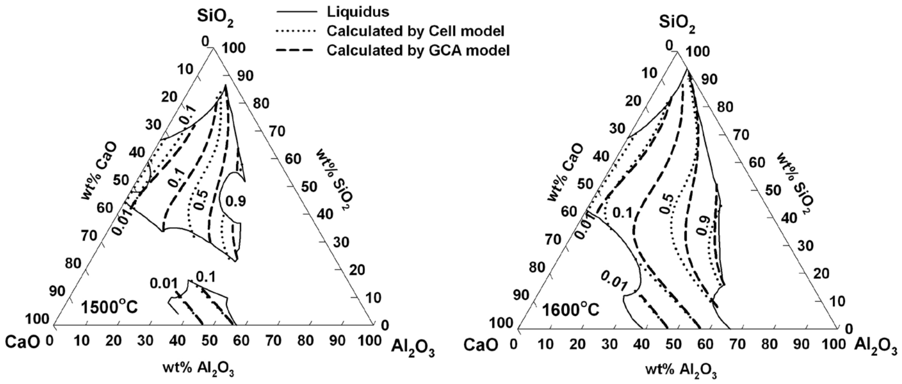

Figure 4: Calculated activity of Al_2O_3 in slags at 1500 and 1600ºC in the $CaO-Al_2O_3-SiO_2$ system

SiO2 Activity in Low Silica Region

The SiO_2 activity in the low silica region is of particular interest to the steelmakers. Here the uncertainties associated with the published data are significant. This may partly relate to difficulties with the measurements. Taking a_{SiO_2} = 0.0001 iso-activity curve as an example, there are three sets of data shown in Figure 5 which were by extrapolation of the measured points [4, 12, 13]. The discrepancy among the data is quite obvious. The silica composition varies from 1.1 to 7.7 wt%, a factor of 7 for a_{SiO_2} = 0.0001 along the CaO/Al_2O_3 =1 to SiO_2 join.

The calculated iso-activity curves are also shown in Figure 5 for comparison. It can be seen that the calculated values by the GCA model is slightly higher than those of the cell model. Both modelling results are in closer agreement with the data by Kang and co-workers [4] than the other two sets of data [12, 13]. The model predicted higher SiO_2 activity values than the data towards Al_2O_3 rich side (Al_2O_3 wt%>55).

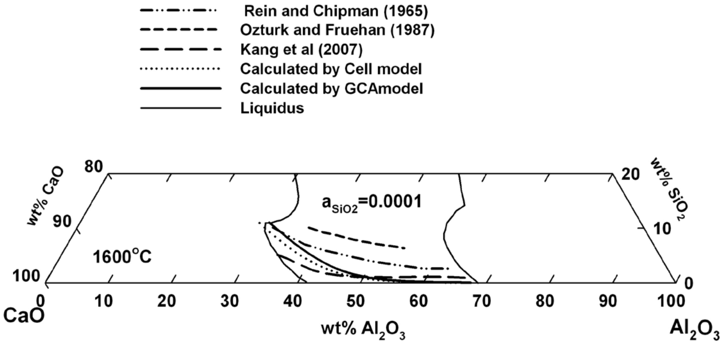

Figure 5: Comparison between the calculated a_{CaO} = 0.0001 iso-activity curves in low silica region and the published data [4, 12, 13] at 1600ºC in the $CaO-Al_2O_3-SiO_2$ system

Modified Cell Model using Ternary Parameters

As mentioned in the introduction, an attempt has been made at CSIRO to introduce ternary parameters in the cell model so as to overcome some of the limitations of this model. The modeling results for the $CaO-Al_2O_3-SiO_2$ system showed that the modified model provided satisfactory fit to the SiO_2 activity and the liquidus surface [21].

In fact the accuracy of the modified cell model is comparable with that of the GCA model presented above. This suggests that in the CaO-Al_2O_3–SiO_2 system the complex behaviour, such as the influence of the third component Al_2O_3 on the interactions between CaO and SiO_2 can be described by either introducing ternary interaction parameters in cell model or detailed short-range order interactions in the GCA model which in essence count for ternary effects and more.

CONCLUSIONS

The applicability of the generalised central atoms (GCA) model has been investigated for oxide slags. The GCA model is able to reproduce published liquidus and component activities with much improved, for the CaO-Al_2O_3–SiO_2 system, comparing with the cell model using binary parameters only. This suggests that the GCA model's description of the short range order is of advantage in modelling complex oxide systems. For example in the CaO-Al_2O_3–SiO_2 system, the influence of the third component Al_2O_3 on the interactions between CaO and SiO_2 can be described well by the GCA model. The applicability and the potential of the GCA model will be explored further for other oxide systems with complex behaviour.

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