

An Approach to Modeling Al₂O₃ Containing Slags with the Cell Model

L. Zhang, S. Sun and S. Jahanshahi

(Submitted October 24, 2006)

The cell model originally developed by Kapoor and Frohberg for binary and ternary silicate melts was later extended to multi-component liquid slags by Gaye and Welfringer. CSIRO has extended the application of this model to describe the behaviour of a large number of oxide species commonly found in metallurgical slags. One limitation of the model was that when using only binary parameters to model ternary or higher order systems, the thermodynamic behaviour of the components in Al₂O₃ containing systems cannot be represented accurately. Based on an analysis of the structural role played by oxide components in the CaO-Al₂O₃-SiO₂ system, two ternary parameters have been introduced to account for the influence of Al₂O₃ on Ca-Si interaction and CaO on Al-Si interaction, respectively. The introduction of the ternary parameters resulted in significant improvements in the model description of Al₂O₃ containing ternary and higher order systems. As a structurally based model, the cell model calculates parameters related to the degree of polymerization in silicate melts. These parameters have been used in a structurally based viscosity model for calculating the viscosity of silicate melts. The fit to a recent set of data has demonstrated the capability of the viscosity model to account closely for the cation effects.

Keywords Al₂O₃, cell model, silicate melts, phase diagram

1. Introduction

In simulation of the processing of alloy materials, thermodynamic models for the liquid alloy, the solid solutions and various intermetallic compounds are widely used. For some processes, such as the production of clean steels, interaction of the alloy phase with solid or liquid oxides (non-metallic inclusions for instance) has critical process implications. Understanding of the interaction is greatly aided by well-developed liquid oxide or slag models.

There are a number of slag models that offer varied levels of success in representing the thermodynamics of liquid slags. Gaskell has presented an excellent review of the earlier developments and a comparison of the models for binary silicate slags.^[1] More recently, Saunders and Mio-

downik provided a review of some of the more commonly used models within various thermodynamic packages.^[2] Among these, the so-called cell model was developed by Kapoor and Frohberg,^[3] initially for binary and ternary silicate melts. Gaye and Welfringer at IRSID extended the model in the 80s to multi-component liquid slags.^[4] It was demonstrated that the model could be applied to multi-component steel making slags (up to six components) by using only binary parameters. This was the first slag model developed for real industrial multi-component slags at the time and was considered to be a remarkable advance in slag modelling. Further extensions of the model by the IRSID researchers include the addition of second and third anions, i.e., S and F species,^[5] and other common oxide species, such as P₂O₅, Cr₂O₃^[5] and TiO₂^[6] in steel making slags. One useful feature of the cell model is that structural information in terms of the fractions of free, bridging and non-bridging oxygen can be generated to describe the degree of polymerization of silicate melts. Subsequently, the calculated structural parameters could be used to correlate properties, such as viscosity, which strongly depend on the structure of the melts.

The CSIRO group adopted and further developed the cell model to 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).^[7,8] The MPE has been used by researchers and plant metallurgists for the prediction of the multiphase equilibria, and the viscosity and electrical conductivity of the slags as well.

One of the unique features of the MPE package is the inclusion of a structurally based predictive model, which calculates the viscosity of homogeneous liquid slags^[9-11] and estimates the viscosity of slags containing up to 30 wt.%

This article was presented at the Multi-Component Alloy Thermodynamics Symposium sponsored by the Alloy Phase Committee of the joint EMPMD/SMD of The Minerals, Metals, and Materials Society (TMS), held in San Antonio, Texas, March 12-16, 2006, to honour the 2006 William Hume-Rothery Award recipient, Professor W. Alan Oates of the University of Salford, UK. The symposium was organized by Y. Austin Chang of the University of Wisconsin, Madison, WI, Patrice Turchi of the Lawrence Livermore National Laboratory, Livermore, CA, and Rainer Schmid-Fetzer of the Technische Universität Clausthal, Clausthal-Zellerfeld, Germany.

L. Zhang, S. Sun, and S. Jahanshahi, CSIRO Minerals, Box 312 Clayton South, VIC 3169, Australia. Contact e-mail: ling.zhang@csiro.au

Section I: Basic and Applied Research

solids^[7]. To support the development of the database, measurements of various properties, such as phase equilibria,^[12,13] viscosity^[14,15] and electrical conductivity^[16] in the relevant regions for both synthetic materials and industrial samples were often carried out to provide critical data for model optimization and validation. The MPE database currently contains optimized parameters for a wide range of oxide components, such as SiO₂, Al₂O₃, Cr₂O₃, TiO₂, Ti₂O₃, Fe₂O₃, FeO, CaO, MgO, MnO, CrO, PbO, NiO, CoO, ZnO, Na₂O and Cu₂O (Na₂O is not yet included in the viscosity model).

The so-called CALPHAD approach^[2] was generally taken in the development of the multiphase thermodynamic database. In this process the published thermodynamic and phase equilibria data on various systems of interest are compiled and critically assessed. Then appropriate thermodynamic models are adapted and/or extended to obtain sets of self-consistent parameters for solution phases. In most cases the parameters of thermodynamic models were obtained for lower order systems, such as binary and ternary systems. One of the challenges in applying the CALPHAD technique to industrial systems is the extrapolation of the model descriptions beyond binary and ternary systems. Although a high degree of accuracy can be achieved for lower order systems, the success of the extrapolation of the models to higher order systems is often not guaranteed. The degree of success of the extrapolations can vary significantly with the constituents that form the real system.

Although covering a broad range of applications, such as, non-ferrous, ferro-alloy as well as iron and steelmaking, an approach was taken at CSIRO in the development of the slag database by using a single set of unified and critically assessed thermochemical data. The cell model parameters were obtained for binary systems of interest by fitting available thermodynamic data and phase diagrams. The model descriptions for ternary and higher order systems were examined and validated against the measured activity and phase equilibrium data. In some cases refinement of the binary parameters was required in order to provide reasonable fit to both binary and higher order systems.

It was found that if a ternary is made of the same type of binary systems, for example, CaO-SiO₂, MgO-SiO₂, MnO-SiO₂ and FeO-SiO₂, the model can represent the measured activity and phase diagram satisfactorily by using only binary parameters. The CaO-MgO-SiO₂ ternary can be considered to be formed by mixing two binaries of CaO-SiO₂ and MgO-SiO₂. The behaviour of the two binaries was found to be similar; i.e., the component activities in the slag phase showed very strong negative deviations from ideality. The formation of the ternary can be considered as substitution of MgO for CaO in the CaO-SiO₂ binary at a given silica content or vice versa. Significant structural changes are not expected in this case and the activities of the components are not expected to vary greatly. This relates to the fact that the CaO-MgO binary exhibits nearly ideal behaviour in the liquid phase, and the value of the cell formation energy $W_{\text{Ca-Mg}}$ is close to zero. This justifies the consideration of simple cation substitution by replacing a Ca²⁺ with a Mg²⁺ cation.

However, for Al₂O₃ containing ternary systems, such as the CaO-Al₂O₃-SiO₂ system, it was found that the binary parameters determined for Al₂O₃-SiO₂, CaO-Al₂O₃, CaO-SiO₂ were not able to predict accurately the SiO₂ activity nor the liquidus surface in the ternary system. It is expected that the model representation of the higher order Al₂O₃ containing systems will also be in error for the same reason.

In the CaO-Al₂O₃-SiO₂ ternary, the two silica containing binaries, CaO-SiO₂ and Al₂O₃-SiO₂, are also very different from each other. Unlike the CaO-SiO₂ system, where the component activities showed very strong negative deviations from ideality, the calculated component activity (using parameters obtained by fitting the phase diagram) in the Al₂O₃-SiO₂ binary showed slightly positive deviation from ideality. When the two binaries are mixed to form a ternary system, it is no longer a case of cation substitution of Al₂O₃ for CaO in the CaO-SiO₂ binary at a given silica content. Strong Ca-Al interactions exist in the CaO-Al₂O₃ binary system, i.e., both Al₂O₃ and SiO₂ compete for CaO. Thermodynamic properties seem to suggest that the effect could be two-fold; on the one hand, addition of CaO to the Al₂O₃-SiO₂ binary appears to make Al-O-Si cells more stable. Addition of Al₂O₃ to the CaO-SiO₂ binary could lead to weakening of the interactions in Ca-O-Si cells. The uneven interactions are likely to impose some structural changes from the binary. In the cell model, binary parameters alone seem unable to describe such complex behaviour.

The modeling results of Gaye and Welfringer^[4] showed that the agreement between the calculated liquidus surface and the published phase diagram was very poor towards the Al₂O₃-SiO₂ rich region in the CaO-Al₂O₃-SiO₂ system. A compromise was made that the set of parameters adopted was able to produce accurate SiO₂ activity for the domain of interest for iron and steel making slags. However, the model is not suitable for the Al₂O₃-SiO₂ binary and other ternary and higher order systems at the Al₂O₃-SiO₂ rich edge.

Examination of the behaviour of the various components suggests that it may be helpful to introduce some ternary parameters to the cell model to account for the effect of the third component C on an A-B binary system. Similar approaches by using the ternary parameters in the slag model has been shown to be helpful in the case of the modified quasi-chemical model in modeling the CaO-Al₂O₃-SiO₂ system by Eriksson and Pelton.^[17] In the present article modeling of the CaO-Al₂O₃-SiO₂ system including the binaries using the cell model will be discussed. The modification of the cell model by introducing ternary parameters will be described and the modeling results presented. Furthermore the behaviour of the individual oxides on structure, thermodynamic properties and viscosity of the silicate melts in general are analyzed.

2. The Cell Model

A detailed formulation of the cell model has been given for silicate melts in the literature by Kapoor and Froberg^[3]

and Gaye and Welfringer.^[4] The model treats the melt as a mixture of cells formed among oxygen atoms and “cations”. For example, the basic structural units considered in a binary MO-SiO₂ 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 (O²⁻), in a Si-O-Si cell a bridging oxygen (O⁰) and in a M-O-Si cell a non-bridging oxygen (O⁻). Model parameters to be determined are the cell formation energy W_{M-Si} and the cell interaction energy E_{M-Si} used in the expression of the free energy of mixing, while the terms W_{M-Si} and E_{M-Si} can be functions of both temperature and composition. In our work the model parameters were in most cases optimized by using a special version of the PARROT program in the Thermo-Calc package,^[18] which works by minimizing an error sum and is capable of handling various kinds of experimental input data. Details of our modeling methodology and procedures have been given elsewhere.^[7] In our modeling the Gibbs energy of formation of species for common elements and their compounds is derived from the SGTE (Scientific Group Thermodata Europe) database^[19,20] and Thermochemical Data of Pure Substances by Barin.^[21] A systematic approach was taken in the modeling work and the attempt was made to build up the model description of the ternary and higher order systems based on binary systems where accurate descriptions were obtained.

2.1 The Binary Systems CaO-SiO₂, CaO-Al₂O₃ and Al₂O₃-SiO₂

In the current MPE database, the thermodynamic data as well as the cell model parameters assessed by Taylor and Dinsdale^[22] for the CaO-SiO₂ system are used. As shown in their article,^[22] a satisfactory fit to the published silica activities and phase diagram, except the miscibility region on the silica rich side, was obtained. The assessment of the CaO-Al₂O₃ and Al₂O₃-SiO₂ binary systems were carried out by the present authors. The slag model parameters of the two binary systems were optimized to reproduce the published component activities in the liquid phase and the phase diagrams. Figures 1 and 2 show the comparison between the calculated and the published phase diagrams for the CaO-Al₂O₃^[23-26] and Al₂O₃-SiO₂^[23,24,26-29] binary systems, respectively. Figure 3 shows a comparison between the published activity data (solid as standard state) and calculated values for CaO and Al₂O₃ in slags at 1500^[30,31] and 1787 °C^[32] in the CaO-Al₂O₃ system. It can be seen that the calculated liquidus and activities are in close agreement with the published data. The results are also comparable with other published modeling results by the modified quasi-chemical model^[17] and ionic model.^[33] It should be pointed out that the mullite in the Al₂O₃-SiO₂ binary was treated as a stoichiometric compound in the MPE rather than a solid solution phase as in the other two models. Nevertheless, such an approach may cause some error in the solid region and will not have a great effect on the description of the liquid phase. In other words the difference in the slag model parameters for the two cases should be minor.

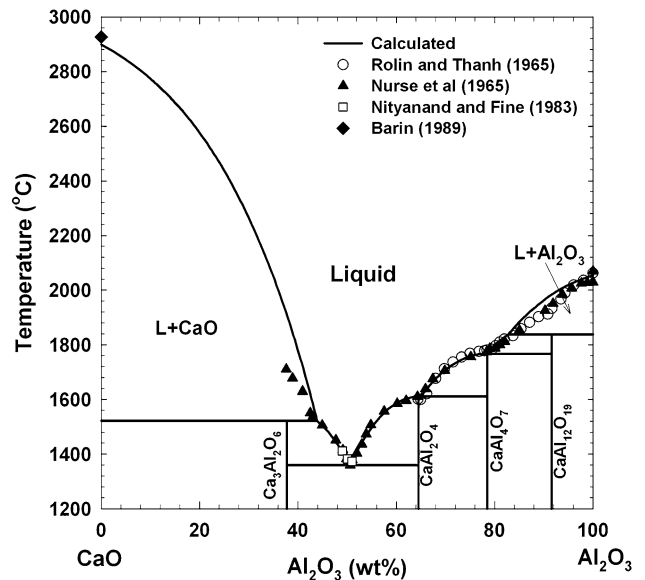


Fig. 1 Comparison between the calculated phase diagram and the experimental data^[23-26] for the CaO-Al₂O₃ system

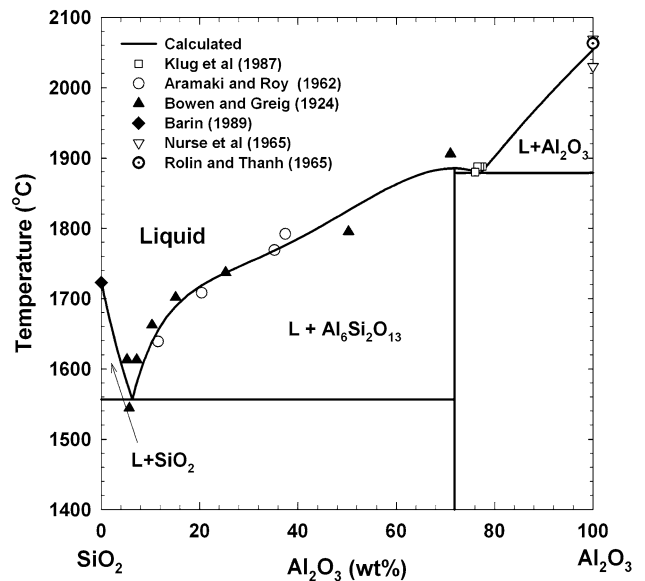


Fig. 2 Comparison between the calculated phase diagram and the experimental data^[23,24,26-29] for the Al₂O₃-SiO₂ system

2.2 The CaO-Al₂O₃-SiO₂ Ternary System

The CaO-Al₂O₃-SiO₂ ternary system can be considered as a base system for various types of slags. There are some well-established activity data^[34,35] and a phase diagram^[36] for this system.

Our first attempt was to use the binary parameters only to predict the ternary behaviour. Figure 4 shows the comparison between the calculated SiO₂ activity values and the published data at 1550 and 1600 °C, respectively.^[34,35]

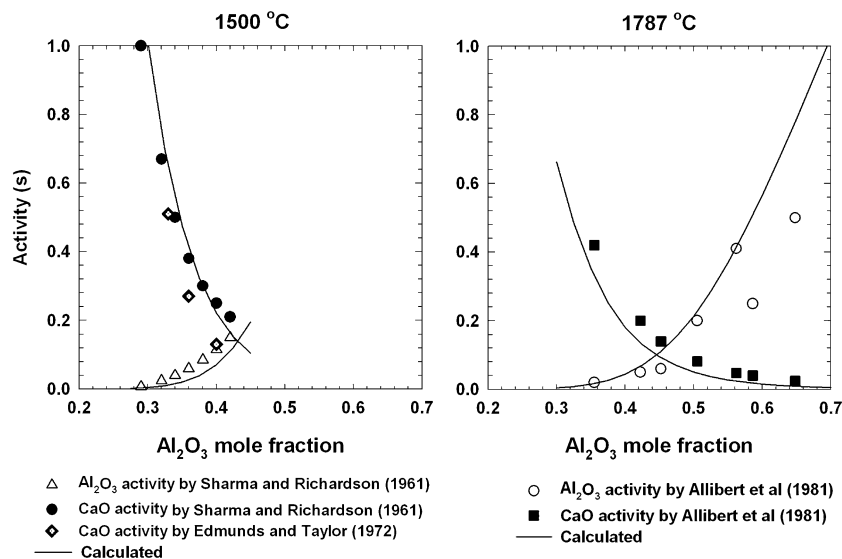


Fig. 3 Comparison between the published^[30-32] and the calculated activity of CaO and Al₂O₃ in slags at 1500 and 1787 °C in the CaO-Al₂O₃ system

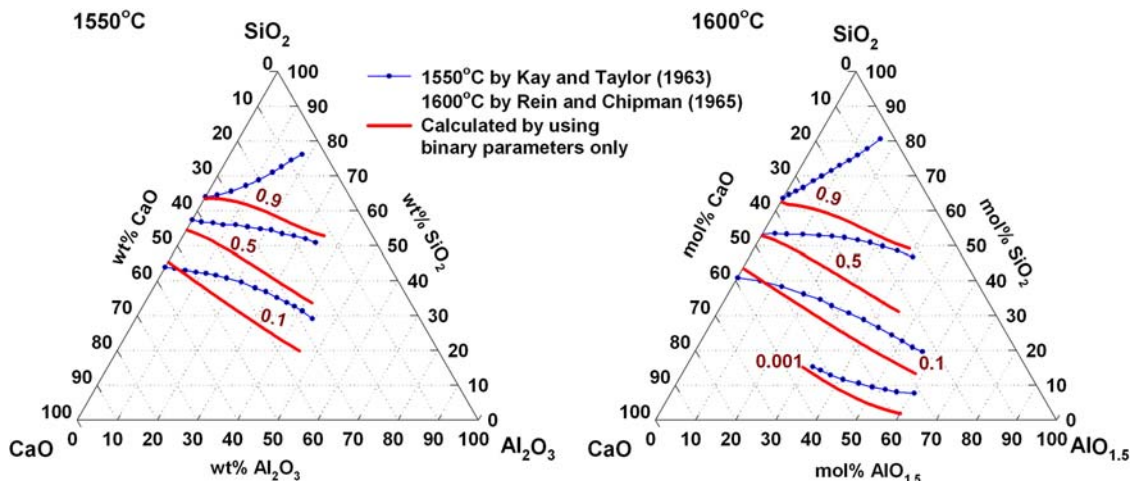


Fig. 4 Comparison between the published^[30-32] and the calculated activity of SiO₂ in slags at 1550 and 1600 °C in the CaO-Al₂O₃-SiO₂ system by using binary parameters only in the cell model

It can be seen that activity values in the CaO-SiO₂ binary side are in close agreement with the experimental data. It should be noted that experimental activity data were not found for the Al₂O₃-SiO₂ binary side. However, the model provides good fit to the binary phase diagram by using generally accepted thermochemical data for phases of Al₂O₃,^[19] mullite,^[21] and SiO₂^[22] in the Al₂O₃-SiO₂ binary. The accuracy of the activities for both Al₂O₃ and SiO₂ should match that of the thermochemical data used. Furthermore, the binary results are in close agreement with extrapolation of the ternary experimental data. Despite good descriptions of the binaries, disagreement between the model and the experimental data grows as Al₂O₃ content increases in the ternary. For example, when the Al₂O₃ content approaches 40 wt.%, the calculated isoactivity curve for a_{SiO₂} = 0.9 is almost at the same composition as that at

which the measured a_{SiO₂} is 0.5. In other words, the model overestimates SiO₂ activity by about 0.4, almost twice the measured values at these compositions. Due to such large errors in the calculated component activities, the calculated liquid regions, in particular at 1400 °C, are also inaccurate as shown in Fig. 5. The published phase diagram^[36] shows that at 1400 °C the liquid region in the centre part of the ternary system is bound by solid phases of SiO₂, CaSiO₃, Ca₂SiO₄, Ca₃Si₂O₇, Al₆Si₂O₁₃, CaAl₂Si₂O₈ and Ca₂Al₂SiO₇. The calculated liquid region is, however, much smaller and only borders three solid phases, i.e., SiO₂, CaSiO₃ and CaAl₂Si₂O₈. The calculated liquid region at 1500 °C is in closer agreement with that determined by experiments than at 1400 °C, especially towards the CaO-SiO₂ binary end. The error becomes greater as Al₂O₃ content increases.

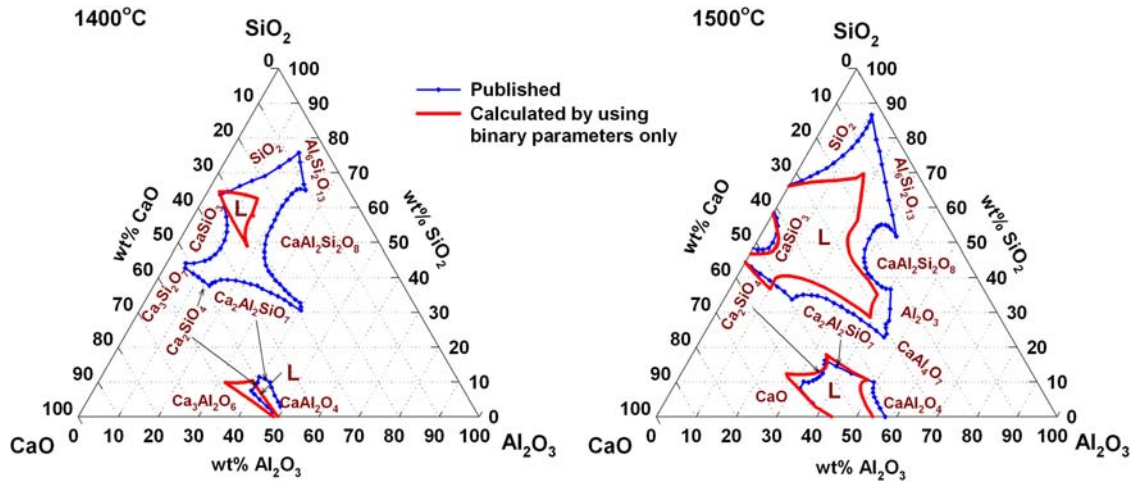


Fig. 5 Comparison between the published^[36] and the calculated liquidus contours at 1400 and 1500 °C in the CaO-Al₂O₃-SiO₂ system by using binary parameters only in the cell model (L stands for liquid)

3. Introduction of Ternary Parameters

In order to improve the accuracy of the calculated component activity values and phase diagrams, an attempt was made to refine the model description by introducing ternary parameters into M(Ca,Mg,Mn,Fe)O-Al₂O₃-SiO₂ systems. Ternary parameters have also been used in the modified quasi-chemical model for the CaO-Al₂O₃-SiO₂ system^[17] to account for the influence of the third component, **k**, upon the Gibbs energies of formation of the binary **i** and **j** pair.^[37] When there are only binary parameters in the model the cell formation energy terms W_{ij} 's were expressed as:

$$W_{ij} = W_{ij}^{(0)} + W_{ij}^{(1)} X_i + W_{ij}^{(2)} X_i^2 \quad (\text{Eq 1})$$

Ternary parameters are introduced in the following form:

$$W_{ij} = W_{ij}^{(0)} + W_{ij}^{(1)} X_i + W_{ij}^{(2)} X_i^2 + \sum_{k=1, k \neq i, j}^m W_{ijk} \frac{X_k}{(1-X_i)} \quad (\text{Eq 2})$$

where $W_{ij}^{(0)}$, $W_{ij}^{(1)}$, $W_{ij}^{(2)}$, are coefficients obtained by fitting the experimental data of the binary systems, X_i is the mole fraction of component **i** and m is the number of components in the slags. The last term in Eq (2) is the sum of the ternary interactions of all non **i**, **j** components upon the **ij** pair. The effect of the third component **k** is proportional to the mole fraction of **k** over the sum of the mole fractions of all non **i** components. It should be noted that the order of the species in the cell model is related to the acidity of the components. The indices **i** and **j** are not interchangeable within the cell model. It can be seen that the second and third terms in Eq (2) are related to X_i only. In other words W_{ij} can only be functions of X_i , not X_j as **i** is more acidic than **j**. In the denominator, $(1-X_i)$ refers to all non-**i** components. It was

found that this functional form is most effective to account for the ternary interactions in the systems modeled.

Two ternary parameters with values of $W_{\text{Si-Al-Ca}} = -15000$ J/mol and $W_{\text{Si-Ca-Al}} = 3000$ J/mol were used for the CaO-Al₂O₃-SiO₂. The calculated iso-activities of SiO₂ and liquidus by using the modified cell model for the CaO-Al₂O₃-SiO₂ are shown in Fig. 6 and 7. The results show that significant improvement in the model descriptions has been achieved by introduction of the ternary parameters. The calculated iso-activities of SiO₂ are in quite close agreement with the experimental data at 1550 by Kay and Taylor^[34] and 1600 °C by Rein and Chipman.^[35] The significant improvement in the calculated activities by the modified cell model has also led to closer agreements between the experimental and the calculated liquid regions at 1400 and 1500 °C, which are now bound to the correct solid phases.

The same approach was also applied to other ternary systems, such as MgO-Al₂O₃-SiO₂, MnO-Al₂O₃-SiO₂ and FeO-Al₂O₃-SiO₂. The accuracy of the model descriptions was also found to be improved by the modified cell model. As a result the model prediction of higher order systems of the M(Ca,Mg,Mn,Fe)O-Al₂O₃-SiO₂ system are expected to be more accurate. Figure 8 presents just one example of liquidus calculations in the system of CaO-MgO-Al₂O₃-SiO₂. The diagram shows the effect of addition of MgO on the phase relations in slags with 15 wt.% Al₂O₃ and CaO/SiO₂ (wt.%/wt.%)=1.0. The published data^[38] show that CaSiO₃ is stable up to 1330 °C without MgO addition. The liquidus temperature drops by about 30 °C with the addition of 1 wt.% MgO. Melilite then becomes the primary solid phase with further addition of MgO and the liquidus temperatures start to increase and level off when MgO addition reaches 8 wt.%. It can be seen that the liquidus temperatures calculated by using binary parameters only in the cell model are in general higher than the published values. Furthermore, only melilite was identified as the primary solid phase in the range of 0-10 wt.% MgO additions. It is also noted that the difference between the calculated and the published liquidus temperatures is about

Section I: Basic and Applied Research

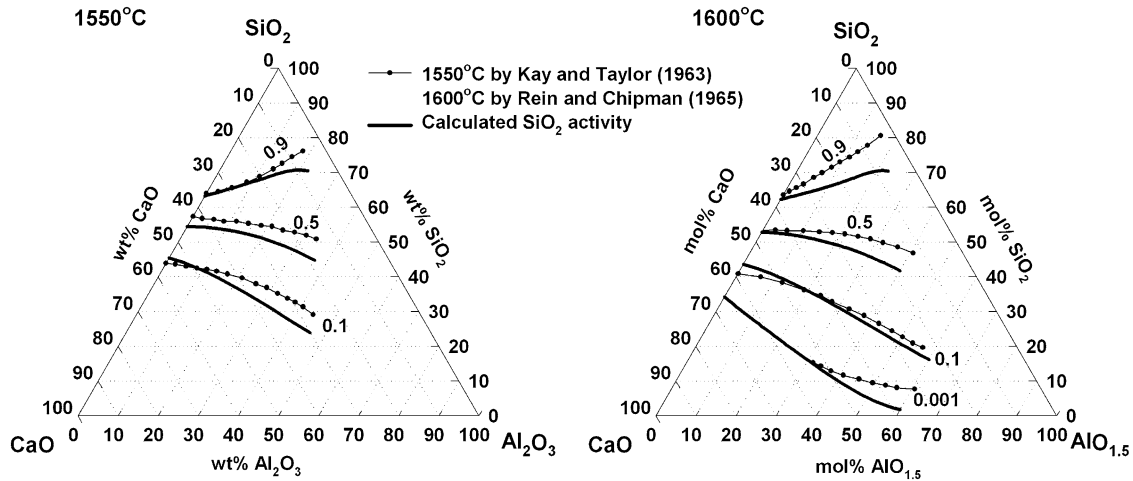


Fig. 6 Comparison between the published^[34,35] and the calculated activity of SiO₂ in slags at 1550 and 1600 °C in the CaO-Al₂O₃-SiO₂ system by using modified cell model with ternary parameters

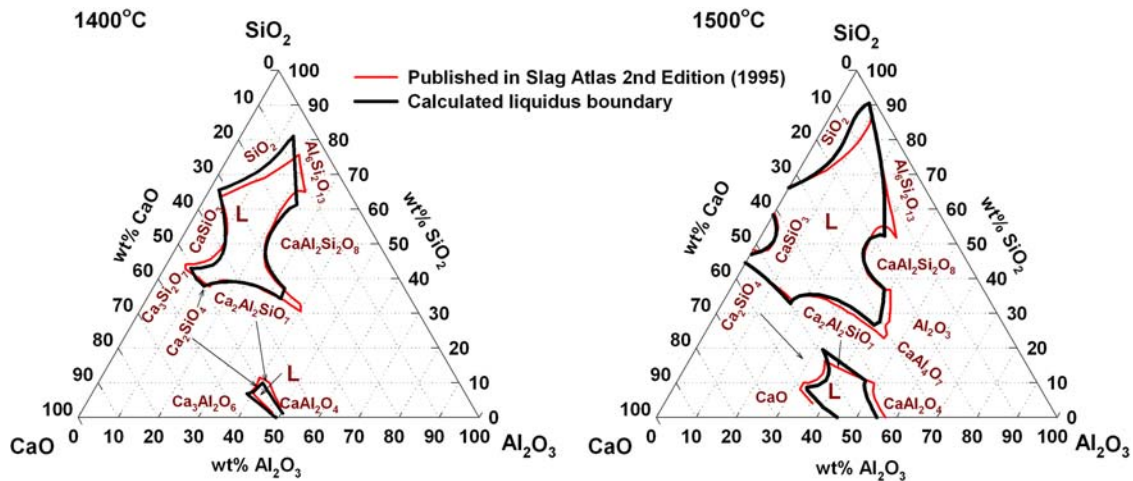


Fig. 7 Comparison between the published^[36] and the calculated liquidus contours at 1400 and 1500 °C in the CaO-Al₂O₃-SiO₂ system by using modified cell model with ternary parameters (L stands for liquid)

130 °C at 0 wt.% MgO and the differences become smaller with more MgO added to the slags. Using the modified cell model with ternary parameters, accurate predictions on the phase relations in the CaO-MgO-Al₂O₃-SiO₂ system were obtained. The results in Fig. 8 show that the model is able to represent both the correct liquidus temperatures and the primary solid phases in equilibrium with the slag in the composition range covered.

It is noted, however, that the modifications introduced in the present study may not be the best approach to resolve the fundamental shortcomings of the cell model. The current approach has been proven to overcome limitations of the model for MO-Al₂O₃-SiO₂ type ternary slags. A new generation of slag models with more realistic physical meaning are needed to overcome the difficulties of the pair-wise like models that require equivalence between various anionic and cationic types when dealing with

polyvalent species as pointed out by Saunders and Miodownik.^[2]

4. Slag Viscosity Model

As mentioned earlier, one of the useful features of the cell model is that structural information in terms of the fractions of free (O²⁻), bridging (O⁰) and non-bridging (O⁻) oxygen can be calculated. These parameters are considered to be a measure of the degree of polymerization of silicate melts, which correlates with slag viscosity. The viscosity model in the MPE package uses the fractions of free and bridging oxygen in calculation of the activation energy term of the viscosity to account for the composition dependence of the viscosity. The model uses binary parameters for the

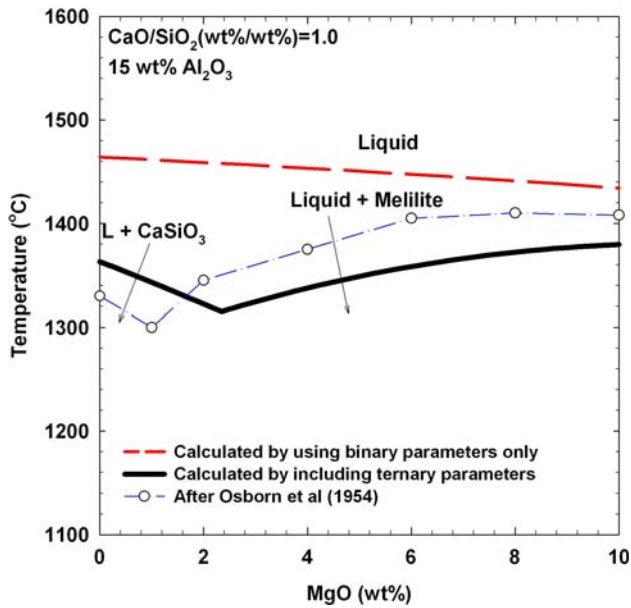


Fig. 8 Comparison between the published^[38] and the calculated phase relations showing the effects of addition of MgO on liquidus in the MgO-CaO-Al₂O₃-SiO₂ system

prediction of viscosity in high order systems. Details of the viscosity model and the major modeling results have been presented elsewhere.^[9,10]

During the development of the viscosity model, Al₂O₃ again presented challenges for that simple approach. In the CaO-Al₂O₃-SiO₂ slags for example, for given silica mole fractions the maximum viscosity was observed about mole ratio of Al₂O₃/CaO = 1 in CaO-Al₂O₃-SiO₂ system.^[39] This phenomenon was confirmed recently by Toplis and Dingwell.^[40] Similar behaviour occurs for both viscosity and electrical conductivity of sodium aluminosilicate glasses.^[41-43] It is believed that it is caused by the so-called amphoteric role played by alumina in the silicate network structure. In order to model such behaviour the concept of classifying oxides as network former (SiO₂), modifier (CaO, MgO, FeO, MnO, PbO, Fe₂O₃) and amphoteric (Al₂O₃) originally introduced by Urbain et al.^[44] in viscosity modeling was adopted. Furthermore, the knowledge gained in the study of the structure of silicate melts via molecular dynamics simulations^[45] helped in a special treatment that enables the viscosity model to describe correctly the behaviour of alumina.^[11]

The viscosity model currently contains 16 oxide components, i.e., SiO₂, Al₂O₃, Cr₂O₃, TiO₂, Ti₂O₃, Fe₂O₃, FeO, CaO, MgO, MnO, CrO, PbO, NiO, CoO, ZnO and Cu₂O. Like the MPE package itself the viscosity model has been constantly extended, validated and refined over the years. The data used for validation cover slags from various operations and types, such as ferrous, non-ferrous, coal ash and PGM (platinum group metals) melter slags.^[8,46-48]

To demonstrate the predictive power of the viscosity model, Fig. 9 shows the comparison between the calculated and the recent set of measured viscosities of blast furnace type slags by Saito et al.^[49,50] and the predicted values at

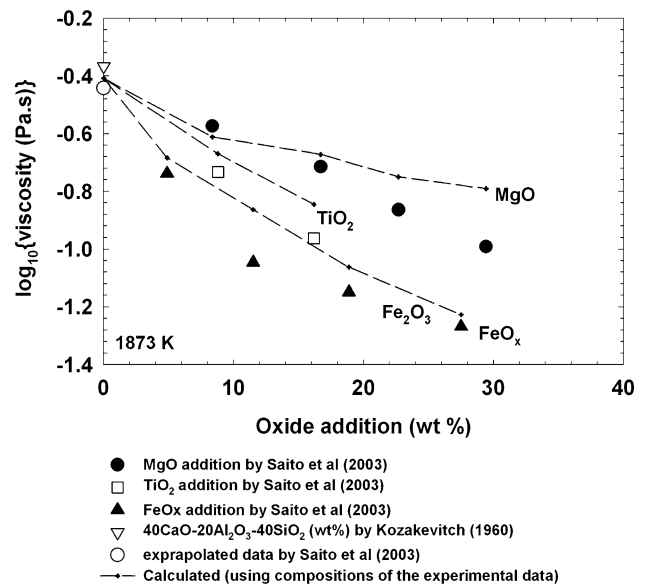


Fig. 9 Comparison between the measured viscosity of blast furnace type slags^[39,49] and the predicted values at 1873 K in the (MgO, TiO₂,Fe₂O₃)-CaO-Al₂O₃-SiO₂ system

1873 K in the (MgO, TiO₂,Fe₂O₃)-CaO-Al₂O₃-SiO₂ system. The aim of the experimental study is to establish the effects of MgO, TiO₂, Fe₂O₃ on the viscosity of 40CaO-20Al₂O₃-40SiO₂(wt.%) slag. Their results show that the viscosity of the CaO-Al₂O₃-SiO₂ slags decreases with increasing MgO, TiO₂, Fe₂O₃. For the same level of addition, viscosity decreases in the order of Fe₂O₃, TiO₂ and MgO. In other words Fe₂O₃ is most effective in reducing the viscosity of the slag, followed by TiO₂ and MgO. They also found the same effects when the three oxides were added to 50CaO-50SiO₂ (wt.%) slags. The predicted values shown in Fig. 9 were calculated using existing viscosity model parameters (binary only) determined when TiO₂ was incorporated.^[48] Good agreement between the predicted values and the experimental data can be seen. The model predicts slightly higher values when the amount of additives increases. Nevertheless, the difference between the predictions and measured values is within 30%, similar to the experimental uncertainties for viscosity measurements as pointed out by Mills and Keene.^[51] Most importantly the model is able to reproduce the correct order in the effectiveness of the cation species in reducing the viscosity of molten oxide slags.

5. Conclusions

Close examination of the cell model revealed that using only binary parameters caused large errors in calculated silica activity and phase diagram in the CaO-Al₂O₃-SiO₂ system even though the binary parameters reproduced the binary behaviour accurately. This was caused by the inability of the model to account for the complex behaviour

Section I: Basic and Applied Research

in the system by mixing of two binary silicates of CaO-SiO₂ and Al₂O₃-SiO₂ with uneven interactions.

An approach was designed to modify the cell model by introducing ternary parameters. The results for the CaO-Al₂O₃-SiO₂ system show that the fit to the SiO₂ activity and the liquidus surface is satisfactory while the accuracy of the binary properties is maintained.

The capability of the structurally based viscosity model has been demonstrated by the close fit to a set of recently measured viscosity and predicting closely the effects of various cations.

Acknowledgments

The authors would like to thank Professor Alan Oates for his guidance and encouragement in extension and refinement of the MPE package. The authors also like to thank an anonymous reviewer for critical comments. This work was financially supported by Bluescope Steel, OneSteel, Rio Tinto, Pasminco, Anglo Platinum, Impala Platinum, Lonmin Platinum, Kumba Resources through AMIRA International and CSIRO Minerals.

References

1. D.R. Gaskell, Thermodynamic Models of Liquid Silicates, *Can. Metall. Q.*, 1981, **20**(1), p 3-19
2. N. Saunders and A.P. Miodownik, *CALPHAD (Calculation of Phase Diagrams): a Comprehensive Guide*. Elsevier Science Ltd, Pergamon, UK, 1998
3. M.L. Kapoor and M.G. Froberg, "Theoretical Treatment of Activities in Silicate Melts", in *Chemical Metallurgy of Iron and Steel*, The Iron and Steel Institute, London, 1971, p 17-22
4. H. Gaye and J. Welfringer, Modelling of the Thermodynamic Properties of Complex Metallurgical Slags, in *Second International Symposium on Metallurgical Slags and Fluxes*, H.A. Fine and D.R. Gaskell, eds. The Metallurgical Society of AIME, Warrendale, 1984, p 357-375
5. H. Gaye, J. Lehmann, T. Matsumiya, and W. Yamada, "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, p 103-108
6. F. Ruby-Meyer, J. Lehmann, and H. Gaye, Thermodynamic Analysis of Inclusions in Ti-deoxidised Steels, *Scan. J. Metall.*, 2000, **29**(5), p 206-212
7. L. Zhang, S. Jahanshahi, S. Sun, M. Lim, B. Bourke, S. Wright, and M. Somerville, Development and Applications of Models for Pyrometallurgical Processes, *Materials Forum*, 2001, **25**, p 136-153
8. L. Zhang, S. Jahanshahi, S. Sun, C. Chen, B. Bourke, S. Wright, and M. Somerville, CSIRO's Multiphase Reaction Models and Their Industrial Applications, *JOM*, 2002, **54**, p 51-56
9. L. Zhang and S. Jahanshahi, Review and Modelling of Viscosity of Silicate Melts: Part I. Viscosity of Binary and Ternary Silicates Containing CaO, MgO and MnO, *Metall. Mater. Trans. B*, 1998, **29B**, p 177-186
10. L. Zhang and S. Jahanshahi, Review and Modelling of Viscosity of Silicate Melts: Part II. Viscosity of Melts Containing Iron Oxide in the CaO-MgO-MnO-FeO-Fe₂O₃-SiO₂ System, *Metall. Mater. Trans. B*, 1998, **29B**, p 187-195
11. L. Zhang and S. Jahanshahi, Modelling Viscosity of Alumina-Containing Silicate Melts, *Scand. J. Metall.*, 2001, **30**, p 364-369
12. M.A. Somerville, S. Wright, S. Sun, and S. Jahanshahi, "Liquidus Temperature and Viscosity of Melter Slags", *7th International Conference on Molten Slags, Fluxes and Salts*, Cape Town, SA. Johannesburg: South African Institute of Mining and Metallurgy, 2004, p 219-224
13. N. Bartie, J. Eksteen, S. Jahanshahi, and S. Sun, "The Effect of Temperature, Oxygen Potential and Slag Chemistry on the Stability of Chromium Spinels in Melter Slags in the Base Metals Industry", In: *22nd International Mineral Processing Congress*, Cape Town, South Africa, L. Lorenzen and D.J. Bradshaw (eds), 2003, p 1364-1369
14. S. Wright, L. Zhang, S. Sun, and S. Jahanshahi, Viscosity of a CaO-MgO-Al₂O₃-SiO₂ Melt Containing Spinel Particles at 1646 K, *Metall. Mater. Trans B*, 2000, **31B**, p 97-104
15. S. Wright, L. Zhang, S. Sun, and S. Jahanshahi, Viscosity of Calcium Ferrite Slags and Calcium Alumino-silicate Slags Containing Spinel Particles, *J. Non-Crystall. Solids*, 2001, **282**, p 15-23
16. R.J. Hundermark, S. Jahanshahi, and S. Sun, "Electrical Conductivity of Melter Type Slags", *22nd International Mineral Processing Congress*, Cape Town, South Africa, L. Lorenzen and D.J. Bradshaw (eds), 2003, p 1370-1377
17. G. Eriksson and A.D. Pelton, Critical Evaluation and Optimization of the Thermodynamic Properties and Phase Diagrams of the CaO-Al₂O₃, Al₂O₃-SiO₂ and CaO-Al₂O₃-SiO₂ Systems, *Metall. Trans. B*, 1993, **24B**, p 807-816
18. B. Sundman, *User Aspects of Phase Diagrams*, F.H. Hayes, Ed., Inst. Metals, London, p 130
19. I. Ansara and B. Sundman, *Computer Handling and Dissemination of Data*, P.S. Glaser, Ed., Elsevier Science Publishers, CODATA, p 154-158
20. A.T. Dinsdale, SGTE Data for Pure Elements, *CALPHAD*, 1991, **15**, p 317-426
21. I. Barin, *Thermochemical Data of Pure Substances*. VCH, Weinheim, Germany, 1989
22. J.R. Taylor and A.T. Dinsdale, Thermodynamic and Phase Diagram Data for the CaO-SiO₂ System, *CALPHAD*, 1990, **14**, p 71-88
23. M. Rolin and P.H. Thanh, Les Diagrammes de Phases des Mélanges ne Réagissant Pas Avec le Molybdène, *Rev. Hautes Temp. Réfract.*, 1965, **2**, p 175-185, in French
24. R.W. Nurse, J.H. Welch, and A.J. Majumdar, The CaO-Al₂O₃ System in a Moisture-Free Atmosphere, *Trans. Br. Ceram. Soc.*, 1965, **64**(9), p 409-418
25. N. Nityanand and H.A. Fine, The Effect of TiO₂ Additions and Oxygen Potential on Liquidus Temperatures of Some CaO-Al₂O₃ Melts, *Metall. Trans. B*, 1983, **14B**, p 685-692
26. I. Barin, *Thermochemical Data of Pure Substances*. VCH, Weinheim, Germany, 1989
27. F.J. Klug and S. Prochazka, Alumina-Silica Phase Diagram in the Mullite Region, *J. Am. Ceram. Soc.*, 1987, **70**(10), p 750-759
28. S. Aramaki and R. Roy, Revised Phase Diagram for the System Al₂O₃-SiO₂, *J. Am. Ceram. Soc.*, 1962, **45**(5), p 229-242
29. N.L. Bowen and J.W. Greig, The System: Al₂O₃-SiO₂, *J. Am. Ceram. Soc.*, 1924, **7**(4), p 238-254; "Errata", *ibid.*, vol 7(5), 1924, p 410
30. R.A. Sharma and F.D. Richardson, Activities in Lime-alumina Melts, *J. Iron Steel Ins.*, 1961, **197**, p 386-390
31. D.M. Edmunds and J. Taylor, Reaction CaO+3C=CaC₂+CO and Activity of Lime in CaO-Al₂O₃-CaF₂ System, *J. Iron Steel Inst. London*, 1972, **210**, p 280-283

32. M. Allibert, C. Chatillon, K.T. Jacob, and R. Lourtau, Mass-spectrometric and Electrochemical Studies of Thermodynamic Properties of Liquid and Solid Phases in the System CaO-Al₂O₃, *J. Am. Ceram. Soc.*, 1981, **64**, p 307-314
33. H. Mao, M. Selleby, and B. Sundman, Phase Equilibria and Thermodynamics in the Al₂O₃-SiO₂ System - Modelling of Mullite and Liquid, *J. Am. Ceram. Soc.*, 2005, **88**(9), p 2544-2551
34. D.A.R. Kay and J. Taylor, The Silica Reduction Reaction in the Blast-furnace, *J. Iron Steel Inst.*, 1963, **201**, p 67-70
35. R.H. Rein and J. Chipman, Activities in the Liquid Solution SiO₂-CaO-MgO-Al₂O₃ at 1600 °C, *Tran. AIME*, 1965, **233**, p 415-425
36. Slag Atlas, 2nd Edition, Ed: Verein Deutscher Eisenhüttenleute. Verlag Stahleisen GmbH, D-Dusseldorf, Germany, 1995
37. P. Chartrand and A.D. Pelton, Modelling the Charge Compensation Effect in Silica-rich Na₂O-K₂O-Al₂O₃-SiO₂ Melts, *CALPHAD*, 1999, **23**(2), p 219-230
38. E.F. Osborn, R.C. DeVries, K.H. Gee, and H.M. Kraner, Optimum Composition of Blast Furnace Slag as Deduced from Liquidus Data for the Quaternary System CaO-MgO-Al₂O₃-SiO₂, *Tran. AIME, J. Metal.*, 1954, **6**(1), p 33-45
39. P. Kozakevitch, Viscosité et Éléments Structuraux des Aluminosilicates Fondus: Laitiers CaO-Al₂O₃-SiO₂ Entre 1600 et 2100 °C, *Revue de Metallurgie*, 1960, **57**, p 149-160, in French
40. M.J. Toplis and D.B. Dingwell, Shear Viscosities of CaO-Al₂O₃-SiO₂ and MgO-Al₂O₃-SiO₂ Liquid: Implications for the Structural Role of Aluminium and the Degree of Polymerisation of Synthetic and Natural Aluminosilicate Melts, *Geochim. Cosmochim. Acta*, 2004, **68**, p 5169-5188
41. D.M. Zirl and S.H. Garofalini, Structure of Sodium Aluminosilicate Glasses, *J. Am. Ceram. Soc.*, 1990, **73**, p 2848-2856
42. J.O. Isard, Electrical Conductivity in Aluminosilicate Glasses, *J. Soc. Glass Technol.*, 1959, **43**, p 113-123
43. T.D. Taylor and G.E. Rindone, Properties of Soda Aluminosilicate Glasses: V, Low-temperature Viscosities, *J. Am. Ceram. Soc.*, 1970, **53**, p 692-695
44. G. Urbain, F. Cambier, M. Deletter, and M.R. Anseau, Viscosity of Silicate Melts, *Trans. J. Br. Ceram. Soc.*, 1981, **80**, p 139-141
45. L. Zhang, S. Sun, and S. Jahanshahi, Molecular Dynamics Simulations of Silicate Slags and Slag-Solid Interfaces, *J. Non-Cryst. Solids*, 2001, **282**, p 24-29
46. S. Sun, L. Zhang, and S. Jahanshahi, From Viscosity and Surface Tension to Marangoni Flow in Melts, *Metall. Mater. Trans. B.*, 2003, **34B**(5), p 517-523
47. L. Zhang, S. Jahanshahi, H.J. Hurst, and J.H. Patterson, "A Predictive Viscosity Model for Coal Ash Slags", *Eighteenth Annual International Pittsburgh Coal Conference*, Newcastle, Australia, December 4-7, 2001, CD-ROM
48. L. Zhang and S. Jahanshahi, "Modelling Viscosity of TiO₂ Containing Silicate Melts", *The Seventh International Conference on Molten Slags, Fluxes and Salts*, Cape Town, South Africa, 25-28 January 2004, p 51-56
49. N. Saito, N. Hori, K. Nakashima, and K. Mori, Viscosity of Blast Furnace Slags, *Metall. Mater. Trans. B.*, 2003, **34B**(10), p 509-516
50. N. Saito, N. Hori, K. Nakashima, and K. Mori, "Viscosity of blast furnace slags", *Mills Symposium*, 22-23 August 2002, London, UK, p 477-485
51. K.C. Mills and B.J. Keene, Viscosities of BOS Slags, *Int. Mat. Reviews*, 1987, **32**, p 1-120