1. Introduction

Slags have a fundamental role in all steelmaking processes, from primary refining to continuous casting. Further to its chemical behavior, normally defined by the slag thermodynamic properties, viscosity and surface tension are among the most important properties considered in the design of slag compositions for steel processing. A brief literature review of the approaches at modeling viscosities shows that viscosity correlations with chemical composition, basicity (both chemical and optical), and more recently with slag constitution have been attempted with different degrees of success. In this work, a model based on the Riboud viscosity model combined with the thermodynamic Kappor-Frohberg-Gaye cell model is described and presented as a potential alternative to obtaining slag viscosity estimates directly from computational thermodynamics software. The first results of the adjustment and application of the model to the CaO-Al$_2$O$_3$-MgO-SiO$_2$-(TiO$_2$) system are presented. The quality of the adjustment is discussed as well as its current limitations. Future steps in the model development involve its extension to include FeO, TiO$_2$, and CaF$_2$.

KEY WORDS: Viscosity; Slag; Computational thermodynamics; Steelmaking.
The shear rate, thus:

\[ \tau = \eta \frac{dv}{dy} \]

where \( \tau \) is the shear stress [Pa], \( \eta \) is the fluid viscosity (a coefficient given [Pa·s]) and \( \frac{dv}{dy} \) is the velocity (v) gradient normal to the shear stress [s⁻¹].

2. Temperature Dependence of Viscosity

As shear should involve the relative movement of layers of atoms, ions or molecules (or “species”) in a structure, and that should depend on their bonding strength, it is reasonable to assume that this force should follow an Arrhenius type relation with temperature. This is assumed by several authors [3-5]. So, viscosity could be described as:

\[ \eta = A \exp \left[ \frac{E_A}{RT} \right] \quad (1) \]

where \( A \) is a pre-exponential coefficient and \( E_A \) is the activation energy for the phenomenon. However, due to the complex nature of the species present in the slag and due to the fact that the slag constitution (i.e. the species present) may also vary with temperature [6,7], Eq. (2) has also been proposed for the description of slag viscosity by Urbain [8,9] based on the Weymann-Frenkel kinetic theory of liquids.

\[ \eta = AT \exp \left[ \frac{E_A}{RT} \right] \quad (2) \]

2.2 Chemical Composition Dependency of Viscosity

Due to the complexity of slag structure and hence the species present in the slag as a function of chemical composition, many different ways of incorporating the effect of chemical composition in viscosity models have been proposed. The simplest approach, classified as empirical models by Kondratiev et al. [10], has been to fit polynomial descriptions to the relation between viscosity, temperature, and composition, not even considering Eqs. (1) or (2). These models have only been successful for interpolation (and minor extrapolations) in limited ranges of composition and temperature. On the other hand, both Eqs. (1) and (2) can have their \( A \) and \( E_A \) coefficients fitted directly to the slag chemical composition, without taking in consideration the species present in the slag, only its constituent compounds. In an attempt to consider the behavior of the various slag forming compounds, Urbain and other authors [11] have proposed the grouping of the slag forming oxides in: glass forming, modifiers, and amphoterics. Silica (SiO₂) is a glass forming oxide. Silica is characterized by strong bonding, polymerization (chains of tetrahedral), and high viscosities. Modifiers are oxides containing Na⁺, K⁺, Ca²⁺, Fe³⁺, and Mg²⁺ ions that modify the polymeric glass structure breaking the strong bonds (or chains) and decreasing the viscosity. Oxides such as Al₂O₃ or Cr₂O₃ can display both behaviors, depending on their concentrations and the other oxides present in the slag [12]. This approach is very similar to the simplified description of steelmaking slags, based on basic concepts [13]. In this approach [3], \( A \) and \( E_A \) in Eqs. (1) and (2) are expressed as shown in Eqs. (3) and (4).

\[ \ln A_w = A_0 + \sum A_i X_i \quad \text{component oxides } i \]

\[ E_w = E_0 + \sum E_i X_i \quad \text{component oxides } i \]

where \( A \) is expressed in Pa.s.K⁻¹ and \( E \) in K.

\[ A_w = \exp[A_0 + A_{\text{mod}} (X_{\text{CaO}} + X_{\text{MnO}} + X_{\text{MgO}} + X_{\text{FeO}}) + A_{\text{fluoride}} X_{\text{CaF}} + A_{\text{alkaline}} (X_{\text{Na}_2O} + X_{\text{K}_2O}) + A_{\text{amph}} X_{\text{Al}_2O}] \]

\[ E_w = E_0 + E_{\text{mod}} (X_{\text{CaO}} + X_{\text{MnO}} + X_{\text{MgO}} + X_{\text{FeO}}) + E_{\text{fluoride}} X_{\text{CaF}} + E_{\text{alkaline}} (X_{\text{Na}_2O} + X_{\text{K}_2O}) + E_{\text{amph}} X_{\text{Al}_2O} \]

Eq. (4) is just a regrouping of terms of Eq. (3) for compounds with the same approximate behavior [3].

More advanced models try to correlate viscosity with structural characteristics or parameters of the slag. Thus, viscosity has been correlated to optical basicity, for instance [12,7]. Kondratiev and Jak [9], on the other hand, have attempted a correlation between viscosity and the concentration of species in the slag, given as the fraction of species in the quasi-chemical thermodynamic model for the slag. These authors have adopted an intermediate temperature dependence as given in Eq. (5):

\[ \eta = AT^{3/2} \exp \left[ \frac{E_A}{T} \right] \quad (5) \]

Using the quasi-chemical model in FACTSAGE software and slag databases they adjusted the coefficients \( A \) and \( E \) as a function of species concentration obtained from thermodynamic calculation.

3. The Present Model

3.1 Model Formulation

In the present work, a model based on Eq. (2) and in a modification of Eq. (3) to consider the concentration of “cells”
(species) in the Gaye-Kapoor-Frohberg\textsuperscript{[10–12]} thermodynamic model for the slag was developed. This way, no correlation with the slag forming components (composition) was attempted. This stems from the observation most models that try to correlate composition and viscosity have limited success. It is the assumption of the present work that this limitation is due to the deviations between slag constitution and composition as discussed above.

The thermodynamic model used in the present viscosity modeling was developed by Gaye \textit{et al.}\textsuperscript{[10,11]} based on the Kapoor-Frohberg\textsuperscript{[12]} proposal. In this model, liquid oxides are described as symmetric (i-O-i) and asymmetric (i-O-j) cells. Other cations can also be considered in an extension of the model\textsuperscript{[11]}. The model considers the cell formation energies as well as the energies of interactions between cells. The Gibbs energy of symmetric cells corresponds to that of the equivalent pure oxide. Thus, for instance:

\begin{equation}
G_{Al2O3-Al2O3} = \kappa^0 G_{Al2O3}
\end{equation}

where the factor \( \kappa \) adjusts for the number of oxygen atoms in the cell and in the oxide formula.

Asymmetric cells have their Gibbs energies given as:

\begin{equation}
G_{i-O-j} = W_{ij} + \kappa^0 G_{iOj} + \kappa^0 G_{jOi}
\end{equation}

where \( W_{ij} \) can be composition-dependent. Furthermore, the model has defined rules for the cell interaction energies:

a) All interactions between similar cells are considered as part of their Gibbs energy;

b) Interaction between different cells obey the following additivity rules:

\begin{equation}
E_{i-j} = 2E_{ij-i}
\end{equation}

\begin{equation}
E_{i-k} = E_{ik-k} + E_{ji-k}
\end{equation}

The \( E_{ij} \) factor can be dependent on the concentration of the highest cation charge concentration.

Thus, the Gibbs energy of the liquid slag can be calculated as:

\begin{equation}
G = \sum_i \sum_j x_i G_{i-O-i} + x_j G_{i-O-j} + \sum_i \sum_j N_{i-j} E_{ij} + RT \sum_i \sum_j x_j \ln x_{ij}
\end{equation}

where the \( x \) coefficients are the cell concentrations. Their variation is limited by the concentration of the oxides forming the slag and determined through the minimization of the Gibbs energy of the liquid phase for a given slag composition. The coefficients \( N_{ij} \) are related to the number of interacting pairs of cells and are determined in the same way. Despite their different formulations, according to Pelton\textsuperscript{[13]}, this model and the quasi-chemical model are formally similar.

It is then possible to describe viscosity by adapting Eq. (2) with \( A \) and \( E \) factors that have linear dependences on the cell concentrations calculated according to this model. Thus, if \( y_j \) is the concentration of cell (in cell fraction or mole fraction of cell) i-O-j in slag (where i and j are cations), the viscosity coefficients in Eq. (2) become:

\begin{equation}
A_w = \exp(A_0 + \sum_i \sum_j y_j A_{ij})
\end{equation}

\begin{equation}
E_w = E_0 + \sum_i \sum_j y_j E_{ij}
\end{equation}

In the present case, the \( y_j \) are calculated using Thermocalc\textsuperscript{[14]} and the Gaye-Kapoor-Frohberg model as implemented in the database SLAG3\textsuperscript{[15]} with basis on Gaye’s assessments\textsuperscript{[10,11]}

Access to structural information of the slag constituents, however, is very limited. The insight proposed by Richard-son in 1954, that there must exist three types of oxygen in slag, namely “those bonded to two silicon atoms (O0), those bonded to one silicon atom (O-1), and those unattached to silicon (O-2)\textsuperscript{[16]} has paved the way for several slag structure models\textsuperscript{[17,18]} (including the Kapoor-Frohberg approach) applied to steelmaking slags. The concentration of these different types of oxygen can be directly measured by X-ray photoelectron spectroscopy (XPS) if one assumes that oxygen bonds are preserved when a liquid slag is quenched to a vitreous sample\textsuperscript{[19]}. Comparison of the measured concentrations of O0, O-1, and O-2 should, thus, give interesting insights on slag structure and adequacy of thermodynamic models. For this reason, the measurements of Park and Rhee\textsuperscript{[19]} in CaO-SiO2 mixtures were compared with the results of the thermodynamic model discussed above. Fig. 1 compares their measurement results, their calculated concentrations obtaining by fitting the degree of dissociation of CaO to the XPS results and using Toops data with the calculated concentrations (\( Y \)) of

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Concentrations of O0 (\( \bullet \)), O-1 (\( \square \)), and O-2 (\( \triangle \)) experimentally measured by XPS at 1,873 K, together with their calculated concentrations fitted to the data by Park and Rhee (see original reference for further discussion\textsuperscript{[16]}). Also presented are the cell concentrations (mole fraction) of Ca-O-Ca, Si-O-Si, and Si-O-Ca cells calculated using Thermo-calc and the SLAG3 database, in the CaO-SiO2 system.}
\end{figure}
Ca-O-Ca, Si-O-Si, and Si-O-Ca cells using the above thermodynamic model. It is evident that the model describes quite well the concentration of the different types of oxygen via the cell concentration. Furthermore, this can give important insights on the relevant cells for the viscosity modeling, as discussed in the next section.

4. Results and Discussion

4.1 First Stage of Modeling

The first stage of modeling was focused on confirming the viability of the PARROT (Parameter Optimization) routine of Thermo-calc\(^\text{[14]}\) in optimizing through least-squares, non-thermodynamic data, and viscosity in the present case. In that stage\(^\text{[20]}\) data concerning viscosities in the SiO\(_2\)-Al\(_2\)O\(_3\)-MgO-CaO system were collected from various sources (for binaries, mostly from Kondratiev and Jak\(^\text{[19]}\) and for ternaries data from Toplis and Dingwell\(^\text{[21]}\)). Data with log \(\eta \geq 2\) has been eliminated since the viscosity for these glasses frequently require two step dependence on temperature.

Data for the quaternary system from Shankar et al.\(^\text{[22]}\) as well as Nakamoto et al.\(^\text{[23]}\) was used. Overall, the data were in the following approximate range of compositions: 7%-80% SiO\(_2\), 0%-70% Al\(_2\)O\(_3\), 0%-16.5% MgO, and 8%-70% CaO. The range of temperatures in the data set was 1623-2273 K.

Thus, the equations to be adjusted were:

\[
A = A_0 + \sum_{ij} y_{ij} A_{ij} = A_0 + y_{SS} A_{SS} + y_{SiCa} A_{SiCa} + y_{SiAl} A_{SiAl} \\
+ y_{SiMg} A_{SiMg} + y_{CaCu} A_{CaCu} + y_{CaAl} A_{CaAl} + y_{CaMg} A_{CaMg} + y_{AlAl} A_{AlAl} + y_{AlMg} A_{AlMg} \\
+ y_{MgMg} A_{MgMg} + y_{CaAl} A_{CaAl} + y_{CaMg} A_{CaMg} + y_{CaMg} A_{CaMg} + y_{CaAl} A_{CaAl} + y_{AlMg} A_{AlMg} + y_{MgMg} A_{MgMg}
\]

4.1.1 Results at the first stage of modeling

The strategy for the optimization of the various parameters is discussed elsewhere\(^\text{[23]}\). It should be noted, however, that the model has only 2x3 adjustable parameters per binary system and no higher order parameter. It is hence expected that optimization should converge to consistent parameters. In the first stage of modeling \(A\) and \(E\) coefficients depending on \(y_{SS-Ca}\) were introduced and only 8 variables were actually used. For the range of MgO contents present in the data only coefficients for \(y_{Si-O-Mg}\) were used. The results of this stage of optimization of the model coefficients are summarized in Fig. 2.

The results of the optimization of the coefficients shown in Fig. 2 indicate that deviation exists for the adjustment of some experimental values but the overall agreement is good for a wide range of viscosity values, associated to temperature and composition variations.

4.2 Second Stage of Modeling

As the optimizing strategy has been proved adequate in the first stage of modeling, the second stage expanded the number of experimental data and attempted to introduce an additional oxide, TiO\(_2\), in the viscosity model. Additional data were selected from Shankar et al.\(^\text{[22]}\), Nakamoto et al.\(^\text{[23]}\), and Saito et al.\(^\text{[24]}\). Special care was taken to eliminate data in which a solid phase could be present. This was done via the equilibrium calculation for the bulk slag composition and temperature in Thermo-calc. This is specially important since the effect of the presence of solid particles on the apparent viscosity is well known\(^\text{[25]}\).

Fig. 3 presents the results of the new optimization for the quaternary system\(^\text{[26]}\). In this optimization no term on \(y_{Si-O-Si}\) was used.

The results in Fig. 3 were obtained with 16 adjustable variables. As at least four of them have low correlation, as indicated in Parrot, it should be possible to achieve similar results with only 12 adjustable variables.

4.2.1 Slags containing TiO\(_2\)

In order to extend the model to slags containing TiO\(_2\), a first attempt was made to identify which cells containing Ti\(^{+4}\) ions would be more relevant. Ti-O-Ca and Si-O-Ti, for the range of slags explored, were the Ti containing cells with higher concentration. Coefficients for these cells were included in \(A\) and \(E\) [Eq. (10)]. Fig. 4(a) shows that the adjustment of the model was not good. The deviations were concentrated in the titanium containing slags. Examining the constitution of these slags, two important facts were observed: (a) the concentration of the Ti containing cells is never high, in the range of TiO\(_2\), contents of 0%-10% mass; and (b) the addition
of TiO₂ causes important changes in the concentration of other more relevant cells, as shown in Fig. 5.

For this reason, a change was introduced in the model and the concentration of Ti containing cells was not considered, while the concentration of the cells already included in the model were normalized to consider the elimination of the Ti containing cells, as shown in Eq. (12). Thus, the direct effect of the concentration of Ti containing cells was not considered in the model.

$$A = A_0 + \sum_i \sum_j Y_{ij} A_j$$
$$E_x = E_0 + \sum_i \sum_j Y_{ij} E_j$$

where:

$$Y_T = Y_{SiSi} + Y_{SiCa} + Y_{SiAl} + Y_{SiMg} + Y_{CaCa} + Y_{CaAl} +$$
$$Y_{CaMg} + Y_{AlAl} + Y_{AlMg} + Y_{MgMg}$$

Fig. 4b shows the improved adjustment of the calculated values when compared to Fig. 4a. This indicates that the most relevant aspect of the structure of the slag (in what concerns viscosity) is probably the concentration of the main types of oxygen ions. This apparently confirms the proposal of other authors[27] that the lower concentration oxides in a slag (such as TiO₂, in the present case) may have a strong influence of the fraction of “bridging” and “non-bridging” oxygen ions and thus affect the slag properties. While the agreement between calculated cell concentration and the measured concentrations of the different oxygen “types” in slags in Fig. 5 is not very good, the trends displayed by the results of thermodynamic model are consistent with the data and the effect of TiO₂ addition on the concentration of Si-O-Si and Si-O-Ca cells is quite evident. One must speculate how would the concentration of other cells such as Al-O-Al and Si-O-Mg contribute to the concentration of the different oxygen “types” measured via XPS.

5. Conclusions

A model for the calculation of viscosity of slags based on the slag constitution calculated by the “cells” thermody-
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The dynamic model of Gaye-Kapoor-Frohberg was implemented and the coefficients adjusted using the least-square routine in Thermo-calc, Parrot. The importance of “censoring” viscosity data in which a solid fraction might be present was highlighted.

The model was adjusted to viscosities in the CaO-MgO-SiO₂-Al₂O₃ system in different ranges of composition and temperature. The agreement was good and the number of adjustable parameters was kept under 16.

It was possible to demonstrate that the “cells” concentration calculated in the present thermodynamic model is related to the types of oxygen in a slag (O₀, O⁻¹, and O⁻²) related to the bridging concept of oxygen in slags.

In view of the physical insight gained by searching the correlation of cells and states of oxygen in the slag, a novel approach was proposed to describe the effect of dilute additions to these slags, in which the effect on the viscosity is modeled by considering only the effect of the minor oxides on the concentration of the most important cells in the system.

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References


Fig. 5 (a) Calculated cell concentrations using Thermo-calc compared to measured[27] O⁻ and O₀ concentration in a slag with B = 1.2 (CaO/SiO₂), 17%Al₂O₃ and 10% MgO, as a function of the SiO₂ content; (b) calculated cell concentrations using Thermo-calc compared to measured[27] O⁻ and O₀ concentration in a slag with B = 0.8 (CaO/SiO₂), 17%Al₂O₃, and 10% MgO, as a function of the SiO₂ content.