Development of a Quasi-chemical Viscosity Model for Fully Liquid Slags in the \( \text{Al}_2\text{O}_3-\text{CaO-'}\text{FeO}'-\text{MgO-\text{SiO}_2} \) System.
The Experimental Data for the ‘\text{FeO}'-\text{MgO-\text{SiO}_2},
\text{CaO-'}\text{FeO}'-\text{MgO-\text{SiO}_2} \) and \( \text{Al}_2\text{O}_3-\text{CaO-'}\text{FeO}'-\text{MgO-\text{SiO}_2} \)
Systems at Iron Saturation

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A structurally-based quasi-chemical viscosity model has been developed for the \( \text{Al}_2\text{O}_3-\text{CaO-'}\text{FeO}'-\text{MgO-\text{SiO}_2} \) system. The model links the slag viscosity to the internal structure of melts through the concentrations of various anion/cation \( \text{Si}_n\text{O}_{5-n} \), \( \text{Me}_{n/2}\text{O} \) and \( \text{Me}_{n/1}\text{Si}_{n/2}\text{O} \) viscous flow structural units. The concentrations of structural units are derived from the quasi-chemical thermodynamic model. The focus of the present paper is the analysis of experimental data for fully liquid slags in the ‘\text{FeO}'-\text{MgO-\text{SiO}_2}, \text{CaO-'}\text{FeO}'-\text{MgO-\text{SiO}_2} \) and \( \text{Al}_2\text{O}_3-\text{CaO-'}\text{FeO}'-\text{MgO-\text{SiO}_2} \) systems at equilibrium with metallic iron. Model parameters for the quasi-chemical viscosity model for the system \( \text{Al}_2\text{O}_3-\text{CaO-'}\text{FeO}'-\text{MgO-\text{SiO}_2} \) are presented. The model has been optimised for the whole composition range at temperatures between \( 1423 \text{ K} \) and \( 1873 \text{ K} \).

KEY WORDS: slag viscosity; viscosity model; \( \text{Al}_2\text{O}_3-\text{CaO-'}\text{FeO}'-\text{MgO-\text{SiO}_2} \).

1. Introduction

The present paper is the fourth in a series describing the development of the structurally-based quasi-chemical viscosity (QCV) model for the \( \text{Al}_2\text{O}_3-\text{CaO-'}\text{FeO}'-\text{MgO-\text{SiO}_2} \) system and its subsystems.\(^{1-3} \) A structurally-based viscosity model for fully liquid silicate slags applied to the \( \text{Al}_2\text{O}_3-\text{CaO-'}\text{FeO}'-\text{MgO-\text{SiO}_2} \) system at metallic iron saturation has previously been developed by authors. The present series of papers describes further extension of the model for the \( \text{Al}_2\text{O}_3-\text{CaO-'}\text{FeO}'-\text{SiO}_2 \) system to incorporate the effect of \( \text{MgO} \).

A wide range of naturally occurring and industrially important compounds are described by the 5-component system \( \text{Al}_2\text{O}_3-\text{CaO-'}\text{FeO}'-\text{MgO-\text{SiO}_2} \). On heating, these materials are transformed to molten igneous rock and slags. Understanding the viscosity characteristics of these materials is a key to predicting the flow behaviour in geological and metallurgical processes. In the case of industrial processes a variety of different raw materials and reactants may be used, leading to bulk compositions that are markedly different from the original. For this reason viscosity models that provide comprehensive descriptions of melt viscosities over wide ranges of compositions are required. In the present paper experimental viscosity data and phase information from all of the sub-systems in the \( \text{Al}_2\text{O}_3-\text{CaO-'}\text{FeO}'-\text{MgO-\text{SiO}_2} \) system are critically evaluated and used to provide a comprehensive liquid phase viscosity model that is accurate and valid for the whole composition range.

2. Summary of the Experimental Data

A summary of the experimental viscosity data available in the literature for the ‘\text{FeO}'-\text{MgO-\text{SiO}_2}, \text{CaO-'}\text{FeO}'-\text{MgO-\text{SiO}_2} \) and \( \text{Al}_2\text{O}_3-\text{CaO-'}\text{FeO}'-\text{MgO-\text{SiO}_2} \) systems at metallic iron saturation is given in Table 1. Blank or partially filled cells in Table 1 (e.g. Gorbachev et al.\(^{12} \)) indicate that corresponding information (i.e. error, atmosphere etc.) was not reported by the investigators.

To achieve iron saturation in Fe-containing slags it is necessary to use Fe crucibles and/or Fe sensors, as employed in some viscosity studies in the \( \text{Al}_2\text{O}_3-\text{CaO-'}\text{FeO}'-\text{MgO-\text{SiO}_2} \) system and its subsystems (see Table 1, for example, Ji et al.\(^{5,9} \) Leiba and Komar,\(^{10} \) Williams et al.\(^{18} \)). However, a number of the researchers used non-iron crucibles. Kucharski et al.\(^{6} \) carried out viscosity measurements in the ‘\text{FeO}'-\text{MgO-\text{SiO}_2} \) system at controlled oxygen partial pressures using Mo crucibles. The values of \( p_{\text{O}_2} \) in this study were low\(( <10^{-3} \text{ atm})\). Calculations of the phase equilibria using the FactSage package\(^{18} \) have shown that \( \text{Fe}_2\text{O}_3 \) concentrations under these conditions are low (less...
than 3 mass%) and iron oxide can be considered to be present only as ‘FeO’.

Toropov et al.\textsuperscript{7)17) carried out post-experimental analysis of rod-quenched slag samples and reported small amounts of Fe\textsubscript{2}O\textsubscript{3} (less than 1 mass%) present in the slags. Bills\textsuperscript{11) used a graphite sleeve surrounding the Ir crucible and N\textsubscript{2} gas to prevent oxidation of the slags; less than 0.6 mass% Fe\textsubscript{2}O\textsubscript{3} content was reported to be present in the samples. Pt or Pt/Rh crucibles/sensors were used in three different studies.\textsuperscript{14–16)} It is well-known that Pt can react with iron to form a Pt–Fe alloy, which can significantly alter the slag composition. No information about the compositional analysis of the slags or reactions between crucible/spindle and the slag was provided in the studies by Kim et al.\textsuperscript{14) and Lee et al.\textsuperscript{15) Sheludyakov et al.\textsuperscript{16)} reported that Mossbauer spectroscopic analysis of the samples showed low concentrations of Fe\textsubscript{2}O\textsubscript{3} in the slags (less than 3–5 mass%).

The column marked PEA in Table 1 refers to Post Experimental Analysis; “+” indicates that the samples were

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
System & Source & Technique & PEA & Material of crucible & Number of comps & Temperature range, K & Uncertainty % Points accepted \\
\hline
FeO-MgO-SiO\textsubscript{2} & Ducret\textsuperscript{10)} & RB & Fe & Fe & - & 1608 - 2031 & 28 \\
\hline
 & JI\textsuperscript{7)} & RB; Ar; t/c & * & Fe or Mo & Fe or Mo & 5 & 32 & - \\
\hline
 & Kucharski\textsuperscript{13)} & RB; CO/CO\textsubscript{2}; t/c & - & Mo & Mo & 8 & 57 & 1543 - 1623 & ±3.5-5.5 & 57 \\
\hline
 & Toropov\textsuperscript{7)} & RB; Ar; t/c & + & Mo & Mo & 15 & 72 & 1523 - 1773 & ±2.2 & 31 \\
\hline
 & Williams\textsuperscript{8)} & RB; Ar; t/c & - & Fe & Fe & 1 & 4 & 1523 - 1673 & ±10.0 & 0 \\
\hline
CaO-FeO-MgO-SiO\textsubscript{2} & JI\textsuperscript{7)} & RB; Ar; t/c & + & Fe & Fe & 4 & 36 & 1543 - 1773 & 33 \\
\hline
 & Leiba\textsuperscript{10)} & RB; t/c & + & Fe & Fe & 30 & 117 & 1423 - 1823 & ±10.0 & 11 \\
\hline
 & Williams\textsuperscript{8)} & RB; Ar; t/c & - & Fe & Fe & 3 & 11 & 1523 - 1673 & ±10.0 & 11 \\
\hline
Al\textsubscript{2}O\textsubscript{3}-CaO-FeO-MgO-SiO\textsubscript{2} & Bills\textsuperscript{11)} & RB; N\textsubscript{2}; t/c & - & Ir (Pt) & Ir & 16 & 82 & 1523 - 1773 & 77 \\
\hline
 & Gorbachev\textsuperscript{12)} & Vibrational & - & & & 32 & 190 & 1573 - 1873 & 190 \\
\hline
 & Higgins\textsuperscript{13)} & RC; N\textsubscript{2}; t/c & - & Mo & Mo & 10 & 175 & 1392 - 1773 & ±8.0 & 175 \\
\hline
 & Kim\textsuperscript{14)} & RB; Ar; & - & Pt/10Rh & Pt/10Rh & 24 & 44 & 1723 - 1773 & 44 \\
\hline
 & Lee\textsuperscript{15)} & RB; Ar; & - & Pt/10Rh & Fe & 24 & 57 & 1623 - 1723 & 57 \\
\hline
 & Sheludyakov\textsuperscript{16)} & Vibrational; t/c & - & Pt & Pt & 9 & 81 & 1523 - 1733 & 81 \\
\hline
 & Vyatkina\textsuperscript{18)} & Rotational; t/c & - & Mo & Mo & 36 & 108 & 1573 - 1673 & 108 \\
\hline
\end{tabular}
\caption{Summary of the experimental viscosity data in the system Al\textsubscript{2}O\textsubscript{3}–CaO–‘FeO’–MgO–SiO\textsubscript{2}.}
\end{table}

RB = rotating bob t/c = thermocouple
analysed chemically following experimentation, “—” means no analysis was reported.

The rotational cylinder method was used by most of the researchers. Gorbachev et al.\(^2\) and Sheludyakov et al.\(^1\) used “vibrational” viscometers, which are accurate at viscosities lower than those reported in the papers.

Viscosity data that was not measured under well-defined and controlled experimental conditions, or which was believed to be obtained under conditions that do not produce fully liquid slags i.e. solid/liquid mixtures, were not included in the model optimisations.

An example of the liquids temperatures and the bulk slag compositions used in viscosity measurements in the system ‘FeO’–MgO–SiO\(_2\) is shown in Fig. 1. It can be seen that using this systematic approach the validity of the reported data are readily evaluated.

3. Development of the Model

The formalism for the quasi-chemical viscosity (QCV) model developed by the authors has been presented in detail in earlier publications.\(^3\)\(^,\)\(^19\) A brief description of the essential features of the model is given below for the benefit of the reader.

Frenkel’s kinetic theory of liquids\(^20\) considers a liquid to possess a solid-like structure with atoms or molecules oscillating about average positions in their energetic cells (potential wells). The oscillations result in the movement of an atom or molecule, or more generally, of a viscous flow structural unit (SU), after a certain time, from its cell into an adjacent cell, provided the latter is vacant. These vacant cells, or “holes” are assumed to be distributed randomly throughout the liquid. From this point of view, the reaction of a liquid (proportional to the viscosity) to the applied shear force is determined by two factors: the ability of structural units to jump over the potential barrier and the concentration of “holes” in the liquid.

Based on the postulates of liquid state and liquid viscosity initially formulated by Frenkel,\(^20\) the Eyring viscosity equation was developed,\(^21\) which was used for the present QCV model:

\[
\eta = \frac{2RT}{\Delta E_v} \left( \frac{2\pi m_{SU} kT}{v_{SU}} \right)^{1/2} \exp \left( \frac{E_v}{RT} \right) \tag{1}
\]

where \(R\) and \(k\) are the gas (JK\(^{-1}\)mol\(^{-1}\)) and Boltzmann (JK\(^{-1}\)) constants, respectively, \(\pi = 3.1416\), \(T\) is the absolute temperature (K), \(\Delta E_v\) and \(E_v\) are the vapourisation and activation energies (J mol\(^{-1}\)), respectively, \(m_{SU}\) and \(v_{SU}\) are the weight and volume of a particular structural unit of viscous flow (kg and m\(^3\), respectively).

The definition of the viscous flow structural unit is based on the understanding that molten slags have complex internal structures dependent on composition and temperature.\(^22\)\(^,\)\(^23\) A silicate slag may be considered to consist of nearly close-packed arrangements of oxygen anions with smaller metal cations occupying the interstitial positions; the cations are distributed through the melt maintaining electroneutrality and interacting over a short range with each other.\(^24\) The conventional description of slag structure includes the silica tetrahedra SiO\(_4\)\(^–\) linked by strong covalent Si–O bonds that are broken by metal cations.\(^22\)\(^,\)\(^23\) Fincham and Richardson\(^25\) further suggested that a silicate slag can schematically be considered to consist of the three different types of oxygens: “bridging” (O\(^–\)– connected to two silicon cations), “non-bridging” (O\(^–\)– connected to only one silicon), and “free” (O\(^2–\)– associated with non-silicon cations). This concept has been successfully used in numerous chemical thermodynamic models related to the silicate slag structure.

Following these concepts, the structural units of viscous flow in the present QCV model applied to the silicate slags are defined as oxygen anions with metal cations partly associated with them: Si\(_0\)O, Me\(_2\)O and Me\(_4\)Si\(_2\)O. Thus, for example, in a ternary system Al\(_2\)O\(_3\)–MgO–SiO\(_2\), there are six different structural units Al–O–Al, Al–O–Mg, Al–O–Si, Mg–O–Mg, Mg–O–Si and Si–O–Si, denoted by the abbreviations Al–Al, Al–Mg, Al–Si, Mg–Mg, Mg–Si and Si–Si, respectively.

The average weights \(m_{SU}\) and volumes \(v_{SU}\) of each structural unit are used in conjunction with Eq. (1), and in the binary MeO–SiO\(_2\) system they are expressed in the following form through the concentrations of different structural units present in the melt:

\[
m_{SU} = m_{Si-Si} X_{Si-Si} + m_{Me-Si} X_{Me-Si} + m_{Me-Me} X_{Me-Me} \ldots \tag{2}
\]

\[
v_{SU} = v_{Si-Si} X_{Si-Si} + v_{Me-Si} X_{Me-Si} + v_{Me-Me} X_{Me-Me} \ldots \tag{3}
\]

where \(m_{Si-Si}\) and \(v_{Si-Si}\), \(m_{Me-Me}\) and \(v_{Me-Me}\), and \(m_{Me-Si}\) and \(v_{Me-Si}\) are the volumes and masses of the Si\(_2\)O, Me\(_4\)O and Me\(_4\)Si\(_2\)O structural units, respectively, where \(n\) is the oxidation state of a metal cation Me\(^{n+}\) and \(X_{Si-Si}, X_{Me-Me}\) and \(X_{Me-Si}\) (here and below) are the molar fractions of respective structural units. The volumes of the corresponding structural units are calculated using the effective diameters of structural units estimated from the ionic radii of different ions (O, Si, Me) composing a particular structural unit; the ionic radii are taken from Shannon\(^26\); the angles between different bonds within a structural unit are not taken into account. The final values of \(m_{SU}\) and \(v_{SU}\) are given in Table 2.
In the QCV model for the binary system MeO–SiO$_2$ the integral molar activation energy $E_a$ is expressed as follows:

$$E_a = \frac{E_{a,Me-Me}}{H_{11005}}X_{Me-Me} + \frac{E_{a,Me-Si}}{H_{11001}}X_{Me-Si}$$

where $E_{a,Me-Me}$ and $E_{a,Me-Si}$ are the partial molar activation energies of each type of structural unit.

The vaporisation energy $D_E$ is expressed as:

$$D_E = \frac{E_{v,Me-Me}}{H_{11005}}X_{Me-Me} + \frac{E_{v,Me-Si}}{H_{11001}}X_{Me-Si}$$

where $E_{v,Me-Me}$ and $E_{v,Me-Si}$ are the dimensionless partial vaporisation energy coefficients of each type of structural unit.

The partial activation energies and vaporisation energy coefficients of a given structural unit depend strongly on the interactions with surrounding structural units. In the QCV model, based on the analysis of the experimental viscosity data, only the interactions between the nearest neighbouring structural units are considered. Moreover, the Si–Si partial molar activation energy $E_{a,SI-SI}$ and the Si–Si vaporisation energy coefficient $e_{v,SI-SI}$ were found to be the only variable parameters in the binary silicate systems:

$$E_{a,SI-SI} = \frac{E_{a,SI-SI,1}}{H_{11005}}X_{SI-SI,1} + \frac{E_{a,SI-SI,2}}{H_{11001}}X_{SI-SI,2}$$

where $E_{a,SI-SI,1}$ and $E_{a,SI-SI,2}$ are adjustable parameters describing influence of neighbouring structural units on the given structural unit. The final set of the model coefficients is given in Table 2.

The concentrations of the structural units $X_{SI-SI}$, $X_{Me-Si}$, and $X_{Me-Me}$ are equal to and derived from, the corresponding concentrations of the second nearest neighbouring bonds (SNNB) calculated using the quasi-chemical thermodynamic model developed by Guggenheim$^{26}$ and then modified by Blander and Pelton. The model takes into account short-range ordering in the ionic melt by considering, for example, in the binary slag system MeO–SiO$_2$, the formation of two nearest-neighbour pairs (Me–Me) and a (Si–Si) pair.$^{27}$ Since its development the quasi-chemical model, as part of the FactSage (earlier F*A*C*T) computer package,$^{18,28}$ has been successfully applied to describe experimental phase equilibria, thermodynamic and other types of data in many slag systems, from binary to multi-component systems.$^{29}$ The quasi-chemical formalism is assumed to accurately describe the internal structural ordering in the slags. Figure 2 gives an example of SNNBs concentrations in the ‘FeO’–MgO–SiO$_2$ system at 1873 K.

![Fig. 2. Predicted (FactSage) SNNB iso-concentrations in the ‘FeO’–MgO–SiO$_2$ system at 1873 K.](image-url)
a complex way; the maximum concentrations in each case occurring about Fe/Si and Mg/Si ratios of 2/1 in each case, these correspond to the ratios to form the orthosilicates, 2FeO·SiO2 and 2MgO·SiO2 respectively.

It has been found experimentally that Al3+ can occupy tetrahedral coordination positions in the oxygen lattice and form strong bonds with neighbouring tetrahedra, in a similar way to Si4+ ions, if the excess negative charge for Al3+ is compensated for by the presence of alkali or alkaline earth cations. This is commonly referred to as the “charge compensation effect”. As a result, the experimental viscosities in the Al-containing silicate slag systems Al2O3–(Me2+, Me3+)–O·SiO2 at constant SiO2 molar concentrations have maxima at Al2O3/(Me2+, Me3+) ratios close to 1. To describe the slag viscosity in these Al-containing systems the following charge compensation term was added to the activation energy of viscous flow (written for the Al2O3–CaO–MgO–SiO2 system):

\[
E_{a}^{vhc} = \left( \sum_{j} X_{Al-j} \right) e_{a,AlMe}^{vhc} \left( \sum_{j} X_{Ca-j} \right)^{\beta} e_{a,AlMe}^{vhc} \left( \sum_{j} X_{Mg-j} \right)^{\beta} \left( \sum_{j} X_{Al-j} + \sum_{j} X_{Ca-j} + \sum_{j} X_{Mg-j} \right) \]

where

\[
\sum_{i} X_{Al-i} = 2X_{Al-Al} + X_{Al-Si} + X_{Al-Ca} + X_{Al-Mg}
\]

\[
\sum_{i} X_{Ca-i} = 2X_{Ca-Ca} + X_{Ca-Si} + X_{Ca-Al} + X_{Ca-Mg}
\]

\[
\sum_{i} X_{Mg-i} = 2X_{Mg-Mg} + X_{Mg-Si} + X_{Mg-Al} + X_{Mg-Ca}
\]

and \( E_{a,AlMe}^{vhc} \) and \( \beta \) are adjustable parameters. The charge compensation term \( E_{a}^{vhc} \) (Eq. (8)) is a function of the concentrations of Al3+, Ca2+, and Mg2+ cations in the melt. In the present study the values of \( \alpha \) and \( \beta \) were selected to achieve the maximum of the charge compensation term, and therefore of the viscosity, at \( X_{Ca,Mg,Al}/X_{Al,O} \approx 1 \), ensuring the best agreement with the experimental data.

In summary, the QCV model links the slag viscosity to the internal structure of melts through the concentrations of various anion/cation structural units that are present in the melt. In the present study the concentrations of these structural units are derived from the quasi-chemical thermodynamic model of the system Al2O3–CaO–FeO–MgO–SiO2 using the FactSage computer package.17,27

The methodology used in optimising the QCV model parameters in the present study involves the following stages: 1) collect and carefully analyse all the experimental data available for the slag systems under investigation; 2) exclude unreliable experimental datasets from the model optimisation (using analysis of phase equilibria and trends in the activation and vapourisation energies obtained from experimental viscosity data); 3) evaluate the variability (internal scatter) of experimental data; 4) analyse the trends in the concentrations of structural units obtained from the quasi-chemical thermodynamic model; 5) calculate the masses and volumes of the structural units using mass balance and available ionic radii data; 6) optimise the model coefficients for the whole compositional range of the slag systems including all unary, binary, ternary etc. sub-systems by repeating optimisation cycles from low- to high-order systems; 7) analyse the model parameters obtained during optimisation to understand general trends and dependencies; 8) repeat steps 6 and 7 until the agreement between model predictions and experimental data is comparable to the data variability over the whole range of conditions.

The final set of model parameters for the Al2O3–CaO–FeO–MgO–SiO2 system is given in Table 3.

4. Comparisons between Model Predictions and Experimental Data

4.1. Binary MgO-containing Systems

Viscosity measurements and QCV model parameters for the binary systems MgO–SiO2, MgO–Al2O3 and MgO–CaO have been presented and discussed in a previous paper by the authors.1 There are no experimental data available on the viscosities of melts in MgO–FeO systems.

4.2. ‘FeO’–MgO–SiO2

Comparison between the model predictions and the experimental data in the ‘FeO’–MgO–SiO2 system at iron saturation is shown in Figs. 3(a)–3(c)), this includes the calculated iso-viscosities [Pa·s] and experimental measurements by Kucharski et al.,8) Toropov et al.,7) Williams et al.,8) Ducret and Rankin5) and Ji et al. at 1 573, 1 723 and 1 873 K. The experimentally-determined viscosities at the various bulk slag compositions are marked on the Figures. The shape of the symbol indicates the first author of the previously published data. Experimental data on the pseudo-binary “FeO”–SiO2 that has been previously evaluated has been included in the optimisation; these data are not marked on the Figures.

It can be seen from Figs. 3(a), 3(b) that all the measurements by Toropov et al.7) at 1 573 and most at 1 723 K were conducted below the liquidus. As a result, these data are significantly higher viscosities than are expected from fully liquid slags, the differences increasing with increasing % solids present in the system at equilibrium, for these reasons these data in the phase regions have not been included in the viscosity model optimisation.

Kucharski et al. data at 1 573 K appears very close to the olivine liquidus surface (Fig. 3(a)); these data and the measurement by Williams8) appear to be consistent with the QCV model predictions. Ji et al.’s measurements5) at 1 573, 1 723 and 1 873 K. Kucharski et al. data at 1 573 K appears very close to the olivine liquidus surface (Fig. 3(a)); these data and the measurement by Williams8) appear to be consistent with the QCV model predictions.
Table 3. Parameters of the quasi-chemical viscosity model for fully liquid slags in the system Al$_2$O$_3$–CaO–FeO$^-$–MgO–SiO$_2$.

Activation energy ($10^7$ kJ/mol):

\[
E_v = E_v_{a-e} X_{a-e} + E_v_{a-g} X_{a-g} + E_v_{a-v} X_{a-v} + E_v_{a-Mg} X_{a-Mg} + E_v_{a-Si} X_{a-Si} +
E_v_{a-Fe} X_{a-Fe} + E_v_{a-Ca} X_{a-Ca} + E_v_{a-Mg} X_{a-Mg} + E_v_{a-Si} X_{a-Si} +
E_v_{a-Fe} X_{a-Fe} + E_v_{a-Ca} X_{a-Ca} + E_v_{a-Mg} X_{a-Mg} + E_v_{a-Si} X_{a-Si} +
E_v^{(1)}_{a-Mg} X_{a-Mg} + E_v^{(1)}_{a-Si} X_{a-Si} +
\frac{2X_{a-e} + \sum X_{a-e}}{4} \left[ E_v^{(1)}_{a-e} X_{a-e} + \sum X_{a-e} \right] + E_v^{(1)}_{a-Ca} \left[ 2X_{a-Ca} + \sum X_{a-Ca} \right] + E_v^{(1)}_{a-Mg} \left[ 2X_{a-Mg} + \sum X_{a-Mg} \right] \right]^\beta \right] Y_{a-Si}^{\alpha} \right)
\]

where

\[
\sum X_{a-e} = X_{a-e} + X_{a-Ca} + X_{a-Mg} + X_{a-Si} +
\sum X_{a-Ca} = X_{a-Ca} + X_{a-Ca} + X_{a-Ca} + X_{a-Ca} +
\sum X_{a-Mg} = X_{a-Mg} + X_{a-Mg} + X_{a-Mg} + X_{a-Mg} +
\sum X_{a-Si} = X_{a-Si} + X_{a-Si} + X_{a-Si} + X_{a-Si} + 1
\alpha = 3, \beta = 1
\]

and

\[
E_v^{(1)}_{a-Si} = 0.79 + 4.65 X_{a-Si}^2 + 4.98 X_{a-Si} + 2.34 X_{a-Si} + 2.17 X_{a-Si} + 2.77 X_{a-Mg} \]
\[
E_v^{(1)}_{a-e} = 1.30, \quad E_v^{(1)}_{a-Ca} = 0.82, \quad E_v^{(1)}_{a-Ca} = 0.50, \quad E_v^{(1)}_{a-Mg} = 1.16, \quad E_v^{(1)}_{a-Si} = 2.78 - 0.96 X_{a-Si} - 3.11 X_{a-Si} - 0.38 X_{a-Mg} + 5.63 X_{a-Ca} + 7.48 X_{a-Fe}, \quad E_v^{(1)}_{a-Fe} = 1.20 - 0.07 X_{a-Fe} + 0.22 X_{a-Mg} + 0.29 X_{a-Ca} + 0.37 X_{a-Fe} + 2.00 X_{a-Ca}, \quad E_v^{(1)}_{a-Mg} = 0.28 + 0.95 X_{a-Mg} + 1.20 X_{a-Mg} - 7.53 X_{a-Ca} - 1.80 X_{a-Fe}, \quad E_v^{(1)}_{a-Ca} = 1.00 + 1.50 X_{a-Mg} + 1.00 X_{a-Mg} + 2.70 X_{a-Ca}, \quad E_v^{(1)}_{a-e} = 1.83 - 0.02 X_{a-si} + 0.56 X_{a-Mg}, \quad E_v^{(1)}_{a-Ca} = \frac{1}{2} \left( E_v^{(1)}_{a-Ca} + E_v^{(1)}_{a-Ca} \right), \quad E_v^{(1)}_{a-Mg} = \frac{1}{2} \left( E_v^{(1)}_{a-Mg} + E_v^{(1)}_{a-Mg} \right), \quad E_v^{(1)}_{a-Si} = \frac{1}{2} \left( E_v^{(1)}_{a-Si} + E_v^{(1)}_{a-Si} \right), \quad E_v^{(1)}_{a-Fe} = 1.90, \quad E_v^{(1)}_{a-Fe} = 2.00, \quad E_v^{(1)}_{a-Fe} = 1.20, \quad E_v^{(1)}_{a-Fe} = 1.29.
tural units, such as Fe–Fe, Mg–Mg and Fe–Mg. It has been shown in earlier reviews of the data that the viscosities of FeO liquids are lower than either MgO or CaO. This leads to the increasing dependence of viscosity on FeO concentration and SiO2/MgO ratio in the liquids.

4.3. CaO–'FeO'–MgO–SiO2

Experimental viscosity measurements in the CaO–'FeO'–MgO–SiO2 systems at iron saturation are available from Leiba and Komar10) and Ji et al.8) By way of illustration the predicted iso-viscosities and experimental data by Leiba10) and Ji 8) in the CaO–'FeO'–MgO–SiO2 at 1773 K and at 5, 10, 15 mass% of MgO are presented in Figs. 4(a)–4(c). It can be seen that some of the measurements by Leiba 10) were carried out below the liquidus at 5 mass% MgO, these data have not been included in the optimisation, and it is clear that the data are both inconsistent and generally higher than expected from fully liquid slags. Note that the experimental data for the CaO–'FeO'–MgO–SiO2 system marked on Figs. 4(a)–4(c) are only for measurements made at 1773 K. The viscosity data at other temperatures generated in the various research studies have been included in the overall QCV model optimisations. In general, the model predictions agree well with the experimental data for the fully liquid slags in the range 1473–1873 K.

4.4. Al2O3–CaO–'FeO'–MgO–SiO2

The experimental viscosity data on the Al2O3–CaO–'FeO'–MgO–SiO2 system by a number of workers (see Table 1) have been included in the QCV model optimisation. The predicted iso-viscosities and experimental data in the Al2O3–CaO–'FeO'–MgO–SiO2 at 1723 K and at 10 mass% Al2O3 and 5 mass% MgO are presented in Fig. 5. Essentially it appears the slag viscosities are dependent on the silica concentrations in the slags. There is considerable scatter between results by different researchers. The experimental results by Kim et al.14) and Lee et al.15) at this temperature are mostly obtained below the liquidus in the olivine primary phase field, this would explain why these measurements are much higher values than expected from fully liquid slags. The crystallisation of olivine from the slag increases the silica concentration in the remaining liquid and this factor, and the presence of solids, will contribute to increased viscosities.

The measurements by Higgins and Jones13) in fully liquid slags appear to be quite variable with values differing by factor of 2 with the same silica concentration and only slightly different CaO/FeO ratios.
The data provided by Bills\textsuperscript{11} indicate viscosities higher than generally predicted from the QCV model; this difference increases with increasing % SiO\textsubscript{2}. It is not clear why this should be.

4.5. Overall Agreement

The agreement between experimental and predicted viscosities for the Al\textsubscript{2}O\textsubscript{3}–CaO–FeO–MgO–SiO\textsubscript{2} system and its sub-systems was evaluated using the Model Evaluation
Parameter (MEP):

\[
\Delta = \frac{1}{N} \sum_{n} \left( \frac{\eta_n^{\text{calc}} - \eta_n^{\text{ex}}}{\eta_n^{\text{ex}}} \right)
\]

where \(N\) is a number of points and \(n\) is a particular slag system, the subscripts “calc” and “ex” refer to the calculated and experimental viscosities at a given composition and process conditions. The results of the overall agreement are given in Table 4.

5. Conclusions

A quasi-chemical viscosity model has been developed for liquid slags in the Al\(_2\)O\(_3\)–CaO–‘FeO’–MgO–SiO\(_2\) system at iron saturation; this model is directly related to the internal slag structure. The structures of the slags have been determined from the second nearest neighbour bond concentrations extracted from the modified quasi-chemical thermodynamic model of the system available in the FactSage package. Critical analysis of the experimental data available on the slag viscosities in this system has been undertaken. Data from a number of systems have been shown to be obtained at sub-liquidus conditions and have not therefore been included in the model optimisation. The Q-C viscosity model parameters are valid for the whole range of compositions in the Al\(_2\)O\(_3\)–CaO–‘FeO’–MgO–SiO\(_2\) system in equilibrium with metallic iron, and generally in the range 1423–1873 K.

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