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 Revised Model to Incorporate Ferric Oxide

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A model has been developed that enables the viscosities of the fully liquid slag in the multi-component $\text{Al}_2\text{O}_3$–$\text{CaO}$–$\text{FeO}$–$\text{Fe}_2\text{O}_3$–$\text{MgO}$–$\text{SiO}_2$ system to be predicted within experimental uncertainties over a wide range of compositions and temperatures based on the Eyring equation to express viscosity. The model links both the activation and pre-exponential energy terms to the slag internal structure through the concentrations of various $\text{SiO}_3\text{O}$, $\text{Me}^{n+}\text{Si}_2\text{O}_3$ and $\text{Me}^{n+}\text{Me}^{2+}\text{Si}_2\text{O}_3$ viscous flow structural units, of which the concentrations are derived from a quasi-chemical thermodynamic model of the liquid slag. The model describes a number of slag viscosity features including the charge-compensation effect specific for the $\text{Al}_2\text{O}_3$-containing systems. The present paper describes application of recent significant improvements in the model formalism to the multi-component system $\text{Al}_2\text{O}_3$–$\text{CaO}$–$\text{FeO}$–$\text{Fe}_2\text{O}_3$–$\text{MgO}$–$\text{SiO}_2$, where both $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ effects on viscosity are individually evaluated. The present model reproduces viscosities of slags equilibrated with metallic iron, which mainly reflects $\text{Fe}^{2+}$ effects on viscosity including the charge compensation effect of the $\text{Fe}^{2+}$ as well as $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ cations on the formation of tetrahedrally-coordinated $\text{Al}^{3+}$. The model can also reproduce the compositional tendency of viscosity of the $\text{SiO}_2$-free $\text{CaO}$–$\text{FeO}$–$\text{Fe}_2\text{O}_3$ slag in air by incorporating the charge compensation effect of $\text{Fe}^{3+}$ to form tetrahedral coordination by basic cations such as $\text{Ca}^{2+}$ and $\text{Fe}^{2+}$ and to indicate viscosity maximum at an intermediate composition. Further analysis of the behaviour of the $\text{Fe}^{3+}$ cation in the silicate structure to describe corresponding effect on viscosities and to improve viscosity predictions is essential.

KEY WORDS: slag viscosity; viscosity model; viscous flow structural unit; ferrous oxide; ferric oxide.

1. Introduction

The present paper is one in a series of papers describing further 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. The QCV model relates the complex viscous behaviour of molten oxide slags to the internal slag structure. The internal slag structure changes systematically with bulk slag composition and temperature, and is derived from the quasi-chemical thermodynamic model incorporated into the FactSage computer package.

Recently, a new significantly improved formalism of the QCV model has been reported by the authors, which expresses a number of slag viscosity features systematically in a comprehensive manner superior to the previous version and enables the viscosities of fully liquid slag in the $\text{Al}_2\text{O}_3$–$\text{CaO}$–$\text{MgO}$–$\text{SiO}_2$ system to be predicted within experimental uncertainties over a wide range of compositions and temperatures above liquidus.

This paper focuses on the effect of ferrous iron oxide and presents extension of the revised QCV model to the $\text{Al}_2\text{O}_3$–$\text{CaO}$–$\text{FeO}$–$\text{Fe}_2\text{O}_3$–$\text{MgO}$–$\text{SiO}_2$ slag system close to and at metallic iron saturation as the first in a series describing the effects of both ferrous and ferric oxides on slag viscosity. Iron in the slag exists as the ferrous and ferric oxides, and the effect of these species on slag viscosity in the present study is individually evaluated. The behaviour of Fe$^{2+}$ and Fe$^{3+}$ with respect to the so-called “charge compensation effect” is paid specific attention in the present study. Experimental viscosity study in the $\text{Al}_2\text{O}_3$–$\text{FeO}$–$\text{SiO}_2$ slag at metallic iron saturation showed possible maximum of viscosity at intermediate Al / (Al + Fe) ratios at constant $\text{SiO}_2$ concentrations indicating that the $\text{Fe}^{3+}$ cation possibly also introduces “the charge compensation effect”, similar to the effects by the $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ in the $\text{Al}_2\text{O}_3$-containing systems. In addition, noticeable charge compensation effect on the $\text{Fe}^{3+}$ cation in slags by basic cations such as $\text{Na}^+$ and $\text{Ca}^{2+}$ have been reported in previous viscosity experimental and analytical studies. Although several structurally-based viscosity models incorporate ferric oxide as chemical components in slag, there is no description of the charge compensation effect on Fe$^{3+}$. The incorporation of ferric oxide in the present model is necessary also for the model development in the future that enables the viscosities of Fe-containing slags under different oxygen partial pressures to be predicted.

Accurate characterization of the effect of iron oxides on slag viscosity is of significant importance also for a wide range of industrial applications; for instance, most of gener-
ated slags in important pyrometallurgical processes consist of ferrous and ferric oxides, lime and silica as main components. In some cases Al₂O₃ and MgO are present in significant concentrations. The slag viscosity is a key property for the pyrometallurgical metal extraction processes.

In the present study, available experimental viscosity data in the multi-component Al₂O₃–CaO–FeO–Fe₂O₃–MgO–SiO₂ system and its subsystems at metallic iron saturation have been critically reviewed with particular attention to the viscosimetry methods and possible contamination of slag samples to select reliable data points. The corresponding model parameters in this system have been optimized to reproduce experimental viscosities over a wide composition and temperature range. The influences of these iron oxides on slag viscosity including charge compensation effect of Fe²⁺ cation to form tetrahedrally-coordinated Al³⁺ are evaluated. The effect of the ferric oxide is also taken into account to achieve accurate description of viscosities. In particular, the notable charge compensation effect to form tetrahedrally-coordinated Fe³⁺ by basic cations such as Ca²⁺ and Fe²⁺ has been introduced into the model using similar formalism to the one used for tetrahedrally-coordinated Al³⁺ evaluated. The effect of the ferric oxide is also taken into account to achieve accurate description of viscosities. In the present study, available experimental viscosity data in the ferrite silicate slags at high Fe³⁺ concentration of liquid as a reaction to the applied shear force there was previously used. A higher power term during optimization.

2. Model

The quasi-chemical viscosity (QCV) model and recent revisions have been presented in detail in previous publications, a brief description of the essential features are given below.

Frenkel’s kinetic theory considers a liquid to have a solid-like structure with structural units (SU), oscillating in their energetic cells (potential wells) near average positions. Oscillations higher in magnitude than the potential barrier result in the movement of a structural unit into an adjacent vacant cell, or “hole”, provided the latter is vacant. The viscosity of a liquid as a reaction to the applied shear force therefore is determined by (a) the ability of a structural unit to jump over the potential barrier and (b) the presence of “holes” in the liquid. The following Eyring Eq. (1) for liquid viscosity was derived using the above principles:

\[ \eta = \frac{2RT}{\Delta E_v} \left( \frac{\Delta V_v}{V_{SU}} \right) \exp \left( \frac{\Delta E_v}{RT} \right) \]  

where \( R \) [J/K/mol] and \( k \) [J/K] are the gas and the Boltzmann constants; \( \tau = 3.1416 \); \( T \) is the absolute temperature [K]; \( m_{SU} \) [kg] and \( v_{SU} \) [m⁴] are the average mass and volume of viscous flow structural units. The activation energy \( E_v \) is determined by the strength of interactions between different structural units composing the liquid. The energy term \( \Delta E_v \) (a product of vaporisation energy and transition probability) is related to the concentration of the holes in the liquid: higher concentration of the holes in the liquid corresponds to the higher \( \Delta E_v \) value and to the lower viscosity.

Four parameters in Eq. (1) – the average mass and volume of structural units, the \( E_v \) and \( \Delta E_v \) energies – are related to the internal structure of liquids, types, concentrations and interactions between structural units at atomic cation/anion level, and require the definition of a viscous flow structural unit.

A silicate slag may be considered as a nearly close-packed arrangement of larger oxygen anions with smaller metal cations that occupy the interstices and interact with each other. A silicate slag structure also is conventionally described as the silicate network of \( \text{SiO}_4^2- \) tetrahedra broken by different metal cations distributed to keep the total electroneutrality. Fincham and Richardson1 related properties of a silicate slag to the internal slag structure through concentrations of three different types of oxygen: “bridging” (O²⁻ – connected to two silicon cations), “non-bridging” (O²⁻ – connected to only one silicon), and “free” (O²⁻ – associated with non-silicon cations). Based on the above background, the viscous flow of the silicate slag in the present model is considered to be a movement of oxygens partly associated with metal cations under the applied shear force, so that the viscous flow structural units (for brevity referred to just as “structural units” SU) are defined as oxygen anions with metal cations partly associated with them, including \( \text{SiO}_4^2- \) (= Si–O–Si = Si–Si), \( \text{Me}^{2+}\text{O} \) (= Me–O–Me = Me–O), \( \text{Me}^{3+}\text{O} \) (= Si–O–Me = Si–Me), where \( n \) denotes the oxidation state of a metal cation Me."³ MSOR. Their molar fractions are indicated as \( X_{\text{Si–Si}} X_{\text{Me–Me}} X_{\text{Me–Si}} \), respectively. Viscous flow structural units are specific to the present viscosity model formulation; they differ from the conventional structural units.²²–²⁵

The values of the \( E_v \) and \( \Delta E_v \) energy terms, and the average mass and volume of structural units \( m_{SU} \) and \( V_{SU} \) in the present model are expressed through the respective molar fractions of the various structural units \( X_{pq} \) with Eq. (2):

\[ m_{SU} = \sum_{p,q} m_{pq} V_{pq}; E_v = \sum_{p,q} E_{a,pq} V_{pq}; \Delta E_v = \Delta E_{v,0} \exp \left( \sum p q \nu_{pq} T \right) \]  

where \( p \) and \( q \) are metal cations; \( m_{pq} \) and \( v_{pq} \) are the masses and volumes of the respective structural units; \( E_{a,pq} \) are partial molar activation energies; \( \Delta E_{v,0} \) is a unit constant; and \( \nu_{pq} \) are the dimensionless partial energy coefficients of the integral energy term \( \Delta E_v \) of each structural unit. In the binary MeO-SiO₂ system, the integral molar activation energy is expressed as follows:

\[ E_v = E_{a,\text{Si–Si}} X_{\text{Si–Si}} + E_{a,\text{Si–Me}} X_{\text{Si–Me}} + E_{a,\text{Me–Me}} X_{\text{Me–Me}} \]  

The \( m_{pq} \) values are the weights of the corresponding molecules, such as \( \text{Si}_2\text{O}_3\text{O} \), \( \text{Me}_2\text{O} \), and \( \text{Me}_2\text{O} \). The \( v_{pq} \) values are calculated using the effective diameters of structural units estimated from the ionic radii of various ions (O, Si, Me) composing a particular structural unit; the ionic radii are taken from Shannon.²⁶ The three-dimensional arrangements of the structural units are not taken into account; this uncertainty is “absorbed” by the model parameters later, during optimization.

In addition to one oxygen, a given structural unit also involves two metal cations, both of them have other neighbours and both are involved into other structural unit(s). The partial properties \( E_{a,pq} \) and \( \nu_{pq} \) of a given structural unit (Me₄-O-Me₄) therefore depend on the type of second nearest neighbours.

The effect of neighbouring structural units on a given partial activation energy is expressed as a function of the concentrations of other types of structural units. The partial molar activation energy of each type of a structural unit was previously expressed using the following Eqs. (3)–(5):

\[ E_{a,\text{Si–Si}} = E_{a,\text{Si–Si}} + E_{a,\text{Si–Me}} X_{\text{Si–Me}} + E_{a,\text{Me–Me}} X_{\text{Me–Me}} \]  

\[ E_{a,\text{Si–Me}} = E_{a,\text{Si–Me}} + E_{a,\text{Me–Me}} X_{\text{Me–Me}} \]  

\[ E_{a,\text{Me–Me}} = E_{a,\text{Me–Me}} \]  

A higher power term \( E_{a,\text{Si–Si}} X_{\text{Si–Si}} \) was previously used in the expression of \( E_{a,\text{Si–Si}} \) to describe the significant viscosity decrease at high SiO₂ concentrations. More complex terms in the expression of \( E_{a,\text{Si–Si}} \) were later introduced for the Na- and K-containing silicate slags.²⁷ The composition dependences of most of the other partial activation energies
except \( \bar{F}_{v_{a-Si}} \) were not taken into account due to the weak dependence on compositions and the lack or uncertainties of experimental data. The partial activation energies \( \bar{E}_{v_{a-Me1-Me2}} \) for the slag systems with limited experimental data available (e.g. CaO–MgO) were taken to be equal to \( \frac{1}{2} \left( \bar{E}_{v_{Me1-Me1}} + \bar{E}_{v_{Me2-Me2}} \right) \). The dimensionless partial energy coefficients \( \bar{E}_{v_{a-Si}}, \bar{E}_{v_{Me-Si}} \) and \( \bar{E}_{v_{Me-Me}} \) were described in a similar way.

To improve reproducibility of reliable experimental viscosity trends for a wide composition range, the model has been critically reviewed and subsequently revised,\(^{10,11} \) the partial properties \( \bar{E}_{v_{Me}} \) and \( \bar{E}_{v_{Me-Si}} \) of a given structural unit (Me\(_{p}\)-O\(_{Me}\)) are described with Eqs. (6)–(8):

\[
F_{v_{a-Si}} = F_{v_{a-Si}}^0 + \sum_{j=Ca,Mg,Al} \frac{X_{jSi}}{X_{Si}} \left( 1 - \frac{X_{jSi}}{X_{Si}} - \gamma_{E_{v_{jSi}}} \right)
+ \sum_{k=Al,Fe^{2+},j=Ca,Mg,Al} \Delta F_{v_{j-kSi}} \left( \frac{p_{AmO_{4}+}}{p_{AmO_{4}}} X_{jSi} \right) + \cdots + \cdots (6)
\]

\[
F_{v_{a-Me}} = F_{v_{a-Me}}^0 + \sum_{j,s,Me} \Delta F_{v_{j-sMe}} \left( \frac{p_{AmO_{4}+}}{p_{AmO_{4}}} \right) \quad (8)
\]

where: \( i = Ca, Mg, Fe^{2+}, Fe^{3+}, Al, \ldots (i \neq Si) \) and \( j = Ca, Mg, Fe^{2+}, \ldots, (j \neq i \neq Si) \) and \( t = Ca, Mg, Fe^{2+}, Al, \ldots t \neq Si \). The dimensionless partial energy coefficients \( \varepsilon_{ij} \) and \( \varepsilon_{k} \) of the present formalism is a system-dependent parameter; \( p_{AmO_{4}+}^{0} \) (i.e. \( Al, Fe^{3+} \)) in Eqs. (6) and (8) is a probability function that expresses the probability to have a tetrahedrally-coordinated \( Al^{3+} \) or \( Fe^{2+} \) among existing \( Am_{-}O_{-}Me_{-} \) structural units (the symbol “Am” corresponds to Amphoteric oxide); \( K_{ij}^{m} \) is an individual constant for each cation and determines the magnitude of the probability to form tetrahedrally-coordinated \( [AmO_{4}]^{2+} \) structure as a result of charge compensation by basic cations; \( \alpha_{ij} \) is the power which determines the composition dependence of the probability function \( p_{AmO_{4}}^{0} \) and in turn the proportion of the \( Am_{-}O_{-}Me_{-} \) structural units with the tetrahedrally-coordinated \( Am_{-}O_{-}Me_{-} \) ion, and this parameter is specific for each \( Al_{2}O_{3} \)–MeO or \( Fe_{2}O_{3} \)–MeO system; \( \Delta F_{v_{j-sMe}} \) and \( \Delta F_{v_{j-kSi}} \) describe additional contributions to the partial energy coefficients \( \bar{E}_{v} \) and \( \varepsilon_{ij} \) of corresponding structural units due to the presence of tetrahedrally-coordinated \( Al^{3+} \) or \( Fe^{2+} \) containing structural units.

The significant decrease of viscosities at high SiO\(_2\) concentrations with the additions of basic metal oxides is commonly attributed to the disturbance of the strong covalent bonds in the silicate tetrahedral network structures by basic cations; the degree of this viscosity decrease therefore should be related to such characteristics as cation size, valence, inner and outer electronic arrangement, the “ease” for cations to donate valent electrons to the oxygen anions in the melt, and therefore, is described in the present revised model with the parameter \( \gamma_{E_{v_{Si}}} \). 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calculations have shown that the Fe $^{3+}$/Fe$^{2+}$ ratio is low (the MgO–SiO$_2$ system and its Fe-containing subsystems close to the literatures 12,13,28–40) for the Al$_2$O$_3$–CaO–FeO–Fe$_2$O$_3$–MgO–SiO$_2$ system to prevent the contamination of container material into slag. The Fe$^{3+}$/Fe$^{2+}$ ratio in slag has not been provided so that it was calculated from the phase equilibria using FactSage. $^9$ These calculations have shown that the Fe$^{3+}$/Fe$^{2+}$ ratio is low (the order of 0.01) in ferrosilicate slag under these atmospheres; however, the Fe$^{3+}$/Fe$^{2+}$ ratio increases as total iron concentration in slag increases and as temperature decreases, and it approaches to 0.1 in maximum (e.g. 0.08 in molten iron oxide equilibrated with metallic iron at 1673 K).

3.2. Determination of the Experimental $E_a$ and $\Delta E_F$ Values

Experimental values of the integral $E_a$ and $\Delta E_F$ energies were derived using Eq. (1) from the gradient and intercept, respectively, of the relationship of $\ln(n/\eta)$ versus inverse temperature $1/T$ for a given composition. $^1$–$^4$, $^{10}$ These $E_a$ and $\Delta E_F$ values were used along with the viscosity experimental data for optimizations of model parameters.

3.3. Physical Meaning of the Model Parameters and Systematic Analysis of the Model Parameters

Present model parameters (partial $E_a$ and $\Delta E_F$ energies) have physical basis and are directly related to the internal slag structure and to the physics of interactions at atomic scale. Strong, mostly covalent bonds linking silicate tetrahedrons in the melt result in high activation energy and high viscosities in the silica-rich slags. Addition of basic metal oxides (e.g. CaO, MgO, ...) strongly affects the bonds between silicate tetrahedrons, and as a result decrease viscosity of the high-silicate slags significantly. Some cations (e.g. Al$^{3+}$ and Fe$^{3+}$) behave in a different way depending on the chemical environment. The individual effect of various metal oxides on viscosity is determined by a series of factors including atomic structure, cation size, inner and outer electronic arrangement, the “ease” to donate valent electrons to the oxygen anions in the oxide melt, etc.

The physical basis of the parameters in the present viscosity model is a foundation (i) to introduce particular restrictions (e.g. integral $E_a$ and $\Delta E_F$ energies should be positive over the whole composition range), and (ii) to relate these parameters to other known metal cation characteristics (e.g. cation size, ionic potential) or other physicochemical properties (e.g. heat of vaporisation). The optimization procedures involved the use of correlations with other properties. The details on the correlations between model parameters and other physicochemical properties are exhibited in our previous publication. $^10$ The present viscosity model parameters can also help to “de-convolute” relative physicochemical behaviour of different cations in the oxide melt.

Table 1. Experimental conditions of viscosity data for the Al$_2$O$_3$–CaO–FeO–Fe$_2$O$_3$–MgO–SiO$_2$ and its subsystems close to and at metallic iron saturation.

<table>
<thead>
<tr>
<th>Source</th>
<th>Method, Atmosphere, Temp. controlling</th>
<th>Container / Sensor materials</th>
<th>Chemical analysis after measurements</th>
<th>Accepted points</th>
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</thead>
<tbody>
<tr>
<td>Kairw, 1977 [20]</td>
<td>RB, CO–CO$_2$; tc</td>
<td>Mo / Mo</td>
<td>No</td>
<td>31</td>
</tr>
<tr>
<td>Kucharski, 1989 [30]</td>
<td>RB, CO–CO$_2$; tc</td>
<td>Mo / Mo</td>
<td>Yes</td>
<td>308</td>
</tr>
<tr>
<td>Shiraih, 1978 [31]</td>
<td>RB, Ar; tc &amp; p</td>
<td>Fe / Fe</td>
<td>Yes</td>
<td>37</td>
</tr>
<tr>
<td>Urbain, 1982 [28]</td>
<td>RC, Ar–H$_2$CO$_2$; p, tc</td>
<td>Mo / Mo</td>
<td>Yes</td>
<td>57</td>
</tr>
<tr>
<td>Ducret, 2000 [32]</td>
<td>RB, CO–CO$_2$; tc</td>
<td>Fe / Fe</td>
<td>Yes</td>
<td>7</td>
</tr>
<tr>
<td>Chen, 2013 [33]</td>
<td>RB, Ar; tc</td>
<td>Mo / Mo (Fe plate was placed at bottom)</td>
<td>Yes</td>
<td>28</td>
</tr>
<tr>
<td>CaO–FeO–Fe$_2$O$_3$–SiO$_2$ Total: 793</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO–FeO–Fe$_2$O$_3$–MgO–SiO$_2$ Total: 129</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>CaO–FeO–Fe$_2$O$_3$–MgO–SiO$_2$ Total: 48</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Al$_2$O$_3$–CaO–FeO–Fe$_2$O$_3$–MgO–SiO$_2$ Total: 48</td>
<td></td>
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</tr>
</tbody>
</table>

Table 2. The molar weight and volume of the structural units in the Al$_2$O$_3$–CaO–FeO–Fe$_2$O$_3$–MgO–SiO$_2$ system.

<table>
<thead>
<tr>
<th>SU</th>
<th>Al–Al</th>
<th>Ca–Ca</th>
<th>Fe$^{2+}$–Fe$^{3+}$</th>
<th>Fe$^{3+}$–Fe$^{2+}$</th>
<th>Mg–Mg</th>
<th>Si–Si</th>
<th>Al–Ca</th>
<th>Al–Fe$^{2+}$</th>
<th>Al–Fe$^{3+}$</th>
<th>Al–Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>mSU$\times 10^{-26}$ kg</td>
<td>5.64</td>
<td>9.31</td>
<td>11.96</td>
<td>8.84</td>
<td>6.69</td>
<td>4.99</td>
<td>7.48</td>
<td>8.80</td>
<td>7.24</td>
<td>5.32</td>
</tr>
<tr>
<td>vSU$\times 10^{-29}$ m$^3$</td>
<td>3.03</td>
<td>5.79</td>
<td>4.34</td>
<td>3.58</td>
<td>3.99</td>
<td>1.92</td>
<td>4.27</td>
<td>3.65</td>
<td>3.30</td>
<td>2.43</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SU</th>
<th>Ca–Fe$^{3+}$</th>
<th>Ca–Fe$^{2+}$</th>
<th>Ca–Mg</th>
<th>Ca–Si</th>
<th>Fe$^{3+}$–Fe$^{2+}$</th>
<th>Fe$^{2+}$–Mg</th>
<th>Fe$^{3+}$–Si</th>
<th>Fe$^{2+}$–Mg</th>
<th>Fe$^{3+}$–Si</th>
<th>Mg–Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>mSU$\times 10^{-26}$ kg</td>
<td>10.64</td>
<td>9.08</td>
<td>8.00</td>
<td>7.15</td>
<td>10.40</td>
<td>9.33</td>
<td>8.48</td>
<td>7.77</td>
<td>6.92</td>
<td>5.84</td>
</tr>
<tr>
<td>vSU$\times 10^{-29}$ m$^3$</td>
<td>5.03</td>
<td>4.60</td>
<td>4.84</td>
<td>3.50</td>
<td>3.95</td>
<td>4.16</td>
<td>2.96</td>
<td>3.78</td>
<td>2.66</td>
<td>2.83</td>
</tr>
</tbody>
</table>

4. Results and Discussion

4.1. Model Parameters

Systematic optimization of the systems was carried out using above principles in cycles from lower order systems to the multi-component systems and back until satisfactory agreement with all accepted experimental data was achieved. Tables 2 and 3 summarize model parameters used in the multicomponent Al$_2$O$_3$–CaO–FeO–Fe$_2$O$_3$–MgO–SiO$_2$ system and its subsystems at the present stage, which we confirmed that is applicable for these systems close to and at metallic iron saturation. Details on the comparison between calculated and experimental viscosity data are given below.
4.2. The FeO–Fe₂O₃ System

The experimental viscosity data in the CaO–FeO–Fe₂O₃ melts in air by Sumita et al. 14,15) were used to determine the εₐ and Δεᵥ energies of "pure" ferrous and ferric oxides. Figure 1(a) shows the viscosity of the CaO–FeO–Fe₂O₃ slag in air as a function of Fe concentration in slag; the experimental viscosity values of iron oxide in air were estimated from extrapolation of this composition dependence. Figure 1(a) also shows that viscosity maxima may exist at intermediate CaO to iron oxide ratios in air (note that the εₐ and Δεᵥ energies of pure CaO melt had been determined from experimental viscosity data in other CaO-containing systems as well as some correlation with other properties 10)). In these compositions, the Fe³⁺ ions are surrounded by tetrahedral coordination with Ca²⁺ or Fe²⁺ cations; this possible compositional tendency is discussed in Table 3.

Table 3. The coefficients for viscosity molar integral εᵥ, Δεᵥ, and partial energies [J/mol].

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| -- | -- |

The rest, εₑ, Δεᵥ, and partial energies [J/mol].
similar to that in the Na₂O–FeO–Fe₂O₃ melt in air indicated by experimental studies.₁⁴,₁⁵)

Figure 1(b) shows the viscosity of molten iron oxides as a function of Fe³⁺ molar concentration in the melt. The experimental data by Urbain ¹⁷) in equilibrium with metallic iron and the estimated viscosity values in air obtained through data by Sumita et al. ¹⁴,₁⁵) were used to optimize the $E_a$ and $\Delta E_v$ energies of “pure” ferrous and ferric oxides, where Fe³⁺ concentrations of the corresponding experiments were calculated by FactSage.⁸) The $E_a$ and $\Delta E_v$ energies of pure ferrous oxide were both determined as higher than the corresponding energies of pure ferric oxide. A high partial activation energy of a pure component corresponds to high viscosities of the corresponding pure molten oxide, however a high $\Delta E_v$ value corresponds to a low viscosity at a high temperature - as combining these information, it was indicated that the viscosity of ferric oxide was lower than that of ferrous oxide at higher temperatures than liquidus. Although the viscosity increase may occur as a result of the charge compensation effect of Fe³⁺ by Fe²⁺ cation, no viscosity maxima at intermediate compositions were introduced due to the lack of experimental information.

4.3. The Fe-containing Systems in Equilibrium with Metallic Iron

4.3.1. The Binary and Ternary Silicate Systems Containing ‘FeO’

Figure 2 shows (a) distribution of structural units, (b) the integral molar activation energy, (c) the integral energy term $\Delta E_v$, and (d) viscosity of the SiO₂–FeO–Fe₂O₃ melt in equilibrium with metallic iron.

![Fig. 1.](image1)

(a) CaO-FeO-Fe₂O₃ in air
(b) FeO-Fe₂O₃

![Fig. 2.](image2)

(a) Structural unit concentrations
(b) Activation energy
(c) Energy term $\Delta E_v$
(d) Viscosity

Fig. 1. (a) experimental tendency of viscosity in CaO–‘Fe₂O₃’ slag in air used to estimate viscosity of iron oxide in air, (b) calculated viscosity of the FeO–Fe₂O₃ melt as a function of Fe₂O₃ concentration.

Fig. 2. Calculated results of (a) structural unit concentrations, (b) integral molar activation energy, (c) integral energy term $\Delta E_v$, (d) viscosity of the SiO₂–FeO–Fe₂O₃ melt in equilibrium with metallic iron.
properties are available at the low SiO\textsubscript{2} concentrations; therefore, the incorporation of Fe\textsuperscript{3+} as well as Fe\textsuperscript{2+} cations in the system is necessary for accurate description of experimental viscosities. The individual contributions of partial $\bar{E}_p$ and $\Delta \bar{E}_p$ energies ($\bar{E}_{p,q}X_{pq}$ and $\bar{E}_{p,q}^\prime X_{pq}$, where $X_{pq}$ is structural unit concentration, $\bar{E}_{p,q}$ is the dimensionless partial energy coefficient of the integral energy term $\Delta \bar{E}_p$) to the corresponding integral molar energies in the present model can accurately describe all experimental integral $E_a$ and $\Delta E_v$ energies as well as reliable experimental viscosity data. The agreement with experimental data by the present model is almost comparable to the previous version.\textsuperscript{1,4,27} However, composition dependence of viscosity is slightly changed by the present model. Although possible viscosity maximum at around 33 mol\% SiO\textsubscript{2} had been discussed by several authors,\textsuperscript{28–31} the predicted viscosities by the present model do not show the corresponding tendency, i.e. they simply decrease as decreasing SiO\textsubscript{2} concentration. These calculated results are in agreement with the latest reliable experimental results by Chen et al.\textsuperscript{33}

The present model including iron oxides was extended to multi-component Fe-containing silicate systems by extrapolating binary model parameters using Eq. (6).\textsuperscript{10} Figure 3 represents the predicted viscosities of the SiO\textsubscript{2}–CaO–FeO–Fe\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2}–MgO–FeO–Fe\textsubscript{2}O\textsubscript{3} slag in equilibrium with metallic iron with constant SiO\textsubscript{2} concentration of 40 mol\% as a function of Fe/Ca and Fe/Mg molar ratios, and compared with the previous version.\textsuperscript{1,4,27} Unexpected viscosity maxima were indicated by the previous model. On the other hand, the present model indicates that viscosity decreases almost linearly with the increase of Fe concentration, and this compositional tendency is rather reasonable. Experimental data by Ducret et al.\textsuperscript{32} are inconsistent with those by other investigators; these experimental data were given a low weight in optimizing model parameters because post-chemical analysis was not conducted and therefore the change of compositions is considered as a reason for the inconsistence. Figure 4 shows the viscosity of the SiO\textsubscript{2}–CaO–FeO–Fe\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2}–MgO–FeO–Fe\textsubscript{2}O\textsubscript{3} slag in equilibrium with metallic iron as a function of Fe/O and Fe/Mg molar ratios of 90/10; the calculated viscosities indicate similar compositional dependence to that of the SiO\textsubscript{2}–FeO–Fe\textsubscript{2}O\textsubscript{3} slag equilibrated with metallic iron. Figure 4 also indicates that the addition of CaO and MgO increase the viscosity of the ferrosilicate slag.

4.3.2. The Al\textsubscript{2}O\textsubscript{3}–FeO\textsuperscript{3+} and Al\textsubscript{2}O\textsubscript{3}–‘FeO’–SiO\textsubscript{2} Systems

Particular attention in model development for these systems is given to the charge compensation effect by Fe\textsuperscript{2+} to form tetrahedrally-coordinated Al\textsuperscript{3+} using experimental measurements.\textsuperscript{12,13} The probability of Al\textsuperscript{3+} to take a tetrahedral coordination $P_{\text{AlO}^4}$ has been introduced, and the contributions of the charge-compensated Al\textsuperscript{3+} to the partial $E_p$ and $\Delta \bar{E}_p$ energies of the Al-containing structural units are described to be proportional to the partial $E_p$ and $\Delta \bar{E}_p$ energies of the Al-containing structural units. This is described by the addition to the partial $E_p$ and $\Delta \bar{E}_p$ energies of (Si–O–Si) structural unit of special term with positive coefficients, which is proportional to the concentration of tetrahedral (Al–O–Si) structural units affecting one (Si–O–Si) structural unit. To apply these treatments to the Al\textsubscript{2}O\textsubscript{3}–‘FeO’ system, the $\alpha_{\text{Al}^3+/\text{Fe}^2+}$ and $K_{\text{AlO}^4}$ values were assumed to be equal to $\alpha_{\text{Al}^3+/\text{Ca}^2+}$ and $K_{\text{AlO}^4}$ respectively.
tively, where the corresponding parameters for the Al$_2$O$_3$–CaO system were determined from experimental structural data on the concentration of tetrahedrally-coordinated Al$^{3+}$.10)

**Figure 5** represent viscosities of (a) the Al$_2$O$_3$–FeO–(Fe$_2$O$_3$) slag at 1973 K, (b) the Al$_2$O$_3$–FeO–(Fe$_2$O$_3$)–SiO$_2$ slag at 1773 K (SiO$_2$ = 50 mol%) equilibrated with metallic iron, as well as those of other aluminate slags determined in the previous study$^{15,11}$ (Me = Ca, Mg or Fe).

4.3.3. Multi-component Fe-containing Systems at Metallic Iron Saturation

The present model is extended to multi-component systems up to the Al$_2$O$_3$–CaO–FeO–Fe$_2$O$_3$–MgO–SiO$_2$ at metallic iron saturation with the same set of parameters. Several examples of the viscosity predictions are shown in **Fig. 6**; the iso-viscosity contours of the calcium ferrite silicate slags with additions of Al$_2$O$_3$ and MgO, where iron oxide in slag is expressed as ‘FeO’. As mentioned, the viscosity of the calcium ferrite silicate slag is of interest in various pyrometallurgy processes for non-ferrous metal productions, however experimental data are not sufficient on the effects of Al$_2$O$_3$ and MgO on the slag viscosity. In Fig. 6, the calculated viscosities reproduce reported data $^{34–36,40}$ within

![](image-url)
experimental uncertainties, and demonstrate that Al$_2$O$_3$ addition increases but MgO decreases viscosity.

The calculated viscosities were compared with all selected experimental data for each temperature and composition in the Al$_2$O$_3$–CaO–FeO–Fe$_2$O$_3$–MgO–SiO$_2$ system and its subsystems in equilibrium with metallic iron, and the summary is given in Fig. 7. The Round Robin project previously determined experimental uncertainties of the recommended viscosity measurements as approximately 30%. As shown in Fig. 7, present model reproduces almost all available experimental data within experimental uncertainties.

The agreement of the calculated viscosities with experimental values was evaluated by the average of relative errors between the calculated and experimental results, described by the following equation:

$$\text{Average of relative errors} (\%) = \left( \frac{1}{N} \sum_{i=1}^{N} \left( \frac{\eta_{\text{calc},i} - \eta_{\text{exp},i}}{\eta_{\text{exp},i}} \right) \right) \times 100 \ldots (10)$$

where $N$ denotes total number of acceptable experimental data points. Figure 8 summarizes the results of analyses on the average of relative errors for the multi-component system Al$_2$O$_3$–CaO–FeO–Fe$_2$O$_3$–MgO–SiO$_2$ and its subsystems containing iron oxides at metallic iron saturation, and demonstrates that the experimental viscosities have been accurately reproduced by the present model within experimental uncertainties (less than 30% as average of relative errors). A lower agreement in the high order systems at metallic iron saturation than the low order systems may be attributed to the possible errors of experimental data in the literatures, or the limitation of extending the present model to high order systems with the same set of parameters determined for low order systems.

### 4.4. Prediction of Viscosities of High Fe$^{3+}$-containing Slags

To predict viscosities of high Fe$^{3+}$-containing slags, the charge compensation effect to form tetrahedral Fe$^{3+}$ by basic cations such as Ca$^{2+}$ and Fe$^{2+}$ was taken into account by the approach similar to that used for the Al$^{3+}$ cation; the probability function of Fe$^{3+}$ to take a tetrahedral coordination has been introduced, and the contributions of the charge-compensated Fe$^{3+}$ to the partial $E_a$ and $\Delta E^*$ energies of the Fe$^{3+}$-containing structural units are described to be proportional to the $P_{\text{Fe}^{3+}}$ value, using the Eqs. (6)–(8).

![Fig. 7. Comparisons between calculated viscosities and experimental data in the Al$_2$O$_3$–CaO–FeO–Fe$_2$O$_3$–MgO–SiO$_2$ multi-component system and its subsystems: (a) FeO–(Fe$_2$O$_3$)–SiO$_2$; (b) CaO–FeO–(Fe$_2$O$_3$)–SiO$_2$; (c) FeO–(Fe$_2$O$_3$)–MgO–SiO$_2$; (d) Al$_2$O$_3$–FeO–(Fe$_2$O$_3$)–SiO$_2$; (e) Al$_2$O$_3$–CaO–FeO–(Fe$_2$O$_3$)–SiO$_2$; (f) Al$_2$O$_3$–CaO–FeO–(Fe$_2$O$_3$)–MgO–SiO$_2$ where "(Fe$_2$O$_3$)" denotes low content of ferric oxide in the system.](image)

![Fig. 8. Summary of comparisons between calculated results and experimental viscosity data for the Al$_2$O$_3$–CaO–FeO–Fe$_2$O$_3$–MgO–SiO$_2$ and its subsystems where low concentrations of ferric oxide is present (2793 viscosity data were selected).](image)

![Fig. 9. Calculated probability of Fe$^{3+}$ to form tetrahedral coordination in the SiO$_2$–CaO–FeO–Fe$_2$O$_3$ slag in air, where $\alpha_{\text{Fe}^{3+}}$ and $\alpha_{\text{Fe}^{3+}+}$ are 2.1 and $K_{\text{Fe}^{3+}} = K_{\text{Fe}^{3+}} = 8.6$ are used (Molar ratio of CaO/SiO$_2 = 1/1$).](image)
CaO/SiO₂ ratio as a function of total Fe concentration in slag, indicating that the calculated viscosities show systematically evaluated. Additionally, the notable charge of the system as well as of the behaviour of the Fe³⁺ cation viscosity in the SiO₂–CaO–FeO–Fe₂O₃ slag in air, however, the predicted viscosities experiments are necessary to fully evaluate the effect of ferric oxides on slag viscosity for wide range of the Fe³⁺/Fe²⁺ ratios, as well as the thermodynamic behaviour of ferric oxide in the silicate slag.

The revised quasi-chemical viscosity model was developed that enables slag viscosities to be predicted in the Al₂O₃–CaO–FeO–Fe₂O₃–MgO–SiO₂ multi-component system and its subsystems close to and at metallic iron saturation over the wide composition and temperature ranges of above liquidus within experimental uncertainties. For accurate model description as well as for the further extension of the model into high Fe³⁺-containing systems, ferrous and ferric oxides were individually incorporated into the model and various of complex slag viscosity behaviours related to these iron oxides including the charge compensation effect to form tetrahedrally-coordinated Al³⁺ by Fe³⁺ cations were systematically evaluated. Additionally, the notable charge compensation effect for Fe³⁺ to form tetrahedral coordination was introduced into the model, which enables the viscosities of the CaO–FeO–Fe₂O₃ slag in air to be predicted by the present model within experimental uncertainties. However, the calculated viscosities of the high Fe³⁺-containing silicate slags deviate from experimental results. Further studies are necessary to fully evaluate the effect of ferric oxide on slag viscosity for wide range of the Fe³⁺/Fe²⁺ ratios, as well as the thermodynamic behaviour of ferric oxide in the silicate slag.

5. Conclusions

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