VISCOSITY MODEL FOR ALUMINOSILICATE MELT

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dedicated to the memory of Professor Zbigniew Moser

Abstract

The structurally based viscosity model proposed in our previous study is extended to include more components, e.g. SiO2, Al2O3, FeO, MnO, MgO, CaO, Na2O and K2O. A simple method is proposed to calculate the numbers of different types of oxygen ions classified by the different cations they bonded with, which is used to characterize the influence of composition on viscosity. When dealing with the aluminosilicate melts containing several basic oxides, the priority order is established for different cations for charge compensating Al3+ ions, according to the coulombic force between cation and oxygen anion. It is indicated that basic oxides have two paradox influences on viscosity: basic oxide with a higher basicity decreases viscosity more greatly by forming weaker non-bridging oxygen bond; while it increases viscosity more greatly by forming stronger bridging oxygen bond in AlO4 tetrahedron after charge compensating Al3+ ion. The present model can extrapolate its application range to the system without SiO2. Furthermore, it could also give a satisfy interpretation to the abnormal phenomenon that viscosity increases when adding K2O to CaO-Al2O3-SiO2 melt within a certain composition range.

Keywords: Viscosity; Model; Aluminosilicate melts; Non-bridging oxygen; Bridging oxygen

1. Introduction

Aluminosilicate melt plays significant roles in the fields of glass-making, pottery-making, geological research and pyrometallurgy etc., with viscosity as one of the most important physical properties. Therefore, accurate viscosity values for aluminosilicate melts are necessary not only for optimizing and improving the productive processes, but for studying the structure of aluminosilicate melts. Estimating viscosity by model may be a useful method considering experimental measurements are both time consuming and sometimes inaccurate for the difficulty of high temperature operation.

Many viscosity models are proposed to estimate viscosity of aluminosilicate melts [1-11]. Though these models are successful to some extent, many shortcomings still exist: (i) The application ranges of these models are very narrow. They can only obtain good estimation results in or near the composition (or temperature) range, in which the model parameters are optimized, while the results will be inaccurate when away from the range. (ii) For aluminosilicate melts containing several basic oxides, these viscosity models can not well represent the viscosity variation tendency with composition. Sometimes, an inverse tendency with the experimental finding may be given. For instance, it is found that viscosity increases when adding K2O to CaO-Al2O3-SiO2 melt [12], while all the viscosity models can only give a decreasing tendency. (iii) The calculation results of these models for oxide systems without SiO2 are very bad (e.g. Al2O3, CaO-Al2O3, and CaO-FeO-Al2O3 systems, etc.), in other words, they can only be applied to the system containing SiO2. In view of these points, much work still should be done on the viscosity model.

2. Points must be considered in viscosity model

At constant pressure, viscosity is determined by temperature and chemical composition of molten slags. The main object of modeling viscosity of aluminosilicate melt is finding a proper relation to correlate viscosity with composition and temperature. Generally, the temperature dependence of viscosity expressed by Weymann equation [13], \( A \exp(E/RT) \), or Arrhenius equation [14] \( \exp(E/RT) \) which is same as Eyring equation [15]. The Weymann equation is used by Riboud et al. [1], Urbain [6], Kondratieev et al. [7], Zhang et al. [8], Ray et al. [5] and Shu [9] etc; while the Arrhenius equation (or Eyring equation) is used by Iida et al. [10], Nakamoto et al. [4], KTH [3], NPL [2], and Shankar et al. [16]. It was pointed out by Shankar et al. [16] that both the two types can well describe the variation of viscosity with temperature. Then, the problem of incorporating the influence of composition on viscosity is the central issue. Generally, viscosity model must fulfill

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the following four requirements:

(i) Viscosity is sensitive to the structure of aluminosilicate melts, and different components (acidic oxide, e.g. SiO₂; basic oxide, e.g. CaO and MgO: amphoteric oxide, e.g. Al₂O₃) have different influences on the structure. Therefore, viscosity model should be built based on a reasonable description to the structure of aluminosilicate melts. However, the empirical models by Riboud et al. [1], Urbain [6], Kondratiev et al. [7], NPL [2], Ray et al. [5], Shanket et al. [16], etc., didn’t consider the influence of melt structure on the viscosity.

(ii) Generally, in the Arrhenius or Weymann equation, there is a linear relation between the logarithm of pre-exponent factor lnA and activation energy E which is called the temperature compensation effect and is a common rule in the fields of viscosity, kinetics, electrical conductivity and diffusion coefficient [17]. Therefore, the compensation effect should also be taken into consideration in the viscosity model, while it is not considered in viscosity models of Riboud et al. [1], NPL [2], KTH [3], Nakamoto et al. [4], Iida et al. [10], etc.

(iii) After considering the Arrhenius or Weymann equation as well as the temperature compensation effect between lnA and E, the remaining task of modelling viscosity is to find a proper expression to relate the activation energy E and composition. It has been pointed out that the activation energy of viscosity is a non-linear function of composition [18]. A reasonable viscosity model should consider this nonlinear behavior. Among the different viscosity models, the polynomial functions with the highest order of “n” were utilized by different authors to describe this behavior: n=1 in Riboud et al. model [1]; n=2 in Shu model [9]; n=3 in Urbain model [6], Kondratiev et al. model [7] and Zhang et al. model [8].

(iv) When Al₂O₃ exists in the melts, Al³⁺ can form AlO⁴⁻ tetrahedron, and replace the position of Si⁴⁺ ion when there are enough metal cations (e.g. Ca²⁺, and Na⁺) participating into the charge compensation of Al³⁺ ions. It is found that different cations have different abilities of compensating Al³⁺ ions [19], so viscosity model should distinguish the different priorities. However, no model has done this except NPL model [2] which achieves this goal according to the different optical basicity values of different basic oxides. But this way has defect for the reason that in NPL model many basic oxides have the same optical basicity values, for instance optical basicity of Li₂O, CaO, FeO and MnO using the same value of 1.0, but actually the compensating abilities of these cations are different.

New viscosity model considering all the four requirements should be developed. This work has been done in our previous paper [17, 20, 21]. New model is structural based, and the model parameters for silicate melts (absence of Al₂O₃) are closely related to the bond strength [17, 20]. In the presence of Al₂O₃, viscosity of CaO-MgO-Al₂O₃-SiO₂ system is also well modeled [21]. However, the more complex or involving other basic oxides systems (containing Al₂O₃) are not considered, meanwhile, the abnormal phenomenon of viscosity increasing as adding K₂O to CaO-Al₂O₃-SiO₂ melt [12] is still unresolved. In this work, the model will be extended to resolve these problems.

3. Model

Details of the model have been given elsewhere [17, 20, 21]. Only a brief description of the model will be given here. The temperature dependence of viscosity is calculated by Arrhenius equation,

\[ \ln \eta = \ln A + \frac{E}{RT} \]  

(1)

where \( \mu \) is the viscosity, Poise; \( A \) is the pre-exponent factor, Poise; \( E \) is the activation energy, J/mol; \( R \) is the gas constant, 8.314 J/(molK); \( T \) is the absolute temperature, K. The temperature compensation effect is considered,

\[ \ln(\eta) = k(E - E_{572516}) - 17.47 \]  

(2)

For multicomponent system \( \sum M_i O_j-SiO_2 \), the value of parameter \( k \) is assumed to be the linear addition of that of the binary systems \( M_i O_j-SiO_2 \) with the normalized mole fractions of oxides \( M_i O_j \), as the weighting factors,

\[ k = \sum_{i,j} (x_i k_i) / \sum_{i,j} x_i \]  

(3)

The activation energy of viscosity in equation (2) is expressed as follows,

\[ E = 572516 \times \frac{1}{2} \left( n \sum_\alpha \sum_\beta \alpha_\alpha_\beta \sum_\gamma \alpha_\gamma \sum_\Delta \alpha_\Delta \sum_\Sigma \alpha_\Sigma + \sum_\alpha \sum_\beta \sum_\gamma \alpha_\gamma \sum_\Delta \alpha_\Delta \sum_\Sigma \alpha_\Sigma \right) \]  

(4)

where \( n \) is the mole number and \( \alpha \) describes the deforming ability of bond around the corresponding oxygen ion. The first, second, third, fourth, fifth, sixth terms in the denominator are the contributions of bridging oxygen \( O_\alpha \), bonded with \( Si^{4+} \) ion; oxygen \( O_\omega \), bonded with \( Al^{3+} \) ion not charge compensated; bridging oxygen \( O_{\omega,i} \), bonded with \( Al^{3+} \) ion charge compensated by cation \( i \); non-bridging oxygen, bonded with \( Si^{4+} \) ion and metal cation \( i \); non-bridging oxygen \( O_{\omega,j} \), bonded with metal cation \( j \) and \( Al^{3+} \) ion charge compensated by cation \( i \); free oxygen \( O_{\omega,i} \), bonded with metal cation \( i \), respectively.

4. Method of calculating the number of oxygen

Before using equations (1)~(4) to calculate viscosity, the numbers of different types of oxygen
ions must be known. In our previous paper [21], five
assumptions are suggested to calculate the numbers
for CaO-MgO-Al$_2$O$_3$-SiO$_2$ melt.

**Assumption I**: The equilibrium constant for the
reaction of free oxygen from basic oxide with
bridging oxygen to generate non-bridging oxygen is
infinite.

**Assumption II**: For system containing several
basic oxides $\sum$M$_2$O$_3$$\cdot$SiO$_2$, the numbers of different
types of oxygen ions can be calculated by the random
mixing rule: firstly, calculate $\sum n_{O_2}$,$\sum n_{O_4}$ and $\sum n_{O_3}$
following Assumption (I) considering the system to
be a pseudo-binary system; then multiply each term
by the re-normalized mole fractions of basic oxides.

**Assumption III**: The equilibrium constant for the
reaction of M$_2$O charge compensating Al$_2$O$_3$ is
infinite: in the case $x_{Al_2O_3}/x_{M_2O} < 1$ , all M$_2$O act
as charge compensators, while in the case of $x_{Al_2O_3}/x_{M_2O} > 1$
all Al$^{3+}$ ions form AlO$_4$ tetrahedrons, and the extra
M$_2$O acts as network modifiers.

**Assumption IV**: In the case of $x_{Al_2O_3}/x_{M_2O} > 1$ , when
the extra M$_2$O breaks the bridging oxide, it is
assumed that the bridging oxygen in AlO$_4$ and SiO$_4$
tetrahedrons are equivalent, and the numbers of formed
non-bridging oxygen bonded to Al$^{3+}$ ions and Si$^{4+}$ ions
are proportional to the numbers of bridging oxygen in
AlO$_4$ and SiO$_4$ tetrahedrons.

**Assumption V**: Ca$^{2+}$ cation has higher priority
of charge-compensating Al$^{3+}$ ion than Mg$^{2+}$ ion. Only
after all the Ca$^{2+}$ ions have been exhausted, Mg$^{2+}$ ions
will participate into the charge compensation.

Among them, Assumption V endows Ca$^{2+}$ ion an
absolute priority over Mg$^{2+}$ ion when charge
compensating Al$^{3+}$ ion, with which the viscosity
variation of CaO-MgO-Al$_2$O$_3$-SiO$_2$ system can be
well represented. However, the previous work can
only deal with the case of aluminosilicate system
contain two basic oxides: CaO and MgO, whereas,
when the basic oxides are not CaO and MgO or when
there are three or more basic oxides exist in more
complex aluminosilicate system, how to establish the
different priorities of different metal cations. This is
one of the main tasks of the present study. Assumptions
V will be revised into a more general form as follows.

**Assumption V**: Different metal cations have
different abilities of charge-compensating Al$^{3+}$ ions.
When there are several basic oxides in aluminosilicate
melts, a strict priority order exists for different metal
cations. In other words, only after all the cations with
the higher priority have been exhausted to compensate
Al$^{3+}$ ions, cations with the lower priority can
participate the charge compensation. The order for
different cations can be determined as follows.

Theoretically, the cation M$^{n+}$ that has strong bond
strength with O$^{2-}$ ion should possess weaker ability of
compensating Al$^{3+}$ ion, for the reason that itself can
form complex anion with oxygen ion, and strong
repulsive force exists between cation M$^{n+}$ and Al$^{3+}$ ion.
So, in this study, parameter $I$ expressed by the
coulombic force between the cation and oxygen anion
will be introduced to characterize the abilities of
different cations,

$$I = \frac{2Q}{(r_{\text{Me}^+} + r_{\text{O}^2-})}$$

where $Q$ is the valence of M$^{n+}$ ion $r_{\text{Me}^+}$ and $r_{\text{O}^2-}$ are
the radii of M$^{n+}$ and oxygen ions, respectively. The
ion radiuses (taken from the data compiled by
Shannon [22]) of Mg$^{2+}$, Ca$^{2+}$, Na$^{+}$, K$^+$, Fe$^{3+}$, Mn$^{2+}$ and
O$^{2-}$ are 0.66Å, 0.99 Å, 0.97 Å, 1.33 Å, 0.74 Å, 0.8 Å
and 1.44 Å, respectively. So the order of $I$ for different
cations is: K$^+$<Na$^+$<Ca$^{2+}$<Mn$^{2+}$<Fe$^{3+}$<Mg$^{2+}$. The
priority order of charge compensating Al$^{3+}$ ion is:
K$^+$<Ca$^{2+}$<Na$^{+}$<Mn$^{2+}$<Fe$^{3+}$<Mg$^{2+}$. The
order of K$^+$>Na$^+$>Ca$^{2+}$>Mn$^{2+}$>Fe$^{3+}$>Mg$^{2+}$ has been proved by the
evidences from thermochemical [23] and
spectroscopic data [24, 25]. However, it was pointed
out that [17] for chemical bond with a high percentage
of covalent bond, e.g. Fe-O (52.3%), Mn-O (41.0%)
(close to the value of Si-O bond which is 55.3%), the
bond strength can not be characterized simply by $I$.
So the position of Fe$^{3+}$ and Mn$^{2+}$ in the order is only an
approximation. The same approximation in the order
was also suggested by Mysen [19].

Based on Assumption I ~ Assumption IV and
Assumption V, the numbers of different types of
oxygen ions can be calculated easily. The detailed
calculating formulae for $\sum$(M$_2$O$_3$)-SiO$_2$ and
M$_2$O-Al$_2$O$_3$-SiO$_2$ systems are given before, and the
calculating formulae for (M$_2$O)$_x$(M$_2$O)-Al$_2$O$_3$-SiO$_2$
system can be obtained following the formulae of
CaO-MgO-Al$_2$O$_3$-SiO$_2$ system [21]. In the following
sections, model will be applied to aluminosilicate
system containing FeO, MnO, MgO, CaO, NaO and
K$_2$O. The literature data source utilized for the model
parameters optimization and comparisons are shown
in Table 1. The regressed parameters are shown in
Tables 2 and 3, in which the parameters optimized in
previous papers [17, 20, 21] are also included.

Parameters for the present model are obtained as
follows: parameters $k$, $a_i$, and $\alpha_i$ , are optimized
to the data of M$_2$O-SiO$_2$ binary system
(have been accomplished in our previous work [17,
20]); parameters $\alpha_{\text{Me}^+}$ and $\alpha_{\text{Me}^{2+}}$ and are
optimized according to the data of M$_2$O-Al$_2$O$_3$-SiO$_2$
system; while for the system (M$_2$O)$_x$(M$_2$O)-Al$_2$O$_3$-SiO$_2$
with two basic oxides, one more parameter $\alpha_{\text{Me}^+}$
is needed. Theoretically, no more parameter is needed for
even higher order system.

5. Results

5.1. M$_2$O-Al$_2$O$_3$-SiO$_2$ ternary system

The viscosity data of FeO-Al$_2$O$_3$-SiO$_2$ and MnO-

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Table 1. Summary of the literature data source utilized in the present study

| System                 | Source                           | Composition range (mole fraction) |
|------------------------|----------------------------------|----------------------------------|
| FeO-Al₂O₃-SiO₂         | Johannsen et al. [26]            | FeO: 0.44~0.73; SiO₂:0.22~0.44   |
| CaO-Al₂O₃-SiO₂         | Urbain et al. [27]               | SiO₂:0.33~0.74                   |
| Na₂O-Al₂O₃-SiO₂        | Kou et al. [28]                  | Na₂O:0.20~0.50; SiO₂:0.4~0.65    |
| CaO-K₂O-Al₂O₃-SiO₂     | Topleis et al. [29]              | Na₂O:0.08~0.28; SiO₂:0.5~0.82    |
| CaO-K₂O-Al₂O₃-SiO₂     | Topleis et al. [30]              | Na₂O:0.09~0.26; SiO₂:0.5~0.82    |

Table 2. Values of model parameters for different M₂O-SiO₂ and M O-Al₂O₃-SiO₂ systems

| l          | k x 10⁶ | α₁₁ | αᵣ | α₁₂ | αᵣᵣ |
|------------|---------|-----|-----|-----|------|
| Fe         | -2.195  | 10.76 | 33.62 | 8.702 | 6.828 |
| Mn         | -2.147  | 8.452 | 27.83 | 5.857 | 4.204 |
| Mg         | -2.106  | 6.908 | 15.54 | 5.606 | 3.975 |
| Ca         | -2.088  | 7.422 | 17.34 | 4.996 | 4.204 |
| Na         | -2.767  | 13.35 | 40.56 | 4.308 | 10.46 |
| K          | -3.2    | 16.59 | 4.156 | 17.34 |
| Al         | -2.594  | 5.671 |      |      |      |

Al₂O₃-SiO₂ systems are taken from the works of Johannsen et al. [26] and Urbain et al. [27], respectively. Based on the parameters k, αᵣ, and αᵣᵣ optimized in binary systems, two parameters αᵣᵣᵣ and αᵣᵣᵣᵣ are optimized in FeO-Al₂O₃-SiO₂ system (MnO-Al₂O₃-SiO₂ system). The comparisons of calculated values with those by experiments for these two systems are shown in Figure 1 and Figure 2, with the mean deviations 29.8% and 28.8%, respectively. The large deviations for these two systems may result from the reasons that both Fe and Mn are polyvalent metallic elements, and possible existences of Fe³⁺ or Mn²⁺ ions lead to the viscosity behavior departing from melts with pure FeO or MnO.

**Figure 1.** Comparisons between estimated and measured viscosity values for FeO-Al₂O₃-SiO₂ system.

**Figure 2.** Comparisons between estimated and measured viscosity values for MnO-Al₂O₃-SiO₂ system.
The data of Na₂O-Al₂O₃-SiO₂ system are taken from Kou et al. [28] and Toplis et al. [29, 30], with viscosity values varying from 10 to 4×10⁵ poise. Parameters $\alpha_{NaK}$ and $\beta_{NaK}$ are optimized in this system. The comparisons of calculated values with the measured values are shown in Figure 3, with the mean deviation 27.9%. For K₂O-Al₂O₃-SiO₂ system, Urban et al. [27] only measured one composition point with high content of SiO₂ and high viscosity; Mizoguchi et al. [31] measured composition points with high content of K₂O and low viscosity. With the optimized parameters of $\alpha_{NaK}$ and $\beta_{NaK}$, viscosity of this system can be calculated. The comparisons between the estimated values and those by experiments are shown in Figure 4, with the mean deviation 31.8%. The large deviations for these two systems may result from large measure errors at high viscosity and evaporations of Na₂O and K₂O at high temperature.

5.2. (MₐO)ᵢ-(MₐO)ᵣ-Al₂O₃-SiO₂ quaternary system

For (MₐO)ᵢ-(MₐO)ᵣ-Al₂O₃-SiO₂ quaternary system, one more parameter is needed. Parameter $\alpha_{NaK}$ has been optimized in CaO-MgO-Al₂O₃-SiO₂ system [21]. In this work, according to the priority order of different cations when charge compensating Al³⁺ ion: K⁺ > Na⁺ > Ca²⁺ > Fe²⁺, oxygen ions $O_{NaK}^-$, $O_{Na}^-$ and $O_{Na}^{2-}$ exist in CaO-Na₂O-Al₂O₃-SiO₂, CaO-K₂O-Al₂O₃-SiO₂ and CaO-FeO-Al₂O₃-SiO₂ systems, respectively, while oxygen ions $O_{CaK}^-$, $O_{Ca}^-$ and $O_{Ca}^{2-}$ are absent. So, corresponding $\alpha_{NaK}$, $\alpha_{Na}$ and $\alpha_{Ca}$ parameters will be optimized in CaO-Na₂O-Al₂O₃-SiO₂, CaO-K₂O-Al₂O₃-SiO₂ and CaO-FeO-Al₂O₃-SiO₂ systems, respectively.

Viscosity data of CaO-FeO-Al₂O₃-SiO₂ are from Higgins et al. [32] and Kolesov et al. [33], while these for CaO-Na₂O-Al₂O₃-SiO₂ and CaO-K₂O-Al₂O₃-SiO₂ systems are from Sukenaga et al. [12]. The comparisons of calculated values with those by experiments are shown in Figures 5-7, with the mean deviations 28.1%, 24.7% and 23.0%, respectively.

5.3. CaO-FeO-Al₂O₃ ternary system

The viscosity of CaO-FeO-Al₂O₃ system are from Vidacak et al. [34]. When calculating viscosity of this system, no parameter needs to be optimized.
Extrapolating the viscosity calculation of CaO-FeO-Al$_2$O$_3$-SiO$_2$ system to the limiting case of content of SiO$_2$ equal to 0, with parameters optimized in other systems, the viscosity for this system can be obtained. The comparisons of calculated values with measured values are shown in Figure 8, with the mean deviation 24.4%. In the following section, it can be seen that the existing viscosity models can not well represent the viscosity variation behavior of this system which is absence of SiO$_2$.

5.4. Complex systems

**CaO-MgO-Na$_2$O-Al$_2$O$_3$-SiO$_2$ system**

The parameter $\alpha_{\text{MgNa}}$ is optimized in CaO-MgO-Na$_2$O-Al$_2$O$_3$-SiO$_2$ system for the lack of viscosity data in MgO-Na$_2$O-Al$_2$O$_3$-SiO$_2$ system. In this system, there are three types of cations: Na’, Ca$^{2+}$ and Mg$^{2+}$ ions, could compensate Al$^{3+}$ ion, and the priority order is Na’>Ca$^{2+}$>Mg$^{2+}$, thereby, oxygen ions O$_{\alpha\alpha}^\text{Na}$, O$_{\alpha\alpha}^\text{Ca}$ and O$_{\alpha\alpha}^\text{Mg}$ exist. Considering the corresponding parameters $\alpha_{\text{MgNa}}$ and $\alpha_{\text{CaNa}}$, have been optimized in CaO-Na$_2$O-Al$_2$O$_3$-SiO$_2$ and CaO-MgO-Al$_2$O$_3$-SiO$_2$ systems, only parameters $\alpha_{\text{MgNa}}$ is optimized in this system.

Parts of the composition points of Sykes et al. [35] fulfill the condition: $x_{\text{NaO}} > x_{\text{AlO}}$, and, $x_{\text{NaO}} + x_{\text{MgO}} + x_{\text{AlO}} - x_{\text{SiO}} < 2x_{\text{MgO}} + x_{\text{SiO}}$, in which case all the Al$^{3+}$ ions are compensated Na’ ions; the remaining Na’, Ca$^{2+}$ and Mg$^{2+}$ ions participate in forming non-bridging oxygen, but are not enough to break all the bridging oxygen. According to the five assumptions, numbers of different types of oxygen ions can be calculated as follows:

- **Non-bridging oxygen bonded to Al$^{3+}$ ion:**
  
  \[ n_{\text{AlO}} = 2(x_{\text{NaO}} - x_{\text{AlO}}) \frac{2x_{\text{MgO}}}{2x_{\text{AlO}} + x_{\text{SiO}}} \]  
  \[ n_{\text{AlO}} = 2x_{\text{MgO}} \frac{2x_{\text{AlO}}}{2x_{\text{AlO}} + x_{\text{SiO}}} \]  
  \[ n_{\text{SiO}} = 2x_{\text{AlO}} \frac{2x_{\text{MgO}}}{2x_{\text{AlO}} + x_{\text{SiO}}} \]

- **Non-bridging oxygen bonded to Si$^{4+}$ ion:**
  
  \[ n_{\text{SiO}} = 2(x_{\text{NaO}} - x_{\text{AlO}}) \frac{x_{\text{SiO}}}{2x_{\text{AlO}} + x_{\text{SiO}}} \]  
  \[ n_{\text{SiO}} = 2x_{\text{MgO}} \frac{x_{\text{SiO}}}{2x_{\text{AlO}} + x_{\text{SiO}}} \]  
  \[ n_{\text{SiO}} = 2x_{\text{AlO}} \frac{x_{\text{MgO}}}{2x_{\text{AlO}} + x_{\text{SiO}}} \]

- **Bridging oxygen:**

![Figure 6. Comparisons between estimated and measured viscosity values for CaO-Na$_2$O-Al$_2$O$_3$-SiO$_2$ system.](image)

![Figure 7. Comparisons between estimated and measured viscosity values for CaO-FeO-Al$_2$O$_3$ system.](image)

![Figure 8. Comparisons between estimated and measured viscosity values for CaO-FeO-Al$_2$O$_3$ system.](image)
The other parts of composition points measured by Sykes et al. [35] and those measured by Kim et al. [36] fulfill the conditions: 
\[ x_{\text{NaO}} < x_{\text{AlO}} + x_{\text{NaO}} > 2x_{\text{AlO}} + x_{\text{NaO}} \]
and 
\[ x_{\text{NaO}} + x_{\text{AlO}} + x_{\text{NaO}} - x_{\text{AlO}} < 2x_{\text{AlO}} + x_{\text{NaO}} \].
In this case, all the Na\(^+\) ions compensate Al\(^{3+}\) ion; while Al\(^{3+}\) ions not compensated by Na\(^+\) ions are completed by Ca\(^{2+}\) ions; the remaining Ca\(^{2+}\) ions and Mg\(^{2+}\) ions participate in forming the non-bridging oxygen, but are not enough to break all the bridging oxygen. The numbers of different types of oxygen ions can be calculated as follows:

Non-bridging oxygen bonded to Ca\(^{2+}\) ion:

\[ n_{\text{O}_{\text{Ca}}} = 2x_{\text{CaO}} + x_{\text{AlO}} - x_{\text{AlO}} \frac{2x_{\text{CaO}}}{2x_{\text{AlO}} + x_{\text{NaO}}} \]

Non-bridging oxygen bonded to Mg\(^{2+}\) ion:

\[ n_{\text{O}_{\text{Mg}}} = 2x_{\text{MgO}} + x_{\text{AlO}} - x_{\text{AlO}} \frac{2x_{\text{MgO}}}{2x_{\text{AlO}} + x_{\text{NaO}}} \]

Bridging oxygen:

\[ n_{\text{O}_{\text{Br}}} = 4x_{\text{CaO}} - x_{\text{CaO}} \frac{n_{\text{O}_{\text{Ca}}}}{2} - n_{\text{O}_{\text{Ca}}} \]

\[ n_{\text{O}_{\text{Br}}} = 4x_{\text{MgO}} - x_{\text{MgO}} \frac{n_{\text{O}_{\text{Mg}}}}{2} - n_{\text{O}_{\text{Mg}}} \]

\[ n_{\text{O}_{\text{Br}}} = 2x_{\text{AlO}} - n_{\text{O}_{\text{Al}}} \frac{n_{\text{O}_{\text{Al}}}}{2} \]

The viscosity values for CaO-MgO-Al\(_2\)O\(_3\)-SiO\(_2\) system can be optimized which are shown in Table 3. The comparisons of calculated viscosities with those measured by experiments are shown in Figure 9, with the mean deviation 13.5%. Thereby, to some extent, the present model has strong extrapolation ability.

**Table 3. Value of model parameter α\(_{\text{Na}}\)**

| Parameters | α\(_{\text{Na}}\) | α\(_{\text{Ca}}\) | α\(_{\text{Mg}}\) | α\(_{\text{Al}}\) | α\(_{\text{Si}}\) |
|------------|-----------------|----------------|----------------|----------------|----------------|
|            | 8.334           | 8.694          | 9.787          | 7.593          | 8.015          |

**Figure 9. Comparisons between estimated and measured viscosity values for CaO-MgO-NaO-Al\(_2\)O\(_3\)-SiO\(_2\) system.**
6. Discussion

(1) According to the results of our previous paper [21], the model can be extrapolated to Al$_2$O$_3$, CaO-Al$_2$O$_3$ systems without optimizing new parameters. In this work, the model can also well describe the composition and temperature dependences of viscosity for CaO-FeO-Al$_2$O$_3$ system. Therefore, the present model can be applied to system without SiO$_2$.

(2) From the values of parameters shown in Table 2, it can be seen that the following orders exist: $a_{Al}^{3+} > a_{Ca}^{2+} > a_{Na}^{+}$. Therefore, the deforming ability of bonds around the non-bridging oxygen bonded with different cations increase following the order: Mg$^2+$<Ca$^2+$<Na$^+$<K$^+$. While, the order is opposed for the bridging oxygen bonded with Al$^{3+}$ ions compensated by different cations: Mg$^2+$>Ca$^2+$>Na$^+$>K$^+$. It is known that the basicity order for these four oxides is K$_2$O>Na$_2$O>CaO>MgO. Therefore, basic oxide with a higher basicity leads to the forming of a weaker non-bridging oxygen bond, which decreases viscosity; while forming a stronger bridging oxygen bond in a more stability AlO$_4$ tetrahedron structure by charge compensating Al$^{3+}$ ion, which increases viscosity. So basic oxide plays a paradox role in influencing viscosity when Al$_2$O$_3$ exists. 

(3) It is found by Sukenaga et al. [12] that the addition of K$_2$O to CaO-Al$_2$O$_3$-SiO$_2$ slag increases viscosity. However, all the theoretical models cannot interpret this abnormal phenomenon, and only give a decreasing tendency. Nakamoto et al. [4] claimed that their model was a progressive for this problem relative to other models. However, it can only decrease the decreasing tendency, but still cannot give an increasing tendency. Figure 11 shows the variations of viscosity for CaO-K$_2$O-Al$_2$O$_3$-SiO$_2$ quaternary system with content of K$_2$O, in which the theoretical lines estimated by Nakamoto et al. model and the present model are also given. It can be seen that the present model can well describe this phenomenon.

According to the description of aluminosilicate melt structure in our model, the reason for the increase of viscosity may be that when adding K$_2$O to CaO-Al$_2$O$_3$-SiO$_2$ system, K$^+$ ion will substitute the position of Ca$^{2+}$ ion to compensate Al$^{3+}$ ion for its higher priority relative to Ca$^{2+}$ ion. The replaced Ca$^{2+}$ ions will form more non-bridging oxygen ions, and this factor decreases viscosity. But as the contents of basic oxides ($x_{Na} + x_{Ca}$) are not very high, and there are still enough bridging oxygen ions (including those bonded with Al$^{3+}$ ion and Si$^{4+}$ ion). In the case that content of K$_2$O is smaller than that of Al$_2$O$_3$ (the case of Sukenaga et al. [12]), all the added K$^+$ ion will substitute the position of Ca$^{2+}$ ion to compensate Al$^{3+}$ ion, therefore, parts of the bridging oxygen bonded with Al$^{3+}$ ion will transform from $O_{\alpha \kappa}$ to $O_{\alpha \kappa \kappa}$. According to parameters values shown in Table 2 ($a_{Al^{3+}}$=4.156 < $a_{Ca^{2+}}$=4.996), the bond around $O_{\alpha \kappa}$ is stronger than that around $O_{\alpha \kappa \kappa}$, thus substitution of K$^+$ ion for Ca$^{2+}$ ion leads to the forming of more stability bridging oxygen bond, and this factor increases viscosity. When the increasing tendency (resulting from the change of bridging oxygen type) exceeds the decreasing tendency (resulting from the increase of the non-bridging oxygen number), viscosity increases, which may be the cause of experiment finding by Sukenaga et al. [12].

It is conceivable that when the content of Al$_2$O$_3$ is very small relative to the content of K$_2$O addition, the decreasing tendency of viscosity will be dominated, since in this case most of the added K$^+$ ions do not form bridging oxygen $O_{\alpha \kappa}$ but non-bridging oxygen ($O_{\alpha \kappa \kappa}$ and $O_{\kappa}$), thereby, viscosity may decrease. In the limiting case of content of Al$_2$O$_3$ equal to 0, the addition of K$_2$O to CaO-SiO$_2$ melts will obviously decrease viscosity for the decrease of absolute content of SiO$_2$ and forming of more non-bridging oxygen. In another cases that the contents of basic oxides ($x_{Na} + x_{Ca}$) is very high to break all the bridging oxygen or only few bridging oxygen ions remaining, the viscosity may also decrease with the addition of K$_2$O, because it is the forming of bridging oxygen $O_{\alpha \kappa}$ increasing viscosity, while its number is very limited in this case.

(4) In order to see clearly the accuracy of the present model relative to other models, the mean deviations of our model and models of Riboud et al. [1], NPL [2], Nakamoto et al. [4], Ray et al. [5], Urbain [6], Kondratiev et al. [7] and Iida et al. [10] are given in Table 4, from which it can be seen that our model has strong ability for viscosity estimation, especially for complex aluminosilicate systems and systems absence of SiO$_2$.

![Figure 11. Variation of viscosity with the content of K$_2$O in CaO-K$_2$O-Al$_2$O$_3$-SiO$_2$ system](image-url)
7. Conclusions

A structurally based viscosity model is proposed for aluminosilicate melt containing MgO, CaO, FeO, MnO, Na$_2$O and K$_2$O, in which a simple method of calculating the numbers of different types of oxygen ions is proposed, to describe influence of structure on viscosity. When several basic oxides exist, the priority order for different cations when compensating Al$^{3+}$ ions is suggested: K$^+$ > Na$^+$ > Ca$^{2+}$ > Mn$^{2+}$ > Fe$^{2+}$ > Mg$^{2+}$, according to the coulombic force between the cation and oxygen anion. The values of the optimized parameters indicate that existence of Al$_2$O$_3$ can lead to two inverse influences of basic oxides on viscosity. The basic oxide with a higher basicity can decrease viscosity by forming weaker non-bridging oxygen bond; while it can also increase viscosity by forming stronger bridging oxygen bond by charge compensating Al$^{3+}$ ion. The present viscosity model can extrapolate its application range to the system without SiO$_2$, and give well results for complex aluminosilicate system. Furthermore, a satisfy interpretation can be given by the present model to the abnormal phenomenon of viscosity increasing when adding K$_2$O to CaO-Al$_2$O$_3$-SiO$_2$ melt.

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References

[1] P.V. Riboud, Y. Roux, L.D. Lucas and H. Gaye, Facber. Hüttenprax. Metallweiter Verarb., 19 (1981) 859.
[2] K.C. Mills and S. Sridhar, Ironmaking & Steelmaking, 26 (1999) 262.
[3] S.C. Du, J. Bygden and S. Seetharaman, Metall. Mater. Trans. B, 25B (1994) 519.
[4] M. Nakamoto, Y. Miyabayashi, L. Holappa and T. Tanaka, ISIJ Int., 47, (2007), 1409.
[5] H.S. Ray and S. Pal, Ironmaking & Steelmaking, 31 (2004) 125.
[6] G. Urbain, Steel Res. Int., 58 (1987) 111.
[7] A. Kondratiev and E. Jak, Fuel, 80 (2001) 1989.
[8] L. Zhang and S. Jahanshahi, Metall. Mater. Trans. B, 29B (1998) 177.
[9] Q.F. Shu, Steel Res. Int., 80 (2009) 107.
[10] T. Iida, H. Sakai, Y. Kita and K. Shigeno, ISIJ Int., 40 (2000) 110.
[11] D. Ghosh, V.A. Krishnamurthy and S.R. Sankaranarayanan, J. Min. Metall. B, 46 B (2010) 41.
[12] S. Sukenaga, N. Saito, K. Kawakami and K. Nakashima, ISIJ Int., 46 (2006) 352.
[13] H.D. Weymann, Colloid Polym. Sci., 181 (1962) 131.
[14] S. Arhenius, Z. Phys. Chem., 1 (1887) 285.
[15] S. Glasstone, K.J. Laider and H. Eyring, The theory of rate processes, McGraw-Hill, New York, 1941.
[16] A. Shankar, M. Gornerup, A.K. Lahiri and S. Seetharaman, Ironmaking & Steelmaking, 34 (2007) 477.
[17] G.H. Zhang, K.C. Chou, Q.G. Xue and K.C. Mills, Metall. Mater. Trans. B, 43B (2012) 64.
[18] J.D. Mackenzie, Chem. Rev., 56 (1956) 455.
[19] B.O. Mysen, Structure and properties of silicate melts, Elsevier Science Publishers B.V., Amsterdam, 1988.
[20] G.H. Zhang and K.C. Chou, J. Min. Metall. B, 48B (2012) 1.
[21] G.H. Zhang, K.C. Chou and K.C. Mills, ISIJ Int., 52 (2012) 355.
[22] D.D. Shannon, Acta Crystallogr., A32 (1976) 751.
[23] A. Navrotsky, G. Peraudeau, P. Mcmillan and J.P. Coutures, Geochem. Cosmochim. Acta, 46 (1982) 2039.

Table 4. Mean deviations for different viscosity models (%)

| Systems                  | Riboud | Urbain | Kondratiev | Iida | NPL | Ray | Nakamoto | Present model |
|--------------------------|--------|--------|------------|------|-----|-----|----------|---------------|
| FeO-Al$_2$O$_3$-SiO$_2$   | 622    | 63     | 324        | 39.1 | 86.4| 34.7| 29.8     |
| MnO-Al$_2$O$_3$-SiO$_2$   | 441    | 45     | x          | 93.6 | 66.2|     | 28.8     |
| Na$_2$O-Al$_2$O$_3$-SiO$_2$| 72.6  | x      | 91.8       | 87.2 |     |     | 27.9     |
| K$_2$O-Al$_2$O$_3$-SiO$_2$| 75.8  | 95.4   | 96.3       | 95.5 | x   |     | 31.8     |
| CaO-FeO-Al$_2$O$_3$      | 200    | x      | 37.4       | 50.6 | 73.3|     | 24.4     |
| CaO-FeO-Al$_2$O$_3$-SiO$_2$| 395   | 25.9   | 95.1       | 58.1 | 75.3| 36.7| 28.1     |
| CaO-Na$_2$O-Al$_2$O$_3$-SiO$_2$| 32.4 | 48.2   | 76.1       | 53.6 | 35.2|     | 24.7     |
| CaO-K$_2$O-Al$_2$O$_3$-SiO$_2$| 42   | 66     | 87.1       | 73.5 | 44  |     | 23       |
| CaO-MgO-FeO-Al$_2$O$_3$-SiO$_2$| 103  | 57.5   | 46.9       | 63.4 | 24.7|     | 13.5     |
| CaO-MgO-Na$_2$O-Al$_2$O$_3$-SiO$_2$| 89.3 | 160    | 95.4       | 179  | 152|     | 25.7     |

* the blank indicates the system can not be calculated for the absence of parameters; ‘x’ represents the mean deviation is higher than 1000%.
[24] F. Domine and B. Piriou, Am. Mineral., 71 (1986) 38.
[25] B.O. Mysen and D. Virgo, Geochem. Cosmochim. Acta, 44 (1980) 1917.
[26] F. Johannsen and H. Brunson, Z. Erz. Metall., 12 (1959) 211.
[27] G. Urbain, Y. Bottinga and P. Richet, Geochem. Cosmochim. Acta, 46 (1982) 1061.
[28] T. Kou, K. Mizoguchi and Y. Suginohara, J. Jpn. Inst. Met., 42 (1978) 775.
[29] M.J. Toplis, D.B. Dingwell, K.U. Hess and T. Lenci, Am. Mineral., 82 (1997) 979.
[30] M.J. Toplis, D.B. Dingwell and T. Lenci, Geochem. Cosmochim. Acta, 61 (1997) 2605.
[31] K. Mizoguchi, K. Okamoto and Y. Suginohara, J. Jpn. Inst. Met., 46 (1982) 1055.
[32] R. Higgins and T.J.B. Jones, Bull. Inst. Min. Metall., 682 (1963) 825.
[33] V.D. Eisenhüttenleute, Slag atlas, Verlag Stahleisen GmbH, Dusseldorf, 1995.
[34] B. Vidacak, S.C. Du and S. Seetharaman, Metall. Mater. Trans. B, 32B (2001) 679.
[35] D. Sykes, J. Dickinson, E. James, R.W. Luth and C.M. Scarfe, Geochem. Cosmochim. Acta, 57 (1993) 1291.
[36] H. Kim, W.H. Kim, J.H. Park and D.J. Min, Steel Res. Int., 81 (2010) 17.
[37] J.R. Kim, Y.S. Lee, D.J. Min, S.M. Jung and S.H. Yi, ISIJ Int., 44 (2004) 1291.