A Semi-empirical Model for Viscosity Estimation of Molten Slags in CaO–FeO–MgO–MnO–SiO₂ Systems

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A semi-empirical viscosity model was proposed for silicate melts in this paper. The binary silicate melts MO–SiO₂ (MO is a bivalent metal oxide) was treated as 2MO · SiO₂–"SiO₂" or "MO"–2MO · SiO₂ system when \( X_{MO}/H_{11349} > 0.667 \) or \( X_{MO}/H_{11022} < 0.667 \). Viscous activation energy of silicate melts was divided into three parts which come from the contributions of "SiO₂", "MO" and 2MO · SiO₂. A relationship between pre-exponential factor \( A \) and activation energy \( E \) in Arrhenius equation was used for silicate melts. The model parameters were extracted from binary silicate melts and applied in ternary or higher order systems. The viscosities of silicate melts within CaO–MgO–MnO–FeO–SiO₂ system were estimated using the present model. Good agreements have been achieved between calculated values and measured values. The mean deviation \( \Delta \) of present model for slag systems investigated in our study is in the vicinity of 20%.

KEY WORDS: viscosity; estimation model; silicate melts.

1. Introduction

As one of important physical properties of silicate melts, viscosity of silicate melts has influence on many metallurgical processes, such as extraction, refining and casting. With the development of mathematical models to describe and simulate these processes, the reliable viscosity data is urgently needed. However, viscosity measurements are difficult, because of high temperature experiments. Hence, for industrial use, development of viscosity estimation model is essential.

Various models have been presented to estimate viscosity of silicate melts by different authors.1–9 Among these models, useful models in practice are empirical or semi-empirical. Most of these models employ parameters extracted from experimental data of viscosity, which ensure the validity of the models in viscosity estimation. However, most of the models are based on limited experimental data. It is usually difficult to extend the model to the estimation for lower order or higher order system. ThermoSlag (or KTH model)11 is an exception. The model was based on a series of self-consistent model parameters extracted from low order system which guarantee its good performance in both low and high order systems, but the model calculation seems some complicated for many parameters are needed.

Recently, there were some attempts to relate the structure to viscosity of silicate melts. Mills et al.5,6 established the relationship between viscosity and structure of silicate melts through optical basicity. Zhang Ling et al.7 related the viscosity to the molar fraction of bridge oxygen and free oxygen ions of silicate melts. Nakamoto et al.8 proposed a model to evaluated the viscosity of silicate melts based on the number of non-bridging oxygen and free oxygen.

These models assume that the ability of cations to depolymerize the silica network is the key factor to the viscosity of silicate melts. It should be mentioned that Zhang and Nakamoto also noticed the impact of interaction between metal and oxygen ion on viscosity of silicate melts. Zhang proposed that the effect of different cations on viscosity may be attributed to the strength of M–O. Nakamoto et al. introduced a parameter \( \alpha \) for individual component, which reflects the weakness of the bonding between cations and oxygen ions. However, it seems that these viewpoints were not consistent with their models, which aimed to relate viscosity to structure of silicate anions. Besides, it is necessary to calculate the number of three type of oxygen ions in silicate melt before applying the Zhang and Nakamoto models. The relative complicated computation will be an obstacle for industrial use.

In this paper, a new semi-empirical viscosity model for silicate melts was proposed. It treated the binary silicate melts MO–SiO₂ (MO is a bivalent metal oxide) as 2MO · SiO₂–"SiO₂" or "MO"–2MO · SiO₂ system when \( X_{MO}/H_{11349} < 0.667 \) or \( X_{MO}/H_{11022} > 0.667 \). It assumes viscous activation energy of silicate melts contains three parts which come from the contributions of "SiO₂", "MO" and 2MO · SiO₂. The model parameters were optimized using binary silicate melts and applied in ternary or higher order systems. The viscosities of silicate melts within CaO–MgO–MnO–FeO–SiO₂ system were estimated using the present model. Good agreements have been achieved between calculated values and measured values. The mean deviation \( \Delta \) of present model for slag systems investigated in our study is in the vicinity of 20%.

2. Model

The temperature dependence of viscosity can be described by the Arrhenius form:
\[ \ln \eta = \ln A + \frac{E}{RT} \] .............................(1)

where \( \eta \) is viscosity, \( T \) is temperature in Kelvin, \( E \) is viscous activation energy, \( A \) is pre-exponential factor, and \( R \) is the gas constant.

Three types of oxygen in silicate melts, bridge oxygen \( O^2- \), non-bridge oxygen \( O^- \) and free oxygen \( O^{2-} \) were introduced by Fincham and Richardson.\(^{10} \) The three types of oxygen are in a chemical equilibrium: \( 2O^{2-} = O^2- + O^- \).

On account of the structure of silicate melts, binary silicate melts MO–SiO\(_2\) (MO was a bivalent metal oxide) can be treated as ternary system “MO”–2MO · SiO\(_2\)–“SiO\(_2\)”. Only free oxygen exists in “MO” and bridge oxygen exists in “SiO\(_2\)”. 2MO · SiO\(_2\) contains solely non-bridge oxygen. When \( X_{SiO_2} > 0.667 \), it is assumed that there is negligible free oxygen, the system was simplified as 2MO · SiO\(_2\)–“SiO\(_2\)”. When \( X_{SiO_2} < 0.667 \), MO–SiO\(_2\) system was treated as 2MO · SiO\(_2\)–“MO”.

The effects of different MO on the composition of three oxygen ions are ignored.

The viscous activation energy \( E \) of binary silicate melts MO–SiO\(_2\) can be expressed by three parts which come from the contributions of “SiO\(_2\)”, “MO” and 2MO · SiO\(_2\).

\[ E = X_{SiO_2}E_{SiO_2} + X_{2MO \cdot SiO_2}E_{2MO \cdot SiO_2} + X_{MO}E_{MO} \] .............................(2)

where \( X_{SiO_2} \), \( X_{2MO \cdot SiO_2} \) and \( X_{MO} \) are molar fractions of “SiO\(_2\)”, 2MO · SiO\(_2\) and “MO” respectively. \( E_{SiO_2} \), \( E_{2MO \cdot SiO_2} \) and \( E_{MO} \) are activation energies of “SiO\(_2\)”, 2MO · SiO\(_2\) and “MO” respectively.

The \( X_{SiO_2} \), \( X_{2MO \cdot SiO_2} \) and \( X_{MO} \) value can be calculated by following equation:

For \( X_{MO} < 0.667 \):

\[ X_{SiO_2} = 1 - X_{MO}/0.67, \quad X_{2MO \cdot SiO_2} = X_{MO}/0.67, \quad X_{MO} = 0 \] .............................(3)

\[ X_{MO} > 0.667 \]

\[ X_{SiO_2} = 0, \quad X_{2MO \cdot SiO_2} = 1 - (X_{MO} - 0.67)/0.33, \quad X_{MO} = (X_{MO} - 0.67)/0.33 \] .............................(4)

The \( E_{SiO_2} \), \( E_{2MO \cdot SiO_2} \) and \( E_{MO} \) values can be optimized according to the experimental data of MO–SiO\(_2\) system. Then activation energy \( E \) can be calculated from the composition of silicate melts.

Urbain\(^{2} \) and Zhang\(^{7} \) have surveyed the relationship between \( \ln A \) and \( B \) in viscosity equation

\[ \ln(\eta/T) = \ln A + B/T \] .............................(5)

They suggested the following expression:

\[ \ln A = mB + n \] .............................(6)

This relationship can be explained by the compensation phenomena which have been observed for many processes. According to the compensation law, the pre-nominal factor is related to the activation energy in Arrhenius equation. As shown in Fig. 1, we correlated \( \ln A \) and \( E/R \) using the experimental data of MO–SiO\(_2\) system,

\[ \ln A = m \frac{E}{R} + n \] .............................(7)

However, the \( m \) and \( n \) value is somewhat different for various MO–SiO\(_2\) system. The values are shown in Table 1.

![Fig. 1. The relationship between ln A and E/R for MO–SiO\(_2\) system.](image)

Table 1. Values of \( m \) and \( n \) used for different MO–SiO\(_2\) systems in this model.

<table>
<thead>
<tr>
<th>System</th>
<th>FeO-SiO(_2)</th>
<th>FeO-SiO(_2)</th>
<th>MnO-SiO(_2)</th>
<th>CaO-SiO(_2)</th>
<th>MgO-SiO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( w )</td>
<td>-2.19</td>
<td>-0.37</td>
<td>-3.94</td>
<td>-4.51</td>
<td>-5.11</td>
</tr>
<tr>
<td>( n )</td>
<td>-0.23e-4</td>
<td>-6.66e-4</td>
<td>-2.92e-4</td>
<td>-2.17e-4</td>
<td>-1.989e-4</td>
</tr>
</tbody>
</table>

Especially for FeO–SiO\(_2\) system, the \( m \) and \( n \) values while \( X_{SiO_2} \leq 0.667 \) are different from the values while \( X_{FeO} > 0.667 \).

The \( E \) and \( \ln A \) values for ternary or higher order systems can be assumed to be linear functions of those of the binary silicate melts. For example, the \( E \) and \( \ln A \) values for CaO–MgO–SiO\(_2\) system can be expressed as follows,

\[ E = X_{CaO}/(X_{CaO} + X_{MgO})E_{CaO-SiO_2} + X_{MgO}/(X_{CaO} + X_{MgO})E_{MgO-SiO_2} \] .............................(8)

\[ \ln A = X_{CaO}/(X_{CaO} + X_{MgO})(\ln A)_{CaO-SiO_2} + X_{MgO}/(X_{CaO} + X_{MgO})(\ln A)_{MgO-SiO_2} \] .............................(9)

Where \( E_{CaO-SiO_2} \) and \( E_{MgO-SiO_2} \) are calculated by setting that \( X_{CaO} \) and \( X_{MgO} \) equal to \( (X_{CaO} + X_{MgO})/2 \).

3. The Optimization of Model Parameters

The viscous activation energy \( (E_{MO}) \) of some divalent metal oxide can be estimated from viscosity data, such as FeO. However, viscosity data of some oxides are missing, because their melting points are too high, such as CaO, MgO, etc. According to the Andrade equation,\(^{11} \) the viscosity of melts at melting point temperature \( T_m \) is proportional to \( (T_m)^{1/2} \). We assume that the activation energy of pure oxide is also proportional to \( (T_m)^{1/2} \) and estimate the viscous activation energy of CaO, MgO, MnO by using viscous activation energy of FeO acquire from experimental data.\(^{12} \) Table 2 showed the estimated \( E_{MO}/R \) values.

It seems as if the \( E_{SiO_2}/R \) value should be estimated by the viscosity data of silica. However, it was shown that the viscosity value will dramatically decrease when minor modifying oxide is added in silicate melts with high silica content. The modifying effect is not obvious when the con-
tent of modifying oxide is higher. Using silica data to optimize $E_{\text{SiO}_2}/R$ will bring significant deviation. Hence, we use the experimental data for MO–SiO$_2$ system instead of the experimental data for silica to optimize the $E_{\text{SiO}_2}/R$ value. In order to achieve better performance in viscosity estimation, the $E_{\text{SiO}_2}/R$ value can be various for different MO–SiO$_2$ system. The $E_{\text{SiO}_2}/R$ values for MO–SiO$_2$ (M=Ca, Fe, Mg, Mn) systems are shown in Table 2.

The $E_{2\text{MO} \cdot \text{SiO}_2}/R$ values for MO–SiO$_2$ (M=Ca, Fe, Mg, Mn) systems can be optimized using the experimental viscosity data. The values are also shown in Table 2.

4. Results
4.1. Binary Systems

The comparison between estimated values and measure values for CaO–SiO$_2$ system is shown in Fig. 2. The measure values are from Bockris et al.,13) Kozakevitch et al.,14) Urbain et al.,15) and Endell et al.16) It can be seen from the figure that the estimated values fit well with the measured values totally. The mean deviation $\Delta$ can be calculated as follows,

$$\Delta = \frac{1}{N} \sum_{n=1}^{N} \left( \frac{\mu_n^{\text{cal}} - \mu_n^{\text{mea}}}{\mu_n^{\text{mea}}} \right) \times 100\% \ldots (10)$$

where ($\mu_n^{\text{cal}}$) and ($\mu_n^{\text{mea}}$) are the estimated and measured viscosities respectively. $N$ are the number of samples. The mean deviation $\Delta$ for CaO–SiO$_2$ system is about 18.2%.

The comparison between estimated values and measure values for MgO–SiO$_2$, MnO–SiO$_2$ system is shown in Figs. 3 and 4. The measure values for MgO–SiO$_2$ system are from Bockris et al.,17) Urbain,15,18) Hofmann,19) Riebling20) and Kawai.21) The estimated values for MgO–SiO$_2$ fit well with the measured values. The mean deviation $\Delta$ for MgO–SiO$_2$ system is about 15.4%. The measured values for MnO–SiO$_2$ system are from Yagi et al.,22) Sokolov et al.,23) Segers et al.,24) and Ji et al.25) The estimated values for MnO–SiO$_2$ agree well with the measured values. The mean deviation $\Delta$ for MnO–SiO$_2$ system is about 13.1%.

The comparison between estimated values and measure values for FeO–SiO$_2$ system is shown in Fig. 5. The mean deviation $\Delta$ for FeO–SiO$_2$ system is about 26.3%. The estimated values fit well with measured value from Ji et al.22)
Some divergences between measured values from other authors and estimated values may be due to the abnormal viscosity of FeO–SiO$_2$ around $X_{FeO}=0.3$. This abnormality may be attributed to the presence of the fayalite cluster in the melts, which is not considered in this work.

4.2. Ternary Systems

The viscosities for three ternary systems, CaO–MgO–SiO$_2$, CaO–MnO–SiO$_2$, and CaO–FeO–SiO$_2$ were estimated using the present model. The comparisons between estimated values and measured values are shown in Figs. 6–8. It can be seen from Figs. 5–6 that the estimated values for CaO–MgO–SiO$_2$ and CaO–MnO–SiO$_2$ are in good agreement with measured values. The mean deviation $\Delta$ for CaO–MgO–SiO$_2$ and CaO–MnO–SiO$_2$ system is about 15.5%, 9.5% respectively. However, for CaO–FeO–SiO$_2$ system, some divergence between predicted and estimated values appeared. The mean deviation $\Delta$ for this system is about 23%. The viscosity of CaO–FeO–SiO$_2$ system was directly estimated by using the parameters of FeO–SiO$_2$ and CaO–SiO$_2$ system. The main reason for deviation may be the strong interaction between FeO–SiO$_2$ and CaO–SiO$_2$ in CaO–FeO–SiO$_2$ system, which is not taken into account in the present model.

4.3. Quaternary and Quinary Systems

The viscosities for three systems, CaO–FeO–MgO–SiO$_2$, CaO–FeO–MnO–SiO$_2$, CaO–FeO–MnO–MgO–SiO$_2$ were estimated using the present model. The comparisons between estimated values and measured values are shown in Figs. 9–11. The estimated values also agree well with the measured values. The mean deviation $\Delta$ for CaO–FeO–MgO–SiO$_2$, CaO–FeO–MnO–SiO$_2$, CaO–FeO–MnO–MgO–SiO$_2$ system is about 17.1, 15.8, 17.7% respectively.

![Fig. 6. Comparison between estimated and measured value for CaO–MgO–SiO$_2$ system.](image)

![Fig. 7. Comparison between estimated and measured value for CaO–MnO–SiO$_2$ system.](image)

![Fig. 8. Comparison between estimated and measured value for CaO–FeO–SiO$_2$ system.](image)

![Fig. 9. Comparison between estimated and measured value for CaO–FeO–MgO–SiO$_2$ system.](image)

![Fig. 10. Comparison between estimated and measured value for CaO–FeO–MnO–SiO$_2$ system.](image)
The order of MO–SiO$_2$ should be MgO, whereas our model parameters clearly show this relationship between melting points of MO and viscosity values. This agreement indicates that the present model can provide accurate estimations for viscosities of silicate slags. Since the present model has a relatively simple form, it can be conveniently used for industrial use.

### 6. Summary

A semi-empirical model for viscosity prediction of silicate melts was presented in this work. In this model, the binary silicate melts MO–SiO$_2$ (MO is a bivalent metal oxide) was treated as 2MO–SiO$_2$–“SiO$_2$” or “MO”–2MO–SiO$_2$ system when $X_{MO} \approx 0.667$, whereas our model parameters did not reflect the relationship between the contributions of “SiO$_2$”, “MO” and 2MO–SiO$_2$. A relationship between pre-exponential factor $A$ and activation energy $E$ in Arrhenius equation was used for individual binary silicate melts.

The model parameters were extracted from binary silicate melts and applied to ternary or higher order systems. The viscosities of silicate melts within CaO–MgO–MnO–FeO–SiO$_2$ system were estimated using the present model. Good agreements have been achieved between calculated values and measured values.

### REFERENCES