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ESTIMATION OF VISCOSITY FOR SOME SILICATE TERNARY SLAGS

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Abstract

A new method, combining KTH model with geometrical model (General solution model by Chou) to estimate viscosity of some ternary silicate slags, was proposed in this work. According to modified KTH model, viscous Gibbs free energy for mixing of ternary slags was estimated by employing general solution model. It was found that viscous Gibbs energy for mixing of ternary system could be calculated using solely viscous Gibbs energy for mixing of sub-binary systems. The viscosities of five ternary slags $CaO-MnO-SiO_2$, $CaO-FeO-SiO_2$, $FeO-MnO-SiO_2$, $CaO-MgO-SiO_2$ *and* $FeO-MgO-SiO_2$ *were estimated in the present work. A good agreement with available experimental data, with mean deviation less than 20%, was achieved. The modified KTH model has advantages with less model parameters and improved estimation ability by comparison to original KTH model.*

Keywords: slag, viscosity, estimation, KTH model, general solution model, silicates

1. Introduction

Viscosity of molten slags is one of thermo-physical properties of most interest and plays an important role in many metallurgical processes. Viscosity of mould fluxes is the key factor for lubrication between mould and strand in continuous casting process and should be well controlled to avoid sticker breakouts [1]. Accurate slag viscosity data is also essential to successful model of fluid flow in ironmaking and steelmaking process. Due to the difficulty and high uncertainty of viscosity measurement at high temperature, the reliable data still cannot meet the increasing demands of industrial use. Accordingly, development of viscosity estimation model for molten slags could be an efficient way to provide accurate data.

During last thirty years, many models [1-11] have been proposed for estimation of viscosity of molten slags. The early-stage models are empirical, using limited experimental data to obtain the model parameters. These models were proposed for given kinds of molten slags, e.g. Riboud model [1] for mould fluxes. Later, several models [2-10] were developed later for estimating viscosity of molten slags with wider compositions. Mills et al. [11] performed a Round Robin projects to assess the performance of these models in different kinds of molten slags and found that models due to KTH (Swedish acronym of Royal institute of technology) [2], Zhang [3,4], Iida [6,7] were ranked as the most reliable models.

KTH model was based on a series of self-consistent model parameters extracted from low order systems which guarantee its good performance in both low and high order systems. However, too many parameters of interaction (especially ternary or high order interaction parameters) were employed in KTH model, which could impair its ability of prediction. It is important to find a suitable way to predict the viscosity of ternary or higher order system from binary interactions.

Geometrical models [12-16] have wide applications in predict thermodynamic properties of ternary systems from information of corresponding sub-binary systems. Among these geometrical models, general solution model [16,17] proposed by Chou has been found superior in predictive ability. In this work, the author explored the way to estimate viscosities of molten slag combining KTH model and general solution model Estimated viscosity values were compared with measured viscosity values to check the accuracy of the method. Moreover, estimation results of modified KTH model were also compared with those of original KTH model and other methods.

2. Model description

The model calculation model for unary and binary

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systems is as same as KTH model [2], and will be briefly introduced here.

According to absolute reaction rate theory by Eyring et al. [18], temperature dependence of melts' viscosity can be described by following equation:

$$\eta = \frac{Nh\rho}{M}\exp(\frac{\Delta G^*}{RT}) \tag{1}$$

where N is Avergadro number, h is Planck constant, R is gas constant, T is temperature, r is density, M is molar weight, and ΔG^* is viscous Gibbs free energy.

Molar weight of multi-component system can be calculated as follows:

$$M = \sum X_i \cdot M_i,\ \rho = \sum X_i \cdot \rho_i \tag{2}$$

where X_i was the mole fraction of component *i*, *Mi* and r_i was the molar weight of density of component i.

Combining Temkin ionic theory [19] with Lumsden theory [20], oxide melts are considered to consist of a matrix of oxygen ions with various cations (including Si^{4+}) distributed in it. In a system containing *m* different oxides, cations and anions can be grouped in two separated subgroups: $(C1^{v1}, C2^{\upsilon 2}, \cdots Ci^{\upsilon i}, \cdots, Cm^{\upsilon m})_p (O^{2-})_q$, where *p* and *q* are stoichiometric numbers. *Ci* stands for cations, and superscript *vi* represents the electrical charge number of *Ci*.

The ionic fraction of cation is defined as:

$y_{Ci} = \frac{N_{Ci}}{\sum N_C}$, where denotes the number of cation *i*.

All cations are included in sum. The viscous Gibbs free energy is expressed as:

$$\Delta G^* = \sum X_i \Delta G_i^* + \Delta G_M^* \tag{3}$$

where ΔG_i^* is viscous Gibbs free energy of pure component *i* and can be described by a linear function of temperature, $\Delta G_i^* = a + bT$.

Viscous Gibbs free energy for mixing ΔG_M^* reflects the interactions among different cations in the presence of oxygen ions. ΔG_{Mix}^* of binary *i-j* system can be expressed using Redlich-Kister polynomial:

$$\begin{aligned}\Delta G_{M(i-j)}^* = y_{Ci} y_{Cj} ((L_{00} + L_{01}T) + (L_{10} + L_{11}T) \cdot \\ \cdot (y_{Ci} - y_{Cj}) + (L_{20} + L_{21}T)(y_{Ci} - y_{Cj})^2)\end{aligned} \tag{4}$$

Original KTH model employs additional ternary parameters to estimate viscosity of ternary system, as follows:

$$\begin{aligned}\Delta G_{Mix}^* = (\sum\sum y_{Ci1} y_{Ci2} L_{Ci1,Ci2(O)} + \\ + \sum\sum\sum y_{Ci1} y_{Ci2} y_{Ci3} L_{Ci1,Ci2,Ci3(O)})\end{aligned} \tag{5}$$

where the first item on the right side of equation represents the summation of different interactions among two cations, while the second item on the right side of equation represents the different interactions among three cations.

In the present work, ΔG_{Mix}^* for the ternary system is estimated from optimized parameters for binary systems, according to geometrical model. Among various geometrical models, general solution model proposed by Chou [16,17] had been widely employed to estimate thermodynamic and physical properties of melts. Better prediction ability had been shown for general solution model than other geometrical model in many reports [21-22]. Consequently, the values of were ΔG_{Mix}^* estimated in the present work by using general solution model.

The formulas for general solution model are summarized here, according to Chou [16,17]. For ternary *i-j-k* system, viscous Gibbs free energy for mixing $\Delta G_M^*(ijk)$ could be calculated in terms of viscous Gibbs free energy for mixing of three sub-binary systems:

$$\begin{aligned}\Delta G_{Mix}^*(ijk) = W_{ij}\Delta G_M^*(X_{i(i-j)}, X_{j(i-j)}) + \\ + W_{jk}\Delta G_M^*(X_{j(j-k)}, X_{k(j-k)}) + W_{ki}\Delta G_M^*(X_{k(k-i)}, X_{i(k-i)})\end{aligned} \tag{6}$$

where is:

$$W_{ij} = \frac{X_i X_j}{X_{i(i-j)} X_{j(i-j)}},\quad W_{ki} = \frac{X_k X_i}{X_{k(k-i)} X_{i(k-i)}},\quad W_{jk} = \frac{X_j X_k}{X_{j(j-k)} X_{k(j-k)}} \tag{7}$$

and

$$X_{i(i-j)} = X_i + \xi_{i(i,j)}^k X_k,\ X_{j(i-j)} = 1 - X_{i(i-j)} \tag{8}$$

$$X_{k(k-i)} = X_k + \xi_{k(k,i)}^j X_j,\ X_{i(k-i)} = 1 - X_{k(k-i)} \tag{9}$$

$$X_{j(j-k)} = X_j + \xi_{j(j,k)}^i X_i,\ X_{k(j-k)} = 1 - X_{j(j-k)} \tag{10}$$

and

$$\xi_{i(i,j)}^k = \frac{\int_0^1 (\Delta G_{M(ij)}^* - \Delta G_{M(ik)}^*)^2 dX}{\int_0^1 (\Delta G_{M(ij)}^* - \Delta G_{M(ik)}^*)^2 dX + \int_0^1 (\Delta G_{M(ji)}^* - \Delta G_{M(jk)}^*)^2 dX} \tag{11}$$

$$\xi_{k(k,i)}^j = \frac{\int_0^1 (\Delta G_{M(ki)}^* - \Delta G_{M(kj)}^*)^2 dX}{\int_0^1 (\Delta G_{M(ki)}^* - \Delta G_{M(ki)}^*)^2 dX + \int_0^1 (\Delta G_{M(ij)}^* - \Delta G_{M(ik)}^*)^2 dX} \tag{12}$$

$$\xi_{j(j,k)}^i = \frac{\int_0^1 (\Delta G_{M(iji)}^* - \Delta G_{M(jk)}^*)^2 dX}{\int_0^1 (\Delta G_{M(ji)}^* - \Delta G_{M(jk)}^*)^2 dX + \int_0^1 (\Delta G_{M(ki)}^* - \Delta G_{M(kj)}^*)^2 dX} \tag{13}$$

Thus, viscous Gibbs energy for mixing of ternary system could be predicted from those of three sub-binary systems. No ternary interaction item is required.

Since no viscosity data for binary system FeO-MnO, CaO-FeO, CaO-MnO, FeO-MgO and CaO-MgO could be found in literature. The model parameters of viscous Gibbs free energy for mixing were estimated using experimental data of ternary systems of FeO-MnO-SiO_2 [23], CaO-FeO-SiO_2 [24], CaO-MnO-SiO_2 [25,26], CaO-MgO-SiO_2 [27-29] and FeO-MgO-SiO_2 [23] and listed in Table 1.

Table 1. *Model parameters for the present work*

Component	Density (g/cm^3)	Molar mass (g/mol)	ΔG_i^* (J/mol)
CaO	3.3	56.1	185327.3
FeO	4.7	71.8	133960.049-18.156345T
MgO	3.58	40.3	186541.828
MnO	5.43	70.9	132713.886
SiO_2	2.3	60.1	529175.3836-51.60776341·T
Interaction parameters			
CaO-SiO_2	$y_{Ca}y_{Si}$(-847733+99.93172· T+260338· (y_{Ca}-y_{Si}))		
FeO- SiO_2	$y_{Fe}y_{Si}$(-964672.09+243.57· T+170109.3686· (y_{Fe}-y_{Si}))		
MgO- SiO_2	$y_{Mg}y_{Si}$(-810037+87.69615· T+132119.3· (y_{Mg}-y_{Si}))		
MnO- SiO_2	$y_{Mn}y_{Si}$(-729657.03+85.8· T-72976.33· (y_{Mn}-y_{Si}))		
CaO-FeO	$y_{Ca}y_{Fe}$(-80000)		
FeO-MnO	$y_{Fe}y_{Mn}$(27500)		
CaO-MnO	$y_{Ca}y_{Mn}$(4750)		
CaO-MgO	$y_{Ca}y_{Mg}$(10000)		
FeO-MgO	$y_{Fe}y_{Mg}$(-29000)		

3. Results and Discussion

Viscosities of four binary systems CaO-SiO_2, MgO-SiO_2, FeO-SiO_2 and MnO-SiO_2 systems were estimated in the present work. Comparisons between estimated and measured values for these systems are shown in Fig.1. A database for experimental viscosity values of binary slag systems from various authors [23-25, 29, 31-34] was established by the present author in a previous work [35], which was used as the data source for comparison. According to Fig.1, estimated values fit well with the measured values in total. The mean deviation D can be defined as follows:

$$\Delta = \frac{1}{N}\sum_{n=1}^{N}\frac{\left|(\mu_n)_{cal}-(\mu_n)_{mea}\right|}{(\mu_n)_{mea}}\times 100\% \qquad (14)$$

where $(m_n)_{cal}$ and $(m_n)_{mea}$ are the estimated and measured viscosities respectively, and N is the number of samples. The mean deviation D for binary systems CaO-SiO_2, MgO-SiO_2, MnO-SiO_2, FeO-SiO_2 is about 14.6%,10.4%, 9.5%, 24.1%, respectively.

Further, the viscosities of several ternary silicate slag systems, such as CaO-MgO-SiO_2, CaO-FeO-SiO_2, CaO-MnO-SiO_2, FeO-MgO-SiO_2 and FeO-MnO-SiO_2, were estimated using presently modified KTH model. Then, estimated viscosities were compared with literature data [23-29] to validate the model.

CaO-FeO-SiO_2 system is a base slag for Linz-Donawitz converter slags. Ji [24] et al measured viscosities of CaO-FeO-SiO_2 system using rotating bob method. To ensure all Fe in valence of +2, iron crucibles and spindles were employed during measurements. Viscosities of slags with compositions in the range of X(CaO)=0.06~0.48 and X(FeO)=0.09~0.65 were determined from 1423 to 1753K. The comparisons between estimated values and measured values for CaO-FeO-SiO_2 system are shown in Fig.2. It could be seen that estimated values agree well with experimental values. The mean deviation for this system is 13.8%.

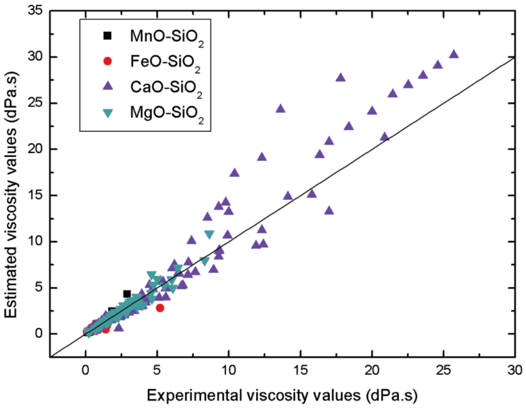

Figure 1. *Comparison between estimated and experimental viscosity values [23-25,29,31-34] for binary systems*

CaO-MnO-SiO_2 slag provides a simplified description for slags in the high carbon ferromanganese production process. Viscosity data of CaO-MnO-SiO_2 system from Ji et al. [25] and Kawahara et al. [26] were employed for comparison with estimated value. Viscosity of the slags with composition in the range of CaO%=8.31%~45% and

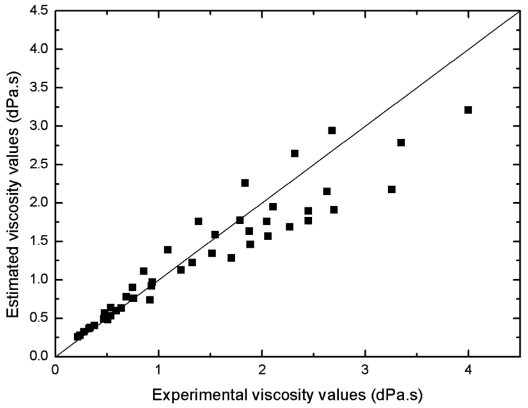

Figure 2. *Comparison between estimated and experimental [24] viscosity values for CaO-FeO-SiO_2 systems*

MnO%=15%~56% were measured by Ji [22] from 1623 to 1753K. The comparisons between estimated values and measured values for CaO-MnO-SiO_2 system are shown in Fig.6-8. It could be seen that the estimated viscosities for CaO-MnO-SiO_2 are in good agreement with measured values. The mean deviation D is about 15.4%.

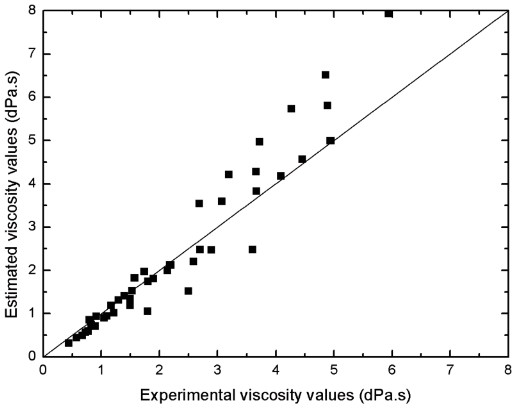

Figure 3. *Comparison between estimated and experimental [25,26] viscosity values for CaO-MnO-SiO_2 systems*

There are several experimental viscosity data sources for CaO-MgO-SiO_2 system. Machin [27] and Licko [28] measured viscosity of CaO-MgO-SiO_2 system using oscillating bob method. Experimental data from Urbain [29] et al were measured using rotating crucible method for CaO-MgO-SiO_2 system (1623-2312K). The comparisons between estimated values and measured values for CaO-MgO-SiO_2 system are shown in Fig.4, and agreement is also very good with a mean deviation D of 11.7%.

Ji et al. [23] measured viscosity values of FeO-MgO-SiO_2 and FeO-MnO-SiO_2 system using rotating bob method with an iron spindle and crucible. Comparisons between estimated values and measured values for FeO-MgO-SiO_2 and FeO-MnO-SiO_2 system are shown in Fig.5 and 6. It is shown that estimated values fit very well with measured values. The mean deviation for FeO-MgO-SiO_2 and FeO-MnO-SiO_2 system is 10.6% and 12.8% , respectively.

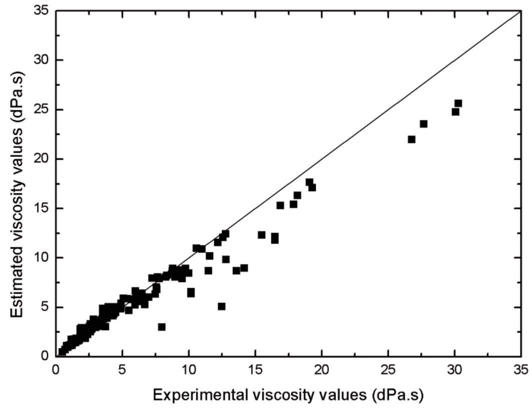

Figure 4. *Comparison between estimated (this work) and experimental [27-29] viscosity values for CaO-MgO-SiO_2 systems*

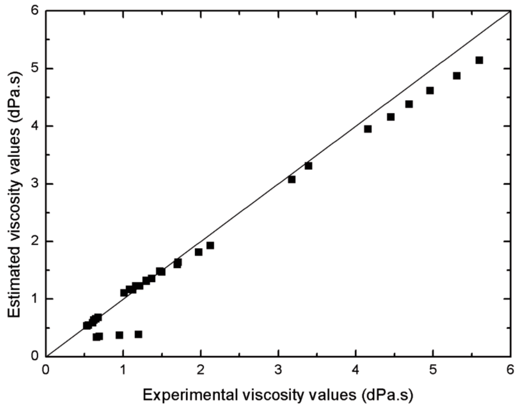

Figure 5. *Comparison between estimated and experimental [23] viscosity values for FeO-MgO-SiO_2 systems*

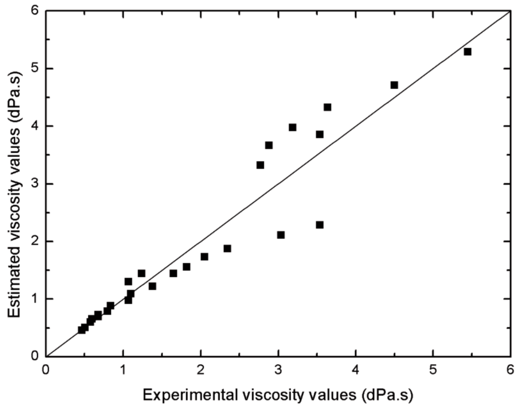

Figure 6. *Comparison between estimated and experimental [23] viscosity values for FeO-MnO-SiO_2 systems*

The viscosities of above ternary systems were also estimated using original KTH model. The parameters of original KTH model could be found in literature [36]. Comparisons between estimated viscosities with experimental data from literature [23-29] were carried out. The deviations between estimated and experimental data were listed in Table 2. It could be found that deviations produced by original KTH model are slightly higher than those obtained in the present work. It should be also noted that the present method includes less model parameters than original KTH model.

Based on the fact that crystalline solid solutions of $MgSiO_3$+$FeSiO_3$, $CaSiO_3$+$FeSiO_3$ and Ca_2SiO_4+Mn_2SiO_4 can all be formed from their separate silicates with very low value of heats of mixing, Richardson [37] assumed that two binary silicates of equal silica mole fraction mix ideally. Further, he proposed an idea on mixing model to calculate the activities of components in ternary silicate solely from activities of binary silicates. This method had been applied to calculate the viscosities of ternary and high order silicate systems from the parameters of binary systems [20].

For ternary AO-BO-SiO_2 system,

$$\Delta G^*_{Mix}(AO-BO-SiO_2) = \frac{X_{AO}}{X_{AO}+X_{BO}}\Delta G^*_{Mix}(AO-SiO_2) + \\ + \frac{X_{BO}}{X_{AO}+X_{BO}}\Delta G^*_{Mix}(BO-SiO_2) \quad (15)$$

where $\Delta G^*_{Mix}(AO-SiO_2)$ are calculated with $X_{AO}(\mathrm{Bin}) = 1 - X_{SiO_2}(\mathrm{Ter})$ and $X_{BO}(\mathrm{Bin}) = 1 - X_{SiO_2}(\mathrm{Ter})$, $X_{AO}(\mathrm{Bin})$ and $X_{BO}(\mathrm{Bin})$ are molar fractions of AO and BO in AO-SiO_2 and BO-SiO_2 respectively. $X_{SiO_2}(\mathrm{Ter})$ is a molar fraction of SiO_2 in ternary AO-BO-SiO_2 system.

The Richardson method was employed to estimated viscosities of five ternary systems. The deviations between estimated viscosities and experimental viscosities were listed in Table 2. It is shown in Table 2 that deviation values for Richardson method is much higher than those for original and the present modified KTH model, apart from CaO-MnO-SiO_2. Especially in the case of CaO-FeO-SiO_2 system, deviation values for Richardson method are four times higher comparing to those given in the present work. This could be due to significant contribution of CaO and FeO interaction (see the CaO-FeO parameters in Table1), which is neglected in Richardson method.

Seetharaman et al. [38] presented a correlation to predict the viscosities of ternary silicate melts using the Gibbs energies of mixing. The main idea is based on modification on Richardson method by adding an item, which could be calculated from excess Gibbs energies of mixing for two network modified oxides, to account for interaction between different network modified cations, as follows:

$$\Delta G^*_{Mix}(AO-BO-SiO_2) = \frac{X_{AO}}{X_{AO}+X_{BO}}\Delta G^*_{Mix}(AO-SiO_2) + \\ \frac{X_{BO}}{X_{AO}+X_{BO}}\Delta G^*_{Mix}(BO-SiO_2) + 3X_{AO}X_{BO}(1-X_{SiO_2})\Delta^E G_{Mix} \quad (16)$$

where $\Delta^E G_{Mix}$ denotes thermodynamic excess Gibbs energy of mixing for AO-BO system.

Estimation using method by Seetharaman et al. [38] was also carried out in the present work. The mean deviation between estimated and experimental viscosities was shown in Table.2. As can be seen, it is found that deviation values of Seetharaman method are slight lower than those of Richardson method, but higher than those of original KTH model and the present method.

There are two network modifying cations presenting in ternary silicate systems studied in this work. The viscosities of these ternary silicate systems are affected by mixing of different network modifying cations. Due to different size and ionicity of network modifying cations, ideal mixing assumption of different network modifying cations is not enough to account the property changes with composition. “Mixed cation effects” have been found to be important to thermodynamic and transport properties of many multicomponent glasses and melts [39,40]. Richardson method completely neglected interaction between different network modifying cations in silicate, therefore leading to larger estimation deviation compared with other methods.

Table 2. *Deviations between estimated and experimental viscosities for different estimation method*

System	Deviations/%			
	Present work	Original KTH model	Richardson method	Seetharaman method
CaO-MgO-SiO_2	11.7	14.8	12.7	36
CaO-FeO-SiO_2	13.8	14	68	59
CaO-MnO-SiO_2	15.4	16.4	16	15.3
FeO-MgO-SiO_2	10.6	13.4	20.8	19.3
FeO-MnO-SiO_2	12.8	13	27.6	27.6

4. Summary

In this work, by combining KTH model with general solution model, a new method was presented to estimate viscosity of ternary slags. Viscous Gibbs free energy for mixing of ternary slags in KTH model was calculated by employing general solution model using solely viscous Gibbs energy for mixing of sub-binary systems. The viscosities of five ternary silicate slags CaO-MnO-SiO_2, CaO-FeO-SiO_2, CaO-MgO-SiO_2, FeO-MnO-SiO_2 and FeO-MgO-SiO_2 were estimated in the present work. A good agreement with mean deviation less than 20% was achieved for comparison of estimated and available experimental values. The modified KTH model has advantages with less model parameters and improved estimation ability by comparison to original KTH model. The present method was also compared with methods presented by Richardson and Seetharaman regarding estimation accuracies. Comparison shows that the present method has the best accuracy on viscosity estimation of ternary slags.

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