ESTIMATION OF VISCOSITIES OF HIGH TEMPERATURE SILICATE MELTS

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ABSTRACT

This paper describes the recent viscosity-modeling studies by present authors in USTB, Beijing. A simple model for non-fluoride containing multi-component silicate melts has been proposed based on the equation of Ering's absolute-rate theory with structure consideration regarding bridge, non-bridge as well as free oxygen in melts. The viscous activation energy has been assumed from contributions of these three types of oxygen. The model has been extended up to CaO-MgO-FeO-MnO-SiO_2 *system, and the results have shown a reasonable agreement between calculated and measured viscosity values. For fluoride-containing silicate melts, the model by Riboud et al.* $\eta = A \cdot T\ exp(\frac{B}{T})$ *was modified using new expressions for A and B involving new sets of parameters optimized from recently published experimental viscosity data. The model applications have shown a better suitability than the Riboud model for* CaO-FeO-Al_2O_3-SiO_2-CaF_2 *melts and mould fluxes with high* CaF_2 *content.*

INTRODUCTION

Viscosities of high temperature melts have impact to metallurgical processes, especially the rate phenomenon that they involve. As the difficulties and high cost of viscosity measurements due to the high temperature and corrosion to the containers, the viscosity estimation has received very close attention since the middle of last century.

Due to the complex structure of the melts, the models for estimating industrial slag viscosities are almost all semi-empirical or empirical with more or less empirical parameters attained from experimental data. Most of the models can be grouped either based on Ering's [1] absolute rate theory [2, 3] or on the hole theory [4, 5, 6, 7, 8]. The Iida model [9] is based on the assumption similar with the Ering equation to link viscosity with activation energy E, and pre-exponential factor *A*. Nevertheless, E, *A* and other parameters have been treated as temperature dependent functions. It has been noted that analogous methodology has been introduced in viscosity modeling. A model for estimation viscosity from Gibbs energy of mixing [11] and the so-called weight triangle model [12] are the typical examples of this type. In the following sections, the authors introduce recent modeling studies in our Lab on viscosity of silicate melts with and without fluoride component [10].

A MODEL FOR MULTI-COMPONENT SYSTEMS WITHOUT FLURIDE

Model Consideration and Formulation

According to the absolute rate theory, viscosity, η can be correlated with temperature *T* (in Kelvin). The equation can be simplified using an Arrehenius form:

$$\eta = A \cdot T \exp\left(\frac{E}{BT}\right) \tag{1}$$

where *A* is pre-exponential factor, and *E* denotes the viscous activation energy. Three types of oxygen in silicate melts, bridge oxygen O^0, non-bridge oxygen O^- and free oxygen O^{2-} were introduced [13]. They are in equilibrium as: $2O^- = O^0 + O^{2-}$. Taking account of the structure of silicate melts, binary melts MO-SiO_2 (M is a bivalent element) in the present model are treated as ternary systems of the type: MO-2MO•SiO_2-SiO_2 with the following assumptions: only free oxygen exists in *MO*, bridge oxygen exists in SiO_2, and 2MO•SiO_2 contains solely non-bridge oxygen. It is also assumed that free oxygen is negligible, and the system can be simplified as 2MO•SiO_2-SiO_2 if $X_{MO} < 0.667$; and be treated as MO-2MO•SiO_2 if $X_{MO} > 0.667$. The effects of different MO on the proposition of three types of oxygen are ignored in the model.

The viscous activation energies for binary melts MO-SiO_2 are regarded coming from the contributions by SiO_2, MO and 2MO•SiO_2 and using the following expression:

$$E = X_{\text{"SiO2}}\,\text{"}E_{\text{"SiO2"}} + X_{\text{"MO"}}E_{\text{"MO"}} + X_{2MO\cdot SiO2}\; E_{2MO\cdot SiO2} \tag{2}$$

where, $E_{\text{"}SiO_2\text{"}}$, $E_{\text{"MO"}}$ and $E_{2MO\cdot SiO_2}$ designate activation energies, and $X_{\text{"}SiO_2\text{"}}$, $X_{\text{"MO"}}$ $X_{2MO\cdot SiO_2}$, the molar ratio values of SiO_2, *MO* and 2MO•SiO_2 respectively. $X_{\text{"}SiO_2\text{"}}$, $X_{\text{"MO"}}$ and $X_{2MO\cdot SiO_2}$ can be calculated using the following expressions:

For $X_{MO} < 0.667$, $X_{\text{"SiO2"}} = 1 - X_{MO}/0.67$, $X_{2MO\cdot SiO2} = X_{MO}/0.67$, $X_{\text{"MO"}} = 0$ (3)

For $X_{MO} > 0.667$, $X_{\text{"SiO2"}} = 0$, $X_{2MO\cdot SiO2} = 1 - (X_{MO} - 0.67)/0.33$, $X_{\text{"MO"}} = (X_{MO} - 0.67)/0.33$ (4)

$E_{"SiO2"}$, $E_{"MO"}$ and $E_{2MO\cdot SiO2}$ values can be optimized using the experimental data of MO- SiO_2 system.

According to the compensation law, the pre-nominal factor is related to the activation energy in Arrhenius equation. ln A and B can be correlated using the experimental data of MO-SiO_2 system,

$$\text{In} \quad A = m + n\frac{E}{R} \tag{5}$$

However, m and n are somewhat different for various MO-SiO_2 systems, and are shown in Table 1.

Table 1: Values of m and n used for different MO-SiO_2 systems in the model

System	FeO-SiO_2	MnO-SiO_2	CaO-SiO_2	MgO-SiO_2
m	-2.37	-3.86	-4.51	-2.51
n	-3.947e-4	-3.198e-4	-2.37e-4	-3.179e-4

* Data m and n were generated using viscosity data with respect to dPa•s unit

The present model assumes that E and ln A have linear relation with the corresponding parameters in the relevant binaries. For instance, E and ln A for CaO- MgO – SiO_2 can be expressed as follows:

$$E = \frac{X_{CaO}}{X_{CaO}+X_{MgO}} E_{"CaO"-SiO_2} + \frac{X_{MgO}}{X_{CaO}+X_{MgO}} E_{"MgO"-SiO_2} \tag{6}$$

$$\ln A = \frac{X_{CaO}}{X_{CaO}+X_{MgO}} \ln A_{"CaO"-SiO_2} + \frac{X_{MgO}}{X_{CaO}+X_{MgO}} \ln A_{"MgO"-SiO_2} \tag{7}$$

where $E_{"CaO"+SiO_2}$ and $E_{"MgO"+SiO_2}$ can be attained by setting $X_{"CaO"}$ and $X_{"MgO"}$ equal to (X_{CaO}+X_{MgO}).

Optimization of Model Parameters

$E_{"MO"}$ values for some divalent metal oxides can be estimated from viscosity data, such as FeO. However, for some oxides like CaO and MgO, the viscosity data are missing due to their extremely high melting temperatures. It is assumed that the activation energy of a pure oxide is proportional to the root square of melting temperature T_m in the model. Using this relation and the activation energy for FeO, $E_{"MO"}$ values for CaO and MgO were attained. E/R values obtained are listed in Table 2.

Table 2: Model parameter values for different MO-SiO_2 system

System	FeO-SiO_2	MnO-SiO_2	CaO-SiO_2	MgO-SiO_2
$E_{"MO"}/R$	20831	23292	17554	28597
$E_{2MO\cdot SiO_2}/R$	6792	10798	14899	16002
$E_{"SiO_2"}/R$	33941	36500	37340	38827

As using silica viscosity data to get optimized $E_{"MO"}/R$ may bring significant deviation, experimental data of MO-SiO_2 binaries rather than those of silica were used for optimization. In order to achieve better fitting, $E_{"SiO_2"}/R$ value is allowed to vary with different MO for MO-SiO_2 binaries.

VISCOSITY ESTIMATION FOR FLUORIDE CONTAINING SYSTEMS

The model proposed to estimate the viscosity of mould powders [7] can be expressed as follows:

$$\eta = A \cdot T \exp(B/T) \tag{8-a}$$

where T denotes the temperature in K, A and B are two empirical parameters linking to mole fractions of slag components.

The present authors renewed the empirical parameters A and B using newly published experimental data for the viscosity of synthetic slags in some CaF_2 containing slags [14, 15, 16]. The error due to fluoride evaporation losses was avoided by determining the composition of the slags periodically between measurements. The two expressions obtained for $CaO\text{-}FeO\text{-}Al_2O_3\text{-}SiO_2\text{-}CaF_2$ are written below:

$$A = \exp(-19.42 - 9.64X_{Al_2O_3} + 2.42X_{CaO} + 6.12X_{FeO} + 8.91X_{CaF_2}) \tag{8-b}$$

$$B = 24619 + 33535X_{Al_2O_3} - 15953X_{CaO} - 23983X_{FeO} - 35314X_{CaF_2} \tag{8-c}$$

Commercial mould fluxes usually contain CaO, MgO, Al_2O_3, FeO, Na_2O, SiO_2, and CaF_2. Equations (8-a), (8-b) and (8-c) cannot directly be used to calculate viscosities of mould fluxes for the lack of parameters with respect to MgO, K_2O and Na_2O. As MgO can be expected to have similar effects as CaO on the slags containing CaF_2, so the parameters of CaO could be used for slags containing MgO. The parameters with respect to K_2O and Na_2O were optimized using experimental data [17, 18], and parameters for K_2O and Na_2O are assumed to be the same. The new correlations to replace Equations (8-b) and (8-c) for the model are shown as follows:

$$A = \exp[-19.42 - 9.64X_{Al_2O_3} + 2.42(X_{CaO} + X_{MgO}) + 6.12X_{FeO} + 8.91X_{CaF_2} - 7.84(X_{Na_2O} + X_{K_2O})] \tag{8-d}$$

$$B = 24619 + 33535X_{Al_2O_3} - 15953(X_{CaO} - X_{MgO}) - 23983X_{FeO} - 35314X_{CaF_2} - 3123 (X_{Na_2O} + 3123(X_{Na_2O} + X_{K_2O}) \tag{8-e}$$

RESULTS

Silicate Melts without Fluoride

Comparison between model estimated and measured viscosity values was firstly made for binary and ternary systems. For $CaO\text{-}SiO_2$ melt, the comparison is illustrated in Figure 1. It can be seen that the model estimated values fit to the measured data well. An index, mean deviation, Δ, has been introduced which is defined as follows:

$$\Delta = \frac{1}{N}\sum_{i=1}^{N} \frac{\left|(\eta_i)_{cal} - (\eta_i)_{expl}\right|}{(\eta_i)_{expl}} \times 100\% \tag{9}$$

where $(\eta_i)_{cal}$ and $(\eta_i)_{expl}$ denote estimated and measured viscosities respectively, N is the number of samples. The mean deviation for $CaO\text{-}SiO_2$ system is as great as about 18.2%. Δ values for all the calculated binaries and ternaries along with sources of the experimental data are listed in Table 3.

Table 3: Mean deviations between estimated and measured viscosities for binaries and ternaries

System	Δ	Sources of experimental data for comparison
$CaO-SiO_2$	18.2%	Bockris(1954), Kozakevitch(1960), Urbain(1982) and Endell(1936)
$MgO-SiO_2$	15.4%	Urbain(1982 and 1986), Hofmann(1959), Riebling(1964) and Kawai(1979)
$MnO-SiO_2$	13.1%	Yagi(1955), Sokolov(1979), Segers(1979) and Ji(1998)
$FeO-SiO_2$	26.3%	Kozakevitch(1949), Urbain(1982), Rontgen(1956) and Ji(1997)
$CaO-MgO-SiO_2$	15.5%	Machin(1954), Guityai(1962), Licko(1986) and Urbain(1982)
$CaO-MnO-SiO_2$	9.5%	Ji(2001) and Kavahara(1979)
$CaO-FeO-SiO_2$	23%	Ji(1997)

*For sources of experimental data in the third column of Table 3, please see Shu *et al.*, 2006

The Δ values obtained for $MgO-SiO_2$ and $MnO-SiO_2$ are 15.4% and 13.1% respectively, for $FeO-SiO_2$ system, is around 26.3%. The calculated values fit to the recent viscosity data well [19]. Some divergences between measured values by other investigators and the calculated data may come from the abnormal viscosity of $FeO-SiO_2$ around $X_{FeO}=0.3$. This abnormity may be attributed to the presence of the fayalite cluster in the melts [20]. Satisfactory fittings have been obtained for ternaries, $CaO-MnO-SiO_2$ and $CaO-FeO-SiO_2$. Only for $CaO-FeO-SiO_2$, the Δ value gets up to about 23% indicating some divergence between experimental and estimated values, which are illustrates in Figure 2. The viscosity of $CaO-FeO-SiO_2$ was directly estimated using the parameters of $CaO-SiO_2$ and $FeO-SiO_2$ systems. The main reason for the deviation may be the strong interactions between $CaO-SiO_2$ and $FeO-SiO_2$ in the ternary, which has not yet been taken into account in the present model.

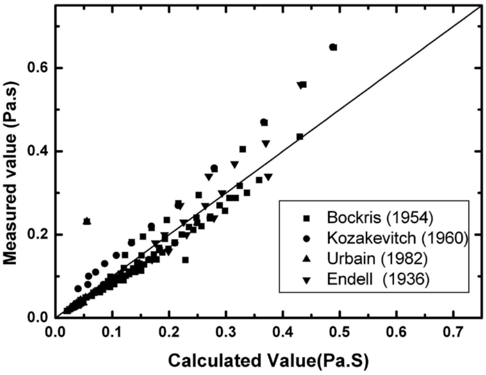


Figure 1: Comparison between estimated and measured viscosity values for $CaO-SiO_2$ system

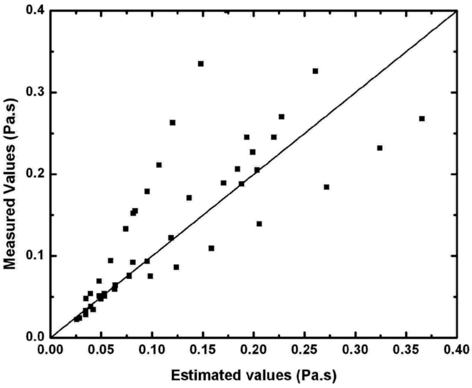


Figure 2: Comparison between estimated and measured viscosities for CaO-FeO-SiO_2 system

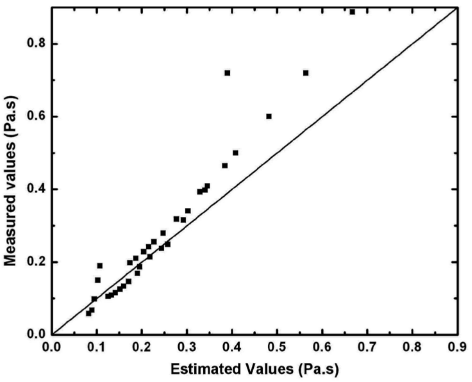
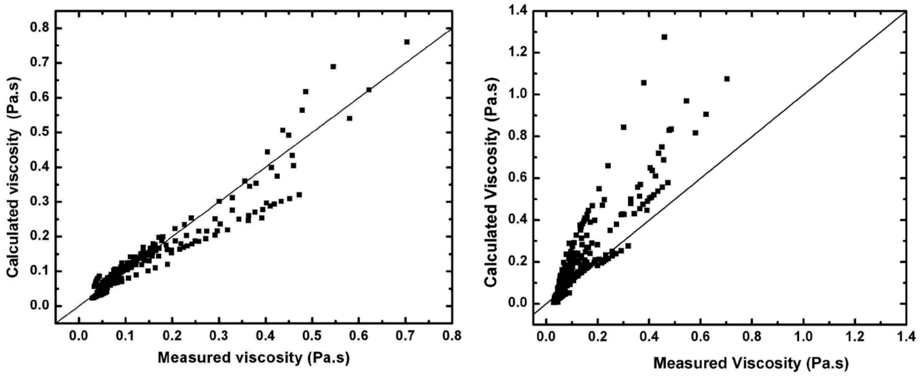


Figure 3: Comparison between estimated and measured viscosities for CaO-FeO-MnO-MgO-SiO_2

The viscosities for CaO-FeO-MgO- SiO_2, CaO-FeO-MnO-SiO_2, and CaO-FeO-MnO-MgO-SiO_2 system were evaluated using the present model, and compared with experimental data [19, 21]. Δ values produced are 17.1%, 15.8% and 17.7% respectively. Figure 3 illustrates the comparison for the quinary system. The comparisons show a satisfactory model extension from binary to quaternary and Quinary.

Fluoride Containing Systems

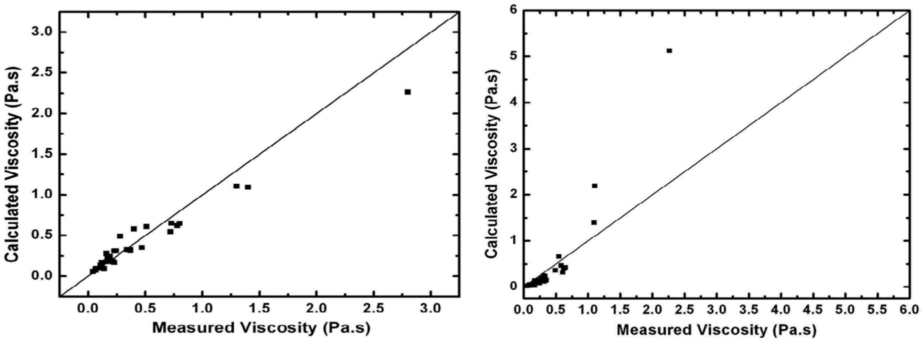
Figure 4(a) shows a comparison of calculated viscosities for CaO-FeO-Al_2O_3-SiO_2-CaF_2 system using Equations (8-a)~ (8-c) in the present model with measured data [14, 15, 16]. The mean deviation Δ defined by Equation (9) was used as a measure of model precision again. The Δ value calculated is as great as ±17.6%. The viscosities calculated using the original Riboud model is shown in Figure 4(b), and produced the mean deviation is as great as 58.4%. Obviously, the present model fits to the measured data much better than the original Riboud model.



(a) Using Present Model: Equations (8-a, b and c)

(b) Using the Original Riboud Model

Figure 4: Comparison between measured and calculated viscosities



(a) Using Present model: Equations (8-a, d and e)

(b) Using the Original Riboud Model

Figure 5: Comparison between Measured and Calculated Viscosities of Mould Fluxes

The comparison of experimental data with model estimated values using the present model (Equations (8-a), (8-d) and (8-e)) for mould fluxes is shown in Figure 5 (a). It can be seen that the present model gives a reasonable estimation. The mean deviation Δ is about 24.4%. The estimated results using the original are shown in Figure 5 (b). The mean deviation is about 42.5%. The mean deviation generated by the present model is much lower than that given by the original Riboud model.

Typical ESR slags usually contain Al_2O_3, CaO, CaF_2 and SiO_2. The CaF_2 content is quite high in slags of this type. The present model has been used to calculate the viscosities of ESR slags [10]. The experimental data used were taken from Reference [23]. The present model has shown a reasonable viscosity estimation of ESR slags, while the original Riboud model provides too low values.

DISCUSSION

In the present model for non-fluoride containing melts, the effects of different MO on the composition of three types of oxygen are neglected. According to reference [6], the composition of non-bridging oxygen follows the order: CaO> MgO >MnO>FeO. If effects of different MO on the composition of three types of oxygen are the dominant factor to the viscosity of the binaries, the viscosity order of MO-SiO_2 systems at the same temperature and composition would be FeO>MnO>MgO> CaO. However, it is not the case for silicate melts of industrial interest. The viscosity order of MgO >CaO> MnO has been proposed [6] when the content of MO is relatively high (X_{MO}> 0.55). Therefore, the effects of different MO on the composition of three types of oxygen ions should not be regarded as a dominant factor in the viscosity of industrial silicate melts. This indicates reasonability of the simplification proposed in the present model.

One may see in Table 1 that $E_{MO\cdot SiO_2}$ follows the order of MgO>CaO>MnO>FeO when X_{MO}>0.67, which is the same as that of the viscosity. This agreement indicates that the present model can represent the effect of different cations on the viscosity of the melts properly.

The viscous activation energy is considered to be the energy required for breaking the bonds necessary for viscous flow, so the $E_{MO\cdot SiO_2}$ should be determined by the strength of M-O-Si bonds. The molten point of an oxide is considered as an indication of the strength of M-O bonds. It is known that melting points of MO follow the order as MgO>CaO>MnO>FeO. The order of $E_{MO\cdot SiO_2}$ is the same as that for the melting points.

The mean deviations of the present two models for the slag systems are around 20%, which is introduced from the high temperature viscosity measurements. Accordingly, it is shown that the present models can provide accurate estimation for viscosities of silicate slags. Since the present models have relatively simple form and a better accuracy, it can be conveniently applied to viscosity estimation for industrial slags.

CONCLUSIONS

A simple model for non-fluoride containing multi- component silicate melts has been proposed based on the equation of Erying's absolute-rate theory with structure consideration regarding bridge, non-bridge and free oxygen. The viscous activation energy has been considered from contributions of these three types of oxygen. The model has been extended up to CaO-MgO-FeO-MnO-SiO_2 system, and has shown reasonable agreements with the corresponding measured values. For fluoride-containing silicate melts, the model by Riboud *et al.* $\eta = A \cdot T \exp(\frac{B}{T})$ was modified using new expressions for A and B with new sets of parameters optimized from recently published experimental viscosity data. The model application has shown a more suitability then the original Riboud model for estimating the viscosities for CaO-FeO-Al_2O_3-SiO_2-CaF_2 melt.

REFERENCES

Eyring, H. (1936). *Viscosity, Plasticity, and Diffusion as Example of Absolute Reaction Rates*. J.Chem.Phys., Vol. 4(2), pp. 283-291. [1]

Du, S., Bygden, J. & Seetharaman, S. (1994). *A Model for Estimation of Viscosities of Complex Metallic and Ionic Melts*. Metall. *Materials*. Trans.B, Vol. 25B(1), pp. 1-7. [2]

Mills, K. C. (1993). *The Influence of Structure on the Physico-chemical Properties of Slags*. ISIJ International, 33(1), pp. 148-155. [3]

Weymann, H. D. (1954). *Theoretical and Experimental Investigations of the Position-change Theory of Viscous Liquids*. Kolloid-Zrits., Vol. 138(1), pp. 41-56. [4]

Bockris, J. O'M. & Reddy A. K. N. (1970). *Modern Electrochemistry*. Vol. 1, Plenum Press, New York, U.S. A., 1970, pp. 574-576. [5]

Zhang, L. & Jahanshahi, S. (1998). *Review and Modeling of Viscosity of Silicate Melts: Part I. Viscosity of Binary and Ternary Silicates Containing CaO, MgO, and MnO. Metall*. Materials. Trans.B, Vol. 29B(1), pp. 177-186. [6]

Riboud, P. V., Roux, Y., Lucas, D. & Gayes, H. (1981). *Improvement of Continuous Casting Powders*. Fachber Huttenprax Metallweiterverarb, Vol. 19(8), pp. 859-869. [7]

Urbain, G. & Boiret, M. (1990). *Viscosity of Liquid Silicates. Ironmaking and Steelmaking*, Vol. 17(4), pp. 255-260. [8]

Iida, T. I, Sakai, H., Kita, Y. & Shigano, K. (2000). *An Equation for Accurate Prediction of the Viscosities of Blast Furnace Type Slags from Chemical Composition*. ISIJ International, Vol. 40 (suppl), S110-S11 4. [9]

Shu, Q. F. & Zhang, J. Y. (2005). *Viscosity Estimation for Slags Containing Calcium Fluoride. J. University of Science and Technology Beijing*, Vol. 12 (3), pp. 221-224. [10]

Seetharaman, S. & Du, S. (1994). *Estimation of the Viscosities of Binary Metallic Melts Using Gibbs Energy of Mixing*. Metall. Materials Trans. B, 1994, 25B (4): pp. 589-595. [11]

Chou, K. C., Zhong, X. M. & Xu, K. D. (2004). *Calculation of Physicochemical Properties in a Ternary System with Miscibility Gap*. Materials Trans. B, Vol.35 B(5), pp. 715-720. [12]

Fincham, C. J. B. & Richardson, F. D. (1954). *The Behavior of Sulphur in Silicate and Aluminate Melts*. Proc. Roy. Soc., Vol. 233(1), pp. 40-62. [13]

Shahbazian, F., Sichen, D. & Seetharaman, S. (1999). *Viscosities of some Fayalitic Slags Containing CaF_2*. ISIJ International, Vol. 39(7), pp. 687-696. [14]

Shahbazian, F. (2001). E*xperimental Studies of the Viscosities in the CaO-FeO-SiO_2-CaF_2 Slags*. Scan. J. Metallurgy, Vol. 30 (5), pp. 302-308. [15]

Shahbazian, F., Sichen, D. & Seetharaman, S. (2002). *The Effect of Addition of Al_2O_3 on the Viscosity of CaO –FeO-SiO_2–CaF_2 slags*. ISIJ International, Vol. 42(2), pp. 155-162. [16]

Mills, K. C. & Sridhar, S. (1999). *Viscosity of Ironmaking and Steelmaking Slags*. Ironmaking and Steelmaking, Vol. 26(4), pp. 262-268. [17]

McCauley, W. L. & Apelian, A. (1980). *Viscosity Characterestics of Continuos Casting Mold Fluxes*. Can. Metall. Q., Vol. 20(2), pp. 247- 262. [18]

Ji, F. Z., Du, S. & Seetharaman, S. (1997). *Experimental Studies of the Viscosity in the CaO –Fe_nO-SiO_2 Slags*. Metall. Materials Trans. B, 28B(4), pp. 827-834. [19]

Shiraishi, Y., Ikeda, K. & Tamura, A. (1978). *On the Viscosity and Density of the Molten FeO-SiO_2 System*. Trans. JIM, vol.19(5), pp. 264-274. [20]

Ji, F. Z. (2001). *Experimental Studies of the Viscosities in CaO-MnO-SiO_2 and CaO-Fe_nO-MnO-SiO_2 Slags*. Metall. Materials Trans. B, vol.32(1), pp. 181-186. [21]

Ji, F. Z., Du, S. & Seetharaman, S. (1999). *Viscosities of Multicomponent Silicate Melts at High Temperatures*. International Journal of Thermophysics, vol. 20(1), pp. 309-323. [22]

Mills, K. C. & Keene, B. J. (1981). *Physico-chemical Properties of Molten CaF_2 - based Slags*. International Metals Reviews, vol. 26(1), pp. 21-69. [23]