A MODEL AND DATABASE FOR THE VISCOSITY OF MOLTEN SLAGS

Sergei Decterov, Nicholas Grundy & Arthur Pelton
École Polytechnique, Canada

ABSTRACT

A new model for the viscosity of slags has been developed. In this model the viscosity is related to the structure of the melt, and the structure in turn is calculated from the thermodynamic description of the melt using the Modified Quasichemical Model. For the binary systems the model requires very few optimized parameters, which is all the more remarkable as the viscosity of silicate slags spans over 20 orders of magnitude as a function of composition. Ternary and higher-order systems without Al_2O_3 *are predicted from the binary parameters within experimental uncertainty without additional model parameters.*

A viscosity maximum arises in ternary systems containing Al_2O_3 *due to the so-called "charge compensation effect" when* Al^{3+} *cations assume tetrahedral coordination and enter the silica network, while the additional negative charge resulting from the fourth oxygen is compensated by the presence of a second cation, such as* Na^+*, in the vicinity of* Al^{3+}*. The viscosity of the multicomponent systems containing* Al_2O_3 *is modeled by assuming that the charge compensated tetrahedral Al has the same effect on the viscosity as Si. The model quantitatively predicts not only the viscosity maximum but also the complex shape of the curves of viscosity versus composition and temperature in ternary systems containing* Al_2O_3 *with only 2 temperature-independent ternary parameters.*

The viscosities of quaternary and higher-order systems are predicted from the binary and ternary subsystems without introducing any additional model parameters. The model has successfully been applied to melts in the multicomponent Na_2O-K_2O-MgO-CaO-MnO-FeO-ZnO-PbO-Al_2O_3-SiO_2 *system.*

INTRODUCTION

The ability to predict slag viscosities accurately is of interest in many industrial areas such as iron, steel and non-ferrous metal production, glassmaking, enamels, coal combustion and gasification, waste disposal, geological magmas, *etc*.

Most systems of technological and scientific interest are multicomponent systems. Estimating the viscosity for a given composition can be virtually impossible using only the available experimental data because of the complex way in which the viscosity varies as a function of composition. The only solution to this dilemma is to develop a model that reliably interpolates and extrapolates to regions where no experimental data are available. Furthermore, a reliable model can help to identify sets of data that are incompatible with other sets of data. What makes the modeling of the viscosity of silicate melts particularly challenging is that it increases by over twenty orders of magnitude at a constant temperature on increasing the SiO_2 content. The reason for this increase is rooted in the structure of silicate melts. A successful viscosity model must therefore take into account the structural changes taking place in the silicate liquid as a function of composition and temperature.

Over the past several years, through critical evaluation of all available thermodynamic and phase equilibrium data, we have developed a quantitative thermodynamic description of multicomponent oxide melts using the Modified Quasichemical Model for short-range ordering. From the resultant database the local structure of the liquid, in terms of the bridging behavior of oxygen as a function of composition and temperature, can be calculated. The structural description of the liquid can be refined by calculating the concentration of structural units, the so-called Q-species, based on the bridging behavior using some simplifying assumptions. The concentrations of Q-species calculated in this manner correspond reasonably well with the experimentally determined concentrations.

We have developed a new model which relates the viscosity to the concentrations of Q-species in silicate melts. The model requires very few optimized parameters. In the present article, the model is outlined and a few examples are given for the description of the viscosity in the Al_2O_3-CaO-MgO-Na_2O-SiO_2 system.

VISCOSITY MODEL

Pure Components

The viscosity η as a function of temperature is given by a simple Arrhenius Equation $\eta = A'\exp[-E'/(RT)]$ with pre-exponential factor A' and activation energy E'. It is equivalent to

$$\ln(\eta) = A + \frac{E}{RT} \tag{1}$$

where $A = \text{In}\,(A')$ and $E = -E'$. If there are experimental data available for a pure molten oxide, the parameters A and E are fitted to the experimental data and are kept fixed when optimizing multicomponent systems. If there are no experimental data available, the viscosities of the pure components are optimized using extrapolated binary viscosity data. Figures 1 and 2 compare the calculated viscosity of pure SiO_2 and Al_2O_3 to experimental data. It is seen that the Arrhenius law is very well obeyed.

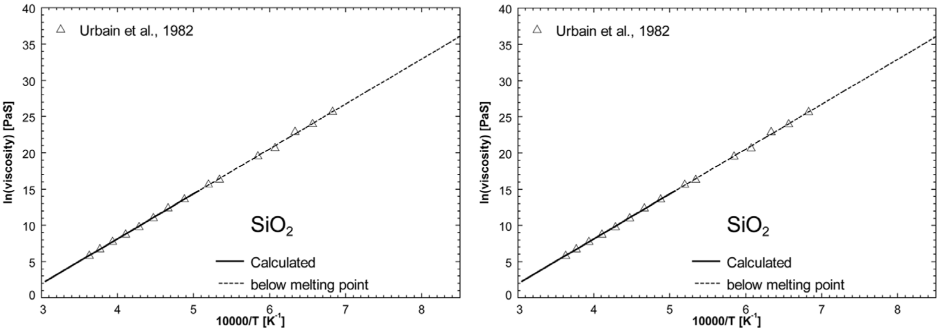

Figure 1: Calculated viscosity of pure liquid SiO_2 and Al_2O_3 compared to selected experimental data

Characterization of the Structure of the SiO_2 Network

The structure of the MeO_x-SiO_2 melts is characterized by the bridging behavior of oxygen. An oxygen atom separating a Me-Me pair is a free oxygen, O^{2-}; an oxygen separating a Me-Si pair is a non-bridging oxygen, O^{-}; and an oxygen separating a Si-Si pair is called a bridging oxygen, O^{0}. The silicon atoms in silicate melts are always tetrahedrally bonded to four oxygen ions. Basic silicate melts consist mainly of Me^{n+}, O^{2-} and SiO_4^{4-} ions. As the silica content increases above the orthosilicate composition, the SiO_4^{4-} tetrahedra start to polymerize, forming more and more bridging oxygens, and gradually a three-dimensional network is formed. The structural change taking place upon formation of the SiO_2 network can be characterized by the amounts of so-called Q^{i}-species [13] which are defined as Si atoms linked to *i* bridging oxygens and (4-*i*) non-bridging oxygens. In pure SiO_2 all four oxygens surrounding each Si are bridging oxygens and the fraction of Q^4-species is 1. An isolated SiO_4^{4-} ion is a Q^0-species.

The Modified Quasichemical Model [14], calculates the number of Me-Me, Me-Si and Si-Si second-nearest-neighbor pairs, which correspond to the fractions of free oxygens, broken bridges and bridging oxygens, as functions of temperature and composition. Therefore, the model also gives the average number of bridging oxygens per Si atom. We calculate the fractions of Q^i-species by applying a binomial distribution to the fraction of bridging oxygens per Si. The calculated concentrations of Q^i-species correspond reasonably well with the experimental data obtained from Raman spectroscopy or nuclear magnetic resonance in melts or quenched glasses. We use a similar statistical method to calculate the interconnectivity between Q^4-species that gives the concentrations of clusters of interconnected Si atoms of a certain size. We postulate that a certain critical cluster size can be defined that mimics the formation of a percolating SiO_2 network. When this cluster size is reached the viscosity will increase dramatically. Our analysis of the viscosity data indicates that a group of 40 interconnected Si-Si pairs is a good choice for the critical cluster size. Clusters which contain at least 40 interconnected Si-Si pairs will be termed $Q^{4,40}$. We further define the difference between Q^4 and $Q^{4,40}$ as $Q^{4,R}$, these are clusters of Q^4 - species which consist of less than 40 interconnected Si-Si pairs.

Modeling the Viscosity of MeO_x-SiO_2 Binary Systems

In our model we assume that the viscosity of pure SiO_2 has two contributions. The first, η^*, is the hypothetical viscosity of SiO_2 if it did not form a network. This would correspond to a liquid consisting of only SiO_4^{4-} tetrahedra with no bridging oxygens. The second contribution, η^E, is due to the formation of the SiO_2 network. The sum of the two contributions is equal to the viscosity of pure SiO_2 :

$$\ln\left(\eta_{SiO_2}\right) = \ln\left(\eta^*_{SiO_2}\right) + \ln\left(\eta^E_{SiO_2}\right) = \left(A^*_{SiO_2} + A^E_{SiO_2}\right) + \frac{\left(E^*_{SiO_2} + E^E_{SiO_2}\right)}{RT} \quad (2)$$

If the viscosity of a binary system is given by Equation (1), the pre-exponential factor A and activation energy E become composition dependent:

$$E = X_{MeO_x} E_{MeO_x} + X_{SiO_2} E^*_{SiO_2} + X_{MeO_x} X_{SiO_2} E_{MeO_x-SiO_2} + X_{Q^{4,40}} E^E_{SiO_2} + X_{Q^{4,R}} E^R_{MeO_x-SiO_2} \quad (3)$$

where X_i are mole fractions of various species. In a first approximation the viscosity of basic silicate liquids up to the orthosilicate composition is modeled to vary linearly as the mole fraction. This is represented by the first two terms of Equation (3). The third term is a small excess term to account for slight non-linearities that are observed in the basic region of silicate melts. This is a first binary viscosity parameter. Above the orthosilicate composition, the viscosity increases dramatically due to the formation of the SiO_2 network. We characterize the formation of the network using the $Q^{4,40}$ species and $Q^{4,R}$ species defined above. The influence of $Q^{4,40}$ on the viscosity, i.e., the contribution of big clusters, is assumed to be the same for all systems. The smaller $Q^{4,R}$ clusters will interact more directly with the basic oxide. Their contribution to the viscosity is therefore expected to be system dependent, so the last term is the second binary viscosity parameter we can optimize to model the viscosity. A similar equation is used for the composition dependence of the pre-exponential factor A. However, binary parameters $A_{MeO_X-SiO_2}$ and $A^R_{MeO_X-SiO_2}$ have never been needed to describe the viscosity of any binary system that we have encountered so far. Therefore, these parameters are set equal to zero and only two binary parameters from Equation (3) are used. The mole fractions $X(Q^4)$, $X(Q^{4,40})$ and $X(Q^{4,R})$ calculated at 1600°C using the thermodynamic database are plotted in Figure 2 for the systems $NaO_{0.5}$ - SiO_2 and CaO-SiO_2.

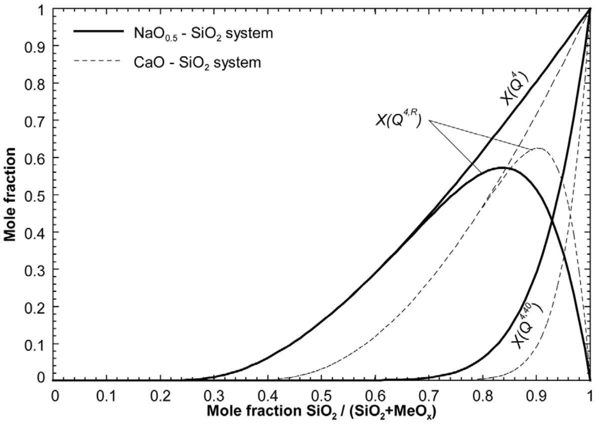

Figure 2: Mole fractions of the species used to model the viscosity

Figures 3 and 4 compare calculated viscosities with selected experimental measurements for the binary Al_2O_3-SiO_2, CaO-SiO_2 and Na_2O-SiO_2 liquids. The dotted lines correspond to calculated viscosities below the liquidus temperature. It can be seen that the composition range for which experimental data are available above the liquidus temperature can be very limited. It is important that the model extrapolates well into regions where the liquid is metastable and no experimental data exist. It can also be seen that the viscosity range that needs to be modeled is vast, covering over 20 orders of magnitude. The calculated viscosity curves reproduce all experimental data within experimental accuracy limits.

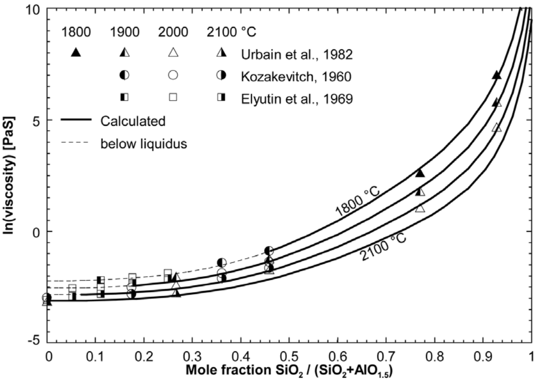

Figure 3: Viscosity of $AlO_{1.5}$-SiO_2 liquids

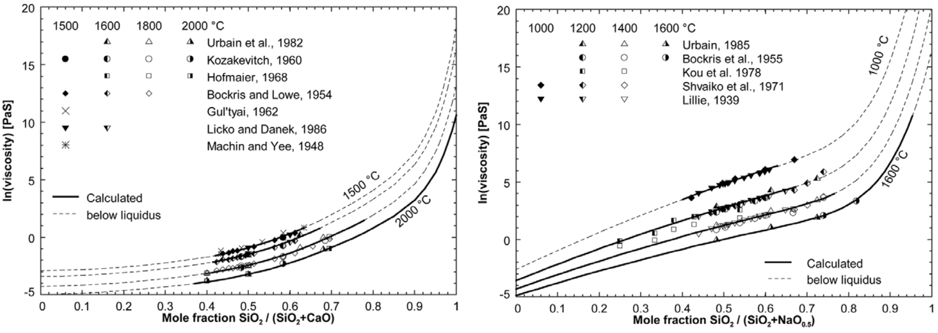

Figure 4: Viscosity of CaO-SiO_2 and $NaO_{0.5}$-SiO_2 liquids

Multicomponent Systems

Analysis of the experimental data shows that ln(η) of multicomponent liquids containing only SiO_2 and basic oxides varies nearly linearly as a function of the mole fractions of the basic oxides MeO_x (CaO, MgO, $NaO_{0.5}$, etc.) at constant SiO_2 mole fraction. Therefore, Equation (3) was generalized for such multicomponent liquids as follows:

$$E = \sum_{\mathrm{Me}} \left(X_{\mathrm{MeO_x}} E_{\mathrm{MeO_x}} + X_{\mathrm{MeO_x}} X_{\mathrm{SiO_2}} E_{\mathrm{MeO_x}-\mathrm{SiO_2}} \right) + X_{\mathrm{SiO_2}} E^{*}_{\mathrm{SiO_2}} + X_{\mathrm{Q}^{4,40}} E^{\mathrm{E}}_{\mathrm{SiO_2}} + X_{Q^{4,R}} \sum_{\mathrm{Me}} \left(\frac{X_{\mathrm{MeO_x}}}{\sum_{\mathrm{Me}} X_{\mathrm{MeO_x}}} E^{R}_{\mathrm{MeO_x}-\mathrm{SiO_2}} \right) \tag{4}$$

A similar equation is used for the pre-exponential factor A. This does not result in an exact linear variation of ln(η) because the mole fractions of clusters $Q^{4,40}$ as $Q^{4,R}$ calculated from the Modified Quasichemical Model do not vary exactly linearly as the ratio of the basic oxides changes. However, the calculated variation is very close to linear. Figure 5 compares the calculated viscosity of the CaO-MgO-SiO_2 slag with selected experimental data. As can be seen from the figure, the model predicts the viscosity of the ternary slag within experimental error limits from the parameters for the CaO-SiO_2 and MgO-SiO_2 binaries without using any additional ternary model parameters.

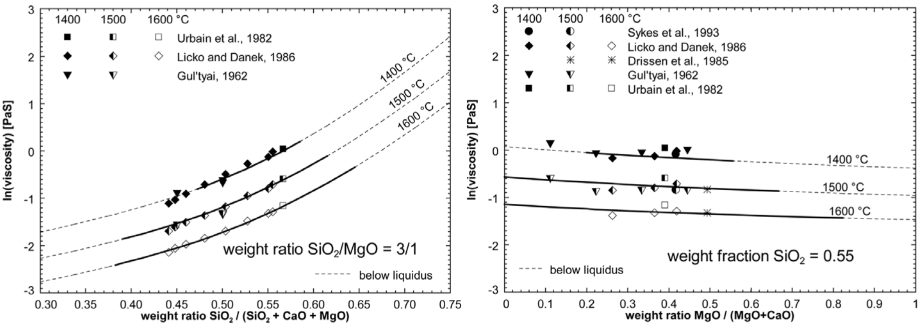

Figure 5: Calculated viscosity of CaO-MgO-SiO_2 liquids compared to experimental data

Viscosity of Systems Showing the Charge Compensation Effect

Al^{3+} ions can behave in profoundly different ways in a silicate melt depending on the overall composition. When added to a pure silica melt, Al_2O_3 acts as a network-modifier, breaking the oxygen bridges of the pure silica network, thereby substantially decreasing the viscosity. On the other hand, when equimolar amounts of MeO or Me_2O and Al_2O_3 are added to SiO_2, some of the Al cations assume tetrahedral coordination and replace Si in the liquid network, so that Al acts as a network-former. The missing charge is compensated by Me ions that stay close to the Al ions. Due to this effect, known as the charge compensation effect [13], there is a maximum in the viscosity when the molar ratio of Al_2O_3 to MeO or Me_2O is unity.

The thermodynamic database of Modified Quasichemical Model parameters, upon which we are basing our viscosity model, does not consider the different structural roles of Al^{3+}, because the thermodynamic properties do not depend strongly on the different structural states. Hence, in order to model the viscosity maximum the amount of network-forming Al^{3+} must be evaluated a *posteriori*. This is done as follows. First, we assume that charge-compensated Al^{3+} in the silica network has the same effect on viscosity as does Si^{4+}. We can then evaluate the amount of network-forming Al^{3+} required to reproduce the experimentally determined viscosity maxima in the various Al-containing systems. The amount of network-forming Al^{3+}, as a function of temperature and composition, may be calculated from the equilibrium constants of the following equilibria between network-forming Al^{3+} associated with charge compensating cations and network-modifying Al^{3+}:

$$AlO_{1.5} + NaO_{0.5} \rightleftharpoons NaAlO_2 \qquad (5)$$

$$2AlO_{1.5} + CaO \rightleftharpoons CaAl_2O_4 \qquad (6)$$

The concentrations of the associates ($NaAlO_2$, $1/2CaAl_2O_4$ and $1/2MgAl_2O_4$) correspond to the concentration of network-forming Al^{3+} while the concentration of $AlO_{1.5}$ corresponds to the concentration of network-modifying Al^{3+}. The network-forming Al^{3+} is assumed to have the same effect on viscosity as does Si^{4+}. The viscosity of Al-containing systems is then calculated from Equations (1) and (3) simply by changing the molar fractions of components: the Si content is increased by the amount of associates calculated from Equations (5) and (6), while the $AlO_{1.5}$ and MeO_x contents are decreased by the corresponding amounts. The model parameters are the Gibbs energies of reactions (5) and (6). These Gibbs energies are not dependent on temperature, but are found to vary linearly as a function of SiO_2 content, becoming more negative at higher SiO_2 concentrations. Hence, only two parameters are required to model the charge compensation effect in each ternary system MeO_x-Al_2O_3-SiO_2 (including the limiting MeO_x-Al_2O_3 binary systems).

Figure 6 compares the calculated viscosity to the experimental data at constant SiO_2 contents for the systems CaO-Al_2O_3-SiO_2 and Na_2O-Al_2O_3-SiO_2. Na is a very effective charge compensator meaning that ΔG for reaction (5) is very negative and most of the Al enters the network leading to a sharp viscosity maximum. Ca is less effective, resulting in a less negative *ΔG* for reaction (6) leading to less of the Al acting as network-former and a less pronounced viscosity maximum.

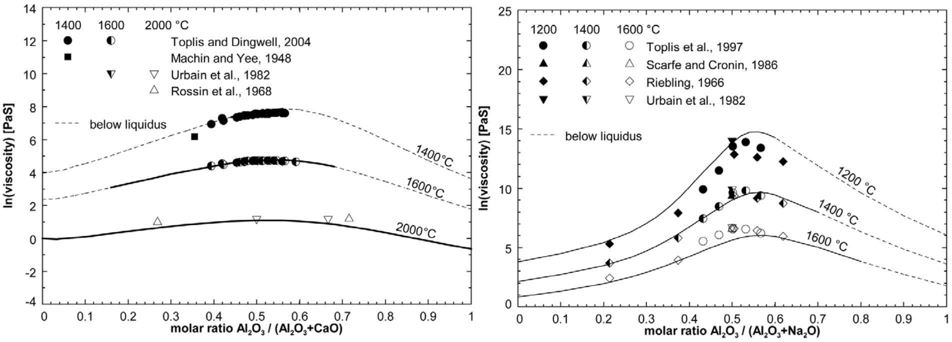

Figure 6: Viscosity of CaO-Al_2O_3-SiO_2 and Na_2O-Al_2O_3-SiO_2 liquids at $X(SiO_2) = 0.75$

In these two systems the experimental data show that the viscosity maximum is not exactly at the 1:1 composition and curves can have different shapes depending on the system. The experiments also show that the temperature dependence of the viscosity changes depending on the Al_2O_3 /(Al_2O_3+MeO_x) ratio. The model reproduces the asymmetry, the shape and also the temperature dependence of the viscosity accurately, even though the two model parameters used to describe this effect depend neither on temperature nor on the Al_2O_3 /(Al_2O_3+MeO_x) ratio, again indicating that the model truly reflects the structural changes taking place in the liquid that cause the viscosity maximum.

The predictive ability of the model can only be tested by comparing the viscosity data for multicomponent systems with the viscosities calculated from the model parameters which were obtained by fitting the viscosities of binary slags and ternary Al_2O_3-containing systems. Such a comparison is shown in Figure 7 for the Al_2O_3-CaO-MgO-SiO_2 and Al_2O_3-CaO-MgO-Na_2O-SiO_2 systems. The former system is of particular importance since many steelmaking slags consist mainly of these four components. The viscosity is calculated at 1500°C, 50 wt% SiO_2 and various MgO contents The diopside-albite ($CaMgSi_2O_6$-$NaAlSi_3O_6$) join is one of the rare examples where systematic experiments are available along a well-defined isopleth through the five -component system. As can be seen from Figure 7, our model correctly predicts the experimental viscosities within the uncertainties of the experimental data.

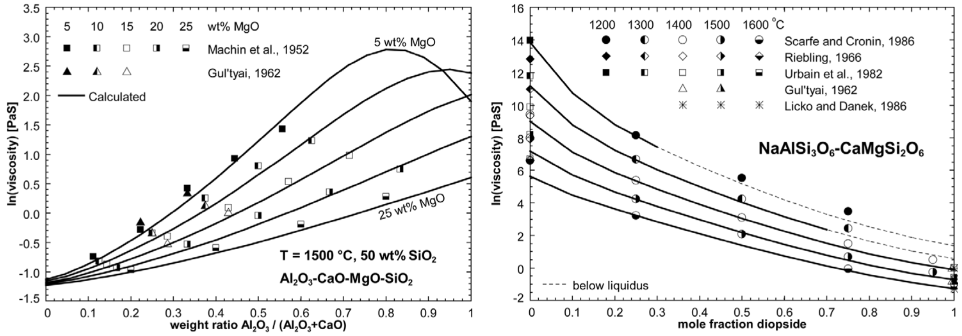

Figure 7: Viscosity of multicomponent slags predicted by the model and compared to experimental data

CONCLUSIONS

In conclusion we find that there is a surprisingly simple link between the structure and the viscosity of multicomponent silicate liquids allowing the development of a simple model to accurately reproduce experimental viscosity data and reliably predict the viscosity at compositions where no experimental data are available. The database of model parameters has been developed for the Na_2O-K_2O-MgO-CaO-MnO-FeO-ZnO-PbO-Al_2O_3-SiO_2 system and more components are currently being added.

ACKNOWLEDGEMENTS

Financial assistance from the Natural Sciences and Engineering Research Council of Canada through a CRD grant in collaboration with POSCO Steel, Rio Tinto, Dupont, INCO and TeckCominco is gratefully acknowledged.

REFERENCES

Bockris, J. O. & Lowe, D. C. (1954). *Viscosity and the Structure of Molten Silicates*. Proc. Roy. Soc. London, Ser. A, Vol. A226, pp. 423-435. [1]

Bockris, J. O. M., Mackenzie, J. D. & Kitchener, J. A. (1955). V*iscous Flow in Silica and Binary Liquid Silicates*. Trans. Faraday Soc., Vol. 51 (12), pp. 1734-1748. [2]

Drissen, P., Engell, H. J. & Janke, D. (1984). *Viscosity of Steelmaking Slags at Elevated Magnesia Content*. Proc. 2nd Int. Symp. on Metall. Slags Fluxes, Metall. Soc. AIME, Warrendale, Pa, pp. 583-592. [3]

Elyutin, V. P., Kostikov, V. I., Mitin, B. S. & Nagibin, Yu. A. (1969). *Measurement of the Viscosity of Aluminum Oxide*. Zhurnal Fizicheskoi Khimii, Vol. 43 (3), pp. 579-583. [4]

Gul'tyai, I. I. (1962). E*ffect of Al_2O_3 on the Viscosity of Slags of the System CaO-MgO-SiO_2*. Izv. Akad. Nauk SSSR, Otd. Tekhn. Nauk, Metall. Toplivo, Vol. 5, pp. 52-65. [5]

Hofmaier, G. (1968). V*iscosity and Structure of Liquid Silicates*. Berg- und Huettenmaennische Monatshefte, Vol. 113 (7), pp. 270-281. [6]

Kou T., Mizoguchi, K. & Suginohara, Y. (1978). *The Effect of Al_2O_3 on the Viscosity of Silicate Melts*. Nippon Kinzoku Gakkaishi, Vol. 42 (8), pp. 775-781. [7]

Kozakevitch, P. (1960). *Viscosité et Éléments Structuraux des Aluminosilicates Fondus: Laitiers CaO-Al_2O_3-SiO_2 entre 1600 et 2100 ºC*. Rev. Métall., Vol. 57, pp. 149-160. [8]

Licko, T. & Danek, V. (1986). *Viscosity and Structure of Melts in the System CaO-MgO-SiO_2*. Phys. Chem. Glasses, vol. 27 (1), pp. 22-26. [9]

Lillie. H.R. (1939). *High-Temperature Viscosities of Soda-Silica Glasses*. J. Am. Ceram. Soc., Vol. 22, pp. 367-374. [10]

Machin, J. S. & Yee, T. B. (1948). *Viscosity Studies of System CaO-MgO-Al_2O_3-SiO_2: II, CaO-Al_2O_3-SiO_2*. J. Am. Ceram. Soc., Vol. 31 (7), pp. 200-204. [11]

Machin, J. S., Yee, T. B. & Hanna, D. L. (1952). *Viscosity Studies of System CaO-MgO-Al_2O_3-SiO_2: III, 35, 45, and 50 % SiO_2*. J. Am. Ceram. Soc., vol. 35 (12), pp. 322-325. [12]

Mysen, B. (2003). *Physics and Chemistry of Silicate Glasses and Melts*. Eur. J. Mineral., Vol. 15 (5), pp. 781-802. [13]

Pelton, A. D. & Blander, M. (1986). *Thermodynamic Analysis of Ordered Liquid Solutions by a Modified Quasi-Chemical Approach*. Application to Silicate Slags. Metall. Trans. B, Vol. 17B, pp. 805-815. [14]

Riebling, E. F. (1966). *Structure of Sodium Aluminosilicate Melts Containing at least 50 Mole % SiO_2 at 1500°*. J. Chem. Phys., Vol. 44 (8), pp. 2857-2865. [15]

Rossin R., Bersan, J. & Urbain G. (1964). *Viscosity of Liquid Slags Belonging to the Ternary System SiO_2-Al $2O_3$-CaO*. Rev. Hautes Temp. Refractaires, Vol. 1 (2), pp. 159-170. [16]

Scarfe, C. M. & Cronin D. J. (1986). *Viscosity-Temperature Relationships of Melts at 1 atm in the System Diopside-Albite*. Am. Mineral., Vol. 81 (5-6), pp. 767-771. [17]

Shvaiko-Shvaikovskaya, T. P., Mazurin, O. V. & Bashun, Z. S. (1971). *Viscosity of Sodium Oxide-silicon Dioxide System Glasses in Molten State*. Izvestiya Akademii Nauk SSSR, Neorganicheskie Materialy, vol. 7 (1), pp. 128-131. [18]

Sykes, D., Dickinson, J. E.Jr., Luth, R. W. & Scarfe, C. M. (1993). *Viscosity-Temperature Relationships at 1 atm in the System Nepheline-Diopside*. Geochim. Cosmochim. Acta, Vol. 57 (6), pp. 1291-1295. [19]

Toplis, M. J. & Dingwell D. B. (2004). *Shear Viscosities of CaO-Al_2O_3-SiO_2 and MgO-Al_2O_3-SiO_2 Liquids: Implications for the Structural Role of Aluminium and the Degree of Polymerisation of Synthetic and Natural Aluminosilicate Melts*. Geochim. Cosmochim. Acta, Vol. 68 (24), pp. 5169-5188. [20]

Toplis, M. J., Dingwell, D. B. & Lenci, T. (1997). *Peraluminous Viscosity Maxima in Na_2O-Al_2O_3-SiO_2 Liquids: the Role of Triclusters in Tectosilicate Melts*. Geochim. Cosmochim. Acta, Vol. 61 (13), pp. 2605-2612. [21]

Urbain, G. (1982). *Viscosité de l'Alumine Liquide*. Rev. Int. Hautes Tempér. Réfract., Vol. 19 (1), pp. 55-57. [22]

Urbain, G. (1985). *Viscosité de Liquides Silice-Alumine-Oxydes Na et K*. Mesures et Estimations. Rev. Int. Hautes Tempér. Réfract., Vol. 22 (1), pp. 39-45. [23]

Urbain, G., Bottinga, Y. & Richet, P. (1982). *Viscosity of Liquid Silica, Silicates and Alumo-Silicates*. Geochim. Cosmochim. Acta, Vol. 46 (6), pp. 1061-1072. [24]