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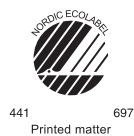
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Publisher School of Chemical Technology**Unit** Department of Materials Science and Engineering**Series** Aalto University publication series SCIENCE + TECHNOLOGY 12/2012**Field of research** Metallurgy**Abstract**

The understanding and optimisation of the metallurgical processes require access to accurate data of the physical properties of slags. Viscosity is one of the most important properties in the case of metallurgical melts, in view of its direct effect on the kinetic conditions of the processes, and is one of the key factors to be taken into consideration in process modeling.

The difficulty and high cost of measuring the viscosity of slags has led to development of number of viscosity models. Most of these models employ parameters extracted from experimental data of viscosity, which ensure the validity of the models in viscosity estimation.

In this report models developed to estimate the viscosity of fully molten oxide slags were discussed. In addition viscosities of converter slags (Basic Oxygen Furnace, Argon-Oxygen Decarburization furnace) predicted with different models were compared.

In the case of BOF-slag the Iida and the modified Urbain models seemed to be more reliable than the other models in predicting the viscosities. The values calculated by KTH model were too high for this high basic slag whereas in the case of NPL model the slag composition was observed to be outside of the working range of the model.

Urbain model modified by Forsbacka as well as the modified Iida models takes account of chromium oxide as a separate component in the calculations and are thus assumed to be more reliable than the other models in predicting viscosities of chromium containing slags. However the reliability of these models is debatable in the case of high chromium containing slags e.g. AOD-slag after oxidising period due to existing of solid phases in the slag.

Iida as well as the Urbain model modified by Forsbacka are also assumed to be reliable predicting viscosity of slag composition corresponding the AOD-slag after reduction period. Also NPL-model seemed to give reliable viscosity values, since in this case the slag composition is inside the working range of the model.

Although there are plenty of experimentally measured viscosity data available for ternary systems, less data in limited ranges are available as the order of the system gets higher. Also lack of experimental data of very basic slag compositions as well as slags containing iron and chromium oxides is apparent. Due to lack of experimental data the performance of these models in predicting viscosities of converter slags was not able to evaluate. Thus more experimental work is necessary to provide the data to test and optimise the models for these very complex slag compositions.

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TABLE OF CONTENTS

1 Introduction.....	6
2 Viscosity.....	7
2.1 Definition	7
2.2 Temperature dependence of viscosity.....	9
2.3 Effect of slag composition on viscosity	10
2.4 Measurement of slag viscosity.....	10
3 Viscosity models for molten slags.....	12
3.1 Urbain Model	13
3.2 Riboud Model.....	17
3.3 Models based on optical basicity (NPL).....	18
3.4 Iida Model	19
3.5 KTH Model.....	22
4 Performance of models in predicting viscosities of industrial slags	25
4.1 BOF slag	25
4.2 AOD slag.....	27
5 Discussion and Conclusions	30
6 References	32

1 Introduction

Slag metallurgy is an essential part of metal manufacturing. Slags are used for refining metal, i.e. dissolving impurity elements from metal (e.g. S) in order to achieve required composition, slags remove detrimental non-metallic inclusions (oxides and sulphides), protect the metal from oxidizing atmosphere and also act as thermal insulation layer on molten metal. Furthermore, slag is often a medium, where reactions take place. The various processes and different purposes in which slags are involved, each obviously demands particular properties of slag, and thus a certain composition.^[1]

The understanding and optimisation of the metallurgical processes require access to accurate data of the physical properties of slags. Viscosity is one of the most important physical property of slag, in view of its direct effect on the kinetic conditions of the processes. The transport of mass and heat, the solubility of slag formers and additions, the separation of metal and slag are improved by the low viscosities. But on the other hand a low viscosity of aggressive slags increases the corrosion of the refractory material of metallurgical vessels.^[2,3]

The significance of slag viscosities in many metallurgical processes involving production, refining and casting, in the area of ironmaking and steelmaking as well as nonferrous metallurgy has long been recognised. Viscosity of molten slag is related to internal structure of oxide melt, and very sensitive to the changes of temperature, slag composition and oxygen partial pressure ^[4].

Generally, slag viscosity has difficulty in being precisely measured, and predicted by empirical methods. Viscosity measurements are also very expensive to perform. Therefore, the development of a reliable viscosity model has been required to accurately and reasonably estimate slag viscosities over whole composition range for multicomponent oxide systems through the structural features of oxide melts.^[4]

Viscosities for molten oxide slags systems have been extensively studied and many models have been developed. This report provides an overview of different viscosity models developed to estimate the viscosity of fully molten oxide slags. In addition the performance of these models in predicting viscosities of some industrial slags will be compared.

2 Viscosity

2.1 Definition

Viscosity (η) is a measure of the internal friction of a fluid. This friction becomes apparent when a layer of a fluid is made to move in relation to another layer (Figure 1).

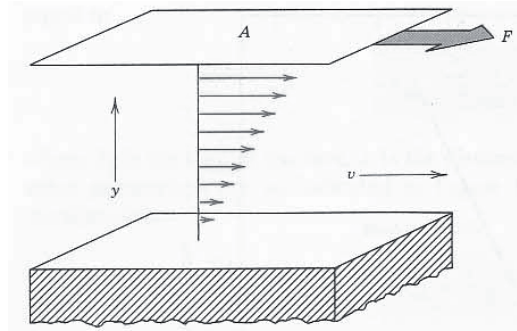


Figure 1. Representation of the viscous flow of a liquid in response to an applied shear force [5].

The greater the friction, the greater amount of force required to cause this movement.[5]

$$\eta = \frac{F/A}{\frac{dv}{dy}} = \frac{\tau}{\frac{dv}{dy}} \quad (1)$$

The term F/A indicates the force per unit area required to produce shearing action “shear stress (τ)” and dv/dy is a measure of the change of speed at which the intermediate layers move with respect to each other and is called “shear rate”.

$$\eta = \frac{\text{shear stress}}{\text{shear rate}} \quad (2)$$

The SI-unit for this dynamic viscosity is $Pa \cdot s$ ($Nm^{-2}s$). A common non-SI unit is P (poise), equal to $0.1 Pa \cdot s$.

In many scenarios, it is practical to use a quantity called the kinematic viscosity ν , which is dynamic viscosity divided by density ($\nu = \eta/\rho$). The SI-unit for kinematic viscosity is m^2s^{-1} , and a common non-SI unit is St (stoke), equal to $0.0001 m^2s^{-1}$.

Most metallic melts and molten slags are Newtonian fluids where the viscosities are independent of the shear rate, and thus the viscosity is defined according to Newton's law as the proportionality constant between the shear stress and the velocity gradient normal to the shear stress (Figure 2) [6, 7].

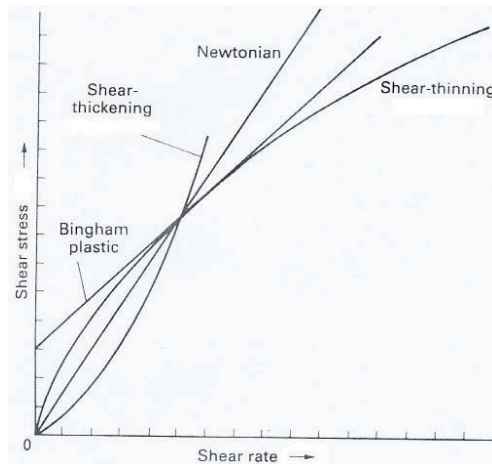


Figure 2. Shear stress - shear rate behaviour of Newtonian and non-Newtonian fluids.[7]

Non-Newtonian fluids exhibit a more complicated relationship between shear stress and velocity gradient than simple linearity. There are several types of non-Newtonian flow behavior, characterised by the way a fluid's viscosity changes in response to variations in shear rate[7]:

Pseudoplastic

This type of fluid will display a decreasing viscosity with an increasing shear rate. This type of flow behavior is sometimes called *shear thinning*.

Dilatant

Increasing viscosity with an increase in shear rate characterises the dilatant fluid. Dilatancy is also referred to as *shear thickening* flow behavior.

Plastic

This type of fluid will behave as a solid under static conditions. A certain amount of force must be applied to the fluid before any flow is induced; this force is called the *yield value*. Once the yield value is exceeded and flow begins, plastic fluids may display Newtonian, pseudoplastic, or dilatant flow characteristics.

Both Newtonian and non-Newtonian behavior has been observed in slag systems. Non-Newtonian behavior is complex and can involve pseudoplastic flow of the fluids. Newtonian behavior has been reported to occur in slag systems containing less than 10–40 vol.% solids. The viscosity behavior of slags containing a high volume percentage of solids has been found to be more accurately described as Bingham plastics.[8]

2.2 Temperature dependence of viscosity

Viscosity of molten slag is related to internal structure of oxide melt, and very sensitive to the changes of temperature and slag composition. The temperature dependence of the viscosity (η) is usually expressed in the forms of the Arrhenius relationship [9]:

$$\eta = A_A \cdot e^{\frac{E_A}{RT}} \quad (3)$$

where A_A is the pre-exponential factor, R is the gas constant, E_A the activation energy and T temperature (K).

However, molten slags are made up of discrete ionic structural units and their activation energy is closely related to the type of ions and ionic complexes present as well as the interionic forces they give rise to. Since types and sizes of ions change with temperature, the activation energy changes with temperature. In order to account for this change, the Wayman-Frankel relationship is sometimes used [6]:

$$\eta = A_W T \cdot e^{\frac{E_W}{RT}} \quad (4)$$

where A_W and E_W are similar to the A_A and E_A parameters in equation (3) but will have different values. In many cases this relationship has been found to give better agreement with experimntal data than can be achieved using th Arrhenius expression (Eq. 3) [5].

Since increased temperature loosens up the structure, the viscosity will deacresae with increasing temperature. Usually viscosity is exponentially proportional to inverse temperature; however at a certain temperature, very small changes in temperature can result in large changes in viscosity. This temperature is called a temperature of critical viscosity (T_{cv} , Figure 3). The nature of a such phenomenon is related to the crystallization of the solid phase from the melt, which in turn, affects the slag viscosity behaviour.[10]

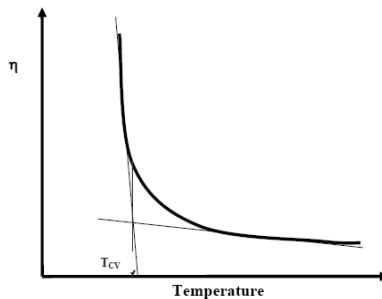


Figure 3. Schematic diagram of the definition of Temperature of critical viscosity (T_{cv}).[10]

2.3 Effect of slag composition on viscosity

As the slags are ionic in nature and as the extent of polymerisation varies with the metal oxide contents in the slag, it can be surmised that the viscosities of slags are extremely sensitive to the size of ions as well as to the electrostatic interactions, and thereby to the structure of slags. [11]

The slag systems in metallurgical process often involve numerous components. The oxides usually found in steel slags are Al_2O_3 , CaO , Cr_2O_3 , MgO , MnO , and SiO_2 , as well as Fe_nO . Most of these oxides are also important components in the slags of nonferrous metals. [12]

Network formers such as SiO_2 , P_2O_5 and B_2O_3 possess strong, highly covalent metal-oxygen bonds, leading to high liquid viscosities. With addition of alkali and alkali earth oxides, Li_2O , Na_2O , K_2O , MgO , CaO , as well as other two-valent oxides like MnO and FeO , the network breaks down and, consequently, the viscosity decreases gradually. The magnitude of the effect is strongly dependent on the components and their proportions present in the slag. Amphoteric oxides, like Al_2O_3 , Fe_2O_3 , may act either network former or breaker following the composition of the slag. [8, 11, 13]

In the case of transition metals (e.g. Fe, Cr) it is important to know the oxidation state (Fe^{2+} or Fe^{3+} , Cr^{2+} or Cr^{3+}) since they have different effect on the viscosity. The oxidation states depend critically on oxygen partial pressure, temperature and bulk composition of the slag, and any of these changes can lead to significant changes in phase equilibria and to variations of the slag viscosity. [8, 14]

2.4 Measurement of slag viscosity

Knowledge on viscosity of molten oxide slag has been of a significant importance in various kinds of metallurgical processes for metal production. A wide range of techniques has, over the years, been developed to measure the viscosity of various liquids at high temperatures. Due to the high temperatures involved in the determination, the following methods are usually adopted: the capillary method, the falling body method, the oscillating methods, as well as the rotating cylinder method [11]. The methods used for measuring viscosities of slags, glasses and fluxes are summarised in Table 1. Detailed descriptions of different methods can be found for example in reference [9].

Table 1. Methods used for measuring viscosities of slags, glasses and fluxes.^[9]

Viscometer	Measurement	Range, Pa-s	Comment
Rotating crucible	Torque measured on static bob	10 ¹ -10 ⁻²	Needs very accurate vertical alignment
Rotating bob	Torque measured on bob—several companies make viscometers	10 ⁰ -10 ²	Alignment problems overcome using flexible joint
Falling body	Time for bob to fall (or drag) through known distance	10 ^{0.5} -10 ⁵	Needs a long, uniform hot zone
Oscillating plate	Amplitude of plate in sample and air	10 ^{-1.5} -10 ¹	Need melt density value
Oscillating viscometer	Measures log decrement of amplitude of twisting	10 ⁻⁴ -10 ⁻¹	1. Need melt density value 2. Roscoe Equation recommended
Shiraishi	Rotating plate-torque	10 ² -10 ¹¹	
	Parallel plate-sample height-time		
	Indentation rate of penetration		
SLS	Damping of scattered waves on surface ('ripples')	10 ⁵ -0.5	Also measures surface tension

The most popular method of measuring slag viscosities is the concentric cylinder method, which consists of centrally - aligned bob in a cylindrical crucible ^[9]. The method can be operated by measuring the torque when rotating either the bob or the crucible; the rotating bob method tends to be more popular because of ease of operation. Rotation speed is determined by the viscosity and torque measured and it is usual to make measurements at least two different speeds to ensure the flow is Newtonian. Falling sphere and capillary viscometers have been used for slags but tend to be difficult to operate at high temperatures because of the need for a large zone of uniform temperature. Oscillating viscometers have been used for measuring de-polymerised slag viscosities ^[9].

As mentioned before viscosity of molten slag is very sensitive to the changes of temperature and slag composition. Hence experimental measurement of slag viscosities at high temperatures is inherently difficult to carry out and the accuracy of the measurements may be influenced by a number of factors. The following three categories of experimental errors may inflect on the accuracy and thereby the reliability of the viscometric evaluations: (i) instrumental factors, (ii) material factors and (iii) hydrodynamic factors. Instrumental factors relate to inadequate temperature control and geometric misalignment within the viscometer. Examples of material factors are inhomogeneities in the liquid due to improper mixing, molecular degradation, solvent evaporation, phase separation and particle agglomeration. Hydrodynamic factors involve flow instabilities, secondary flows, end effects and transient effects due to fluid elasticity. Any one, or a combination of, these factors can lead to significant errors and corresponding misinterpretation of the executed data. The uncertainty in the measurements for many slags is ca. $\pm 20\%$. The very best viscosity measurements are probably subject to an uncertainty of ca. $\pm 10\%$. ^[11, 15].

Knowledge of viscosities is of immense important in the modeling of high temperature processes. Before accepting and using experimentally-determined viscosities a careful and systematic analysis of the experimental results should therefore be carried out in order to identify inaccurate and erroneous measurements, and exclude them from consideration when undertaking optimisation of model parameters ^[14, 16].

A number of compilations and reviews are available that summarise and evaluate the experimental data on slag viscosities published in the literature ^[9, 12, 16, 17].

3 Viscosity models for molten slags

Viscosity of slags is a complex function of the slag composition, temperature and oxygen partial pressure in the system. Slags commonly contain four or more main chemical components that have a complex effect on viscosity. The determination of viscosities of the industrial slags is therefore a complicated task due to large number of variables and can not be solved by means of experimental measurements only.^[18] The difficulty and high cost of measuring the viscosity of slags has led to development of number of viscosity models. Mathematical models can be used to predict the trends in viscosity as a function of the key variables, and so assist in the selection of process conditions and the optimisation of the performance of the system interest. ^[8] An excellent classification of the various models available and their salient features has been presented by Kondratiev et al.^[8] and Mills^[15]. A summary covering most of the published viscosity models suitable for use in metallurgical applications and the particular chemical and metallurgical systems to which they have been applied is given in Table 2.

Table 2. Classification of slag viscosity models.^[8]

Model Type		Name	Chemical Systems	Comments/Validity
Temperature	Composition			
Empirical	Empirical	Sage-McIlroy ¹⁵ Utigard-Warczok ¹⁶ Watt-Fereday ¹⁷ Gupta ¹⁸ Saxen ¹⁹	Coal ash slags "Fayalite-type" slags Coal ash slags Industrial mold fluxes Iron blast furnace slags	Valid only for limited composition-temperature ranges
Empirical	Empirical: Linear (major components)	Bottinga-Weill ²⁰	Binary and ternary alkali and alkali earth-SiO ₂ systems	Validity reported for 1,200–1,800°C and 35–81 mol% SiO ₂ with 470 coefficients
Anhenius	Empirical	Shaw ²¹	Binary and ternary alkali and alkali earth-SiO ₂ systems	
Anhenius	Empirical	S ² ²²	Na ₂ O-K ₂ O-CaO-MgO-FeO-Al ₂ O ₃ -SiO ₂	Valid only for limited composition-temperature ranges
Anhenius	Optical basicity	NPL ²³	Wide range of industrial slags and mold fluxes (Na ₂ O-K ₂ O-CaO-MgO-FeO-MnO-CaF ₂ -Fe ₂ O ₃ -TiO ₂ -Al ₂ O ₃ -SiO ₂)	Optimized using a limited set of experimental data; Requires use of optical basicity data
Weymann-Frenkel	Urbain	Urbain ^{24,25}	(Mg, Ca, Mn)O-Al ₂ O ₃ -SiO ₂ and corresponding binaries + (Ba, Pb, Fe, Sr)O-SiO ₂	Different sets of coefficients for each ternary system
Weymann-Frenkel	Urbain	Riboud ²⁶	Industrial mold fluxes (Na ₂ O-CaO-CaF ₂ -Al ₂ O ₃ -SiO ₂)	Valid only for limited composition-temperature ranges
Weymann-Frenkel	Urbain	Senior-Srinivasachar ²⁷	Coal ash slags (Na ₂ O-K ₂ O-CaO-MgO-FeO-Fe ₂ O ₃ -Al ₂ O ₃ -TiO ₂ -SiO ₂)	Optimized on large set of data, but not valid for whole range of compositions
Weymann-Frenkel	Urbain (+ correction factor)	Streeter ²⁸	Particular set of coal ash slags (Na ₂ O-K ₂ O-CaO-MgO-FeO-TiO ₂ -Al ₂ O ₃ -SiO ₂ -SO ₃)	Valid only for limited composition-temperature ranges
Weymann-Frenkel	Urbain (modified)	Kondratiev-Jak ^{12,13}	CaO-FeO-Al ₂ O ₃ -SiO ₂ at metallic iron saturation	Valid for whole composition range within four-component system
Weymann-Frenkel	Quasi-structural: Cell model	Zhang-Jahanshahi ^{29,30}	CaO-MgO-MnO-FeO-Fe ₂ O ₃ -Al ₂ O ₃ -SiO ₂	Requires use of TD cell model parameters
Bockris-Reddy	Quasi-structural: Atomic pair model	Reddy ³¹	(Ca, Mg, Ba, Sr)O-SiO ₂ + (Na, K) ₂ O-B ₂ O ₃ , Na ₂ O-B ₂ O ₃ -SiO ₂	Yokokawa TD atomic pair model required to calculate the concentrations of bridging O
Quasi-structural: network parameter + basicity index		Iida ³²	Mold fluxes and metallurgical slags	Requires use of basicity index
Eyring	TD: Gibbs free energy of mixing	KTH ^{33,34}	Metallurgical slags	Coefficients are not published
TD: Adam-Gibbs theory	TD: Configurational entropy	Configurational entropy ^{35,36}	General model for silicate systems	Configurational entropy of slag required
TD: Clausius-Clapeyron	Empirical	McCaulley-Apelian ³⁷	Industrial slags (Na ₂ O-K ₂ O-CaO-MgO-FeO-MnO-ZrO ₂ -CaF ₂ -Al ₂ O ₃ -B ₂ O ₃ -SiO ₂)	Valid only for limited composition-temperature ranges

The early-stage models were empirical, using limited experimental data to obtain the model parameters. A number of viscosity models use of the well-known Arrhenius equation (Eq. 3) to describe the temperature dependence of silicate viscosity. However, the compositional dependencies of the models are still fully empirical. More advanced viscosity models introduce a more fundamental physicochemical basis into the viscosity description. For example, the NPL model also uses the Arrhenius equation for temperature dependence of slag viscosity, but links the compositional dependence to the corrected optical basicity of the slag, which in turn can be obtained from experimental data or estimated. Many viscosity models are based on the Weymann-Frenkel kinetic theory of liquids (Eq. 4). In many cases, these models have been found to give better agreement with experimental data than can be achieved using the Arrhenius expression. The quasi-structural models have been developed to take into account the complex internal structures of molten slags. Thermodynamically based viscosity models have been developed using a number of very different approaches.^[8, 19] In recent years, the capabilities of commercial thermodynamic software packages have expanded from the estimation of thermodynamic properties to the estimation of parameters to represent the slag structure and which lead to the calculation of slag densities and viscosities^[20].

In this report models based on fully liquid $\text{Al}_2\text{O}_3\text{-CaO-MgO-SiO}_2$ system have been considered since it is a key slag system for ironmaking and ferroalloys production.

3.1 Urbain Model

The Urbain formalism is one of the most widely used slag viscosity models. The model is based on $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system and in the model the slag constituents are classified into three categories: glass formers (X_G); modifiers (X_M) and amphoteric (X_A)^[9, 20-22].

$$X_G = X_{\text{SiO}_2} + X_{\text{P}_2\text{O}_5} \quad (5)$$

$$X_M = X_{\text{CaO}} + X_{\text{MgO}} + X_{\text{FeO}} + X_{\text{MnO}} + X_{\text{CrO}} + X_{\text{NiO}} + X_{\text{Na}_2\text{O}} + X_{\text{K}_2\text{O}} + X_{\text{Li}_2\text{O}} + 2X_{\text{TiO}_2} + 2X_{\text{ZrO}_2} + 3X_{\text{CaF}_2} \quad (6)$$

$$X_A = X_{\text{Al}_2\text{O}_3} + X_{\text{Fe}_2\text{O}_3} + X_{\text{B}_2\text{O}_3} + X_{\text{Cr}_2\text{O}_3} \quad (7)$$

The Urbain model works predominantly on basis of M_xO so this creates extra ions and it is necessary to normalise X_G , X_M and X_A by dividing them by term $(1 + X_{\text{CaF}_2} + X_{\text{TiO}_2} + X_{\text{ZrO}_2})$ to give X_G^* , X_M^* and X_A^* .^[9]

The model assumes Weymann-Frenkel relation^[22]:

$$\eta(P) = AT \exp\left[\frac{1000B}{T}\right]; -\ln A = mB + n, \quad (8)$$

where A and B are compositionally dependent parameters whereas m and n are empirical parameters.

Urbain found that A and B were linked through the equation ^[22]

$$-\ln A = 0.29B + 11.57 \quad (9)$$

The parameter B can be expressed by third order polynomial equation (10) where B_0 , B_1 , B_2 and B_3 can be obtained by equations (11) and (12)

$$B = B_0 + B_1 X_G^* + B_2 (X_G^*)^2 + B_3 (X_G^*)^3 \quad (10)$$

$$B_i = a_i + b_i \alpha + c_i \alpha^2 \quad (11)$$

where subscript i can be 0, 1, 2 or 3 and a , b and c are given constants for each case.

$$\alpha = X_M^* / (X_M^* + X_A^*) \quad (12)$$

B_0 , B_1 , B_2 and B_3 can be calculated from the equations listed in Table 3. These parameters are then introduced into equation (10) to calculate B . The parameter A can be calculated by equation (9) and the viscosity of the slag can then be determined by using equation (8).

Table 3. Equations for B-parameters in Urbain model.^[21]

$B_0 = 13.8 + 39.9355 \alpha - 44.049 \alpha^2$
$B_1 = 30.481 - 117.1505 \alpha + 139.9978 \alpha^2$
$B_2 = -40.9429 + 234.0486 \alpha - 300.04 \alpha^2$
$B_3 = 60.7619 - 153.9276 \alpha + 211.1616 \alpha^2$

Urbain modified the model later^[22] to calculate separate B-values for different individual modifiers CaO, MgO and MnO and then the mean B is calculated (Eq. 13). Table 4 shows the parameters a_i , b_i and c_i of equation (11) for three cations.

Table 4. Parameters a_i , b_i and c_i for MgO, CaO and MnO.^[22]

	a_i	b_i			c_i		
i	all	Mg	Ca	Mn	Mg	Ca	Mn
0	13.2	15.9	41.5	20.0	-18.6	-45.0	-25.6
1	30.5	-54.1	-117.2	26	33.0	130.0	-56.0
2	-40.4	138	232.1	-110.3	-112.0	-298.6	186.2
3	60.8	-99.8	-156.4	64.3	97.6	213.6	-104.6

Mills et al.^[20] modified X_{MnO} to represent $X_{MnO} + X_{FeO} + X_{NiO} + X_{CrO} + 0.6(X_{Fe_2O_3} + X_{Cr_2O_3})$

It is assumed that Fe_2O_3 and Cr_2O_3 behave both as network breakers and as amphoteric, where f is the fraction behaving as network modifiers and a value $f = 0.6$ is assumed.^[20]

The global B-value is given by:

$$B_{\text{global}} = \frac{X_{CaO}B_{CaO} + X_{MgO}B_{MgO} + X_{MnO}B_{MnO}}{X_{CaO} + X_{MgO} + X_{MnO}} \quad (13)$$

Modified Urbain model

Kondratiev and Jak^[17] modified the Urbain viscosity model in order to describe viscosities of multi-component slags. The modification has been made by introducing more composition-dependence parameters to describe the viscosity behavior of slags over the whole composition range in the four-component system $SiO_2-Al_2O_3-CaO-FeO$ slag. The model is based on the Weymann-Frenkel equation modified by Urbain (Eq. 8).

According to Kondratiev and Jak^[17] constant values of m and n in Eq. (8) proposed by Urbain^[22] can't provide an accurate description of "experimental" values of A and B over the whole compositional range.

In their model reasonable description of A through B could be achieved with a constant n and the following equation for m :

$$m = m_A X_A + m_C X_C + m_F X_F + m_S X_S, \quad (14)$$

where m_A , m_C , m_F and m_S are model parameters; and X_A , X_C , X_F and X_S are the molar fractions of Al_2O_3 , CaO, 'FeO' and SiO_2 , respectively.

They introduced also compositional dependence of B for two different modifiers (CaO and FeO):

$$B = \sum_{i=0}^3 b_i^0 X_s^i + \sum_{i=0}^3 \sum_{j=1}^2 \left[b_i^{C,j} \frac{X_C}{X_C + X_F} + b_i^{F,j} \frac{X_F}{X_C + X_F} \right] \alpha^j X_s^i; \quad (15)$$

$$\alpha = \frac{X_C + X_F}{X_C + X_F + X_A};$$

where b_i^0 values are parameters for the Al_2O_3 - SiO_2 system, and $b_i^{C,j}$ and $b_i^{F,j}$ are sets of parameters for CaO and 'FeO' respectively, which are determined by optimisation.

Optimized model parameters (n , m_i , and b_i^j) are given in Table 5.

Table 5. Viscosity Model Parameters (10^{-1} Pa·s) for Al_2O_3 - SiO_2 -CaO-'FeO' - system.^[17]

j/i	0	1	2	3			
b_i^0	0	13.31	36.98	-177.70	190.03	n	9.322
$b_i^{C,j}$	1	5.50	96.20	117.94	-219.56	m_F	0.665
	2	-4.68	-81.60	-109.80	196.00	m_C	0.587
$b_i^{F,j}$	1	34.30	-143.64	368.94	-254.85	m_A	0.370
	2	-45.63	129.96	-210.28	121.20	m_S	0.212

The model uses one set of parameters (Table 5) and agrees well with more than 3000 experimental points covering four unary, six binary, and four ternary systems, and the liquid in the whole of the quaternary system.^[8]

Forsbacka et al.^[22] extended the modified Urbain model to include MgO, CrO and Cr_2O_3 , in addition to existing Al_2O_3 , CaO, 'FeO' and SiO_2 .

If CrO and Cr_2O_3 are treated as two different modifiers, expressions for m and B for the Al_2O_3 -CaO-'FeO'-CrO- Cr_2O_3 -MgO- SiO_2 system can be written as follows:

$$m = m_A X_A + m_C X_C + m_F X_F + m_{\text{Cr}^n} X_{\text{Cr}^n} + m_{\text{Cr}^m} X_{\text{Cr}^m} + m_M X_M + m_S X_S \quad (16)$$

$$B = \sum_{i=0}^3 b_i^0 X_s^i + \sum_{i=0}^3 \sum_{j=1}^2 \left[b_i^{C,j} \frac{X_C}{X_C + X_F + X_{\text{Cr}^n} + X_{\text{Cr}^m} + X_M} + b_i^{F,j} \frac{X_F}{X_C + X_F + X_{\text{Cr}^n} + X_{\text{Cr}^m} + X_M} + b_i^{\text{Cr}^n,j} \frac{X_{\text{Cr}^n}}{X_C + X_F + X_{\text{Cr}^n} + X_{\text{Cr}^m} + X_M} + b_i^{\text{Cr}^m,j} \frac{X_{\text{Cr}^m}}{X_C + X_F + X_{\text{Cr}^n} + X_{\text{Cr}^m} + X_M} + b_i^{M,j} \frac{X_M}{X_C + X_F + X_{\text{Cr}^n} + X_{\text{Cr}^m} + X_M} \right] \alpha^j X_s^i; \quad (17)$$

$$\alpha = \frac{X_C + X_F + X_{\text{Cr}^n} + X_{\text{Cr}^m} + X_M}{X_A + X_C + X_F + X_{\text{Cr}^n} + X_{\text{Cr}^m} + X_M}$$

where X_A , X_C , X_F , $X_{Cr''}$, $X_{Cr'''}'$, X_M , X_S are the molar fractions of Al_2O_3 , CaO , FeO , CrO , Cr_2O_3 , MgO and SiO_2 , respectively; m_Y , b_i^0 and $b_i^{Y,j}$ adjustable model coefficients ($Y = A, C, F, Cr''$, Cr''' , M, S).

Table 6 show parameters for Al_2O_3 - CaO - CrO - Cr_2O_3 - FeO - MgO - SiO_2 system.

Table 6. Parameters of the modified Urbain model for Al_2O_3 - CaO - CrO - Cr_2O_3 - FeO - MgO - SiO_2 system.^[23]

	j/i	0	1	2	3		
b_i^0	0	13.31	36.98	-177.70	190.03	n	9.322
$b_i^{C,j}$	1	5.50	96.20	117.94	-219.56	m_A	0.37
	2	-4.68	-81.60	-109.80	196.60	m_C	0.587
$b_i^{F,j}$	1	34.30	-143.64	368.94	-254.85	m_F	0.665
	2	-45.63	129.96	-210.28	121.20	m_M	0.522
$b_i^{M,j}$	1	-23.41	159.56	114.40	-303.38	m_S	0.212
	2	20.60	-176.64	2.84	206.02	$m_{Cr''}$	0.75
$b_i^{Cr'',j}$	1	104.70	546.24	408.59	56.32	$m_{Cr'''}$	0.5
	2	-113.01	-523.55	-112.89	-366.40		
$b_i^{Cr''',j}$	1	50.67	-410.14	192.62	-10.48		
	2	-54.98	112.55	440.99	-321.23		

3.2 Riboud Model

Riboud et al.^[24] classified the slag components into five different categories, depending on their ability to break or form polymetric chains in the molten slag. Additional slag constituents were later added to various groups by Mills et al.^[20].

- i. Network formers, $X_{SiO_2} = X_{SiO_2} + X_{P_2O_5} + X_{TiO_2} + X_{ZrO_2}$
- ii. Network breaker, $X_{CaO} = X_{CaO} + X_{MgO} + X_{FeO} + X_{Fe_2O_3} + X_{MnO} + X_{NiO} + X_{CrO} + X_{ZnO} + X_{Cr_2O_3}$
- iii. $X_{Al_2O_3} = X_{Al_2O_3} + X_{B_2O_3}$
- iv. X_{CaF_2}
- v. $X_{Na_2O} = X_{Na_2O} + X_{K_2O} + X_{Li_2O}$

The temperature dependence is expressed via the Weymann-Frenkel equation $\{\eta(dPas) = AT \exp(B/T)\}$ and the viscosity is calculated from this relation where A and B are calculated using equations 18 and 19^[24]

$$A = \exp(-19.81 + 1.73X_{CaO} + 5.82X_{CaF_2} + 7.02X_{Na_2O} - 35.76X_{Al_2O_3}) \quad (18)$$

$$B = 31140 - 23896X_{CaO} - 46356X_{CaF_2} - 39159X_{Na_2O} + 68833X_{Al_2O_3} \quad (19)$$

The model was initially developed to estimate the viscosity of mould powders in the SiO₂-CaO-Al₂O₃-CaF₂-Na₂O system but has also been applied to estimate viscosity of other types of slags. The major disadvantage of this model might be that it fails to differentiate between the various cations, e.g. MgO on a mole fraction basis is treated as if it was CaO etc.

3.3 Models based on optical basicity (NPL)

The NPL (National Physical Laboratory) model was developed by **Mills and Sridhar** [25]. It uses the Arrhenius equation (Eq. 3) for temperature dependence of slag viscosity and relates the viscosity (η) of slag to the structure through the optical basicity corrected for the cations used for charge balancing (Λ^{corr}).

The routine employed for calculating the optical basicity is given by:

$$\Lambda = \frac{\sum x_i n_i \Lambda_i}{\sum x_i n_i} \quad (20)$$

Where x is the mole fraction, n refers to the number of oxygen atoms in the molecule and Λ_i is components optical basicity (Table 7).

Table 7. Optical basicity values of various constituents. [15]

K ₂ O	Na ₂ O	BaO	SrO	Li ₂ O	CaO	MgO	Al ₂ O ₃	TiO ₂	SiO ₂	B ₂ O ₃	P ₂ O ₅	FeO	Fe ₂ O ₃	MnO	Cr ₂ O ₃	CrO	CaF ₂
1.4	1.15	1.15	1.1	1.0	1.0	0.78	0.60	0.61	0.48	0.42	0.40	1.0	0.75	1.0	0.75	1.0	1.2

The correct optical basicity (Λ^{corr}) is calculated similarly to theoretical optical basicity, but the mole fractions x_i have been balanced to take into account the amphoteric AlO₄⁵⁻-anions. The AlO₄⁵⁻-anions are charge balance by cations with higher Λ_i values. These cations are consumed and play no part in the de-polymerisation of the melt. The corrected optical basicity (Λ^{corr}) considers the cations required to balance the AlO₄⁵⁻-anions with cations in basic oxides. The first consumed oxides have higher Λ_i values.[1, 25]

For example, if the melt composition is:

$$X_{\text{SiO}_2} = 0.5, X_{\text{Al}_2\text{O}_3} = 0.15, X_{\text{CaO}} = 0.2, X_{\text{MgO}} = 0.1 \text{ and } X_{\text{K}_2\text{O}} = 0.05$$

the mole fraction values used for calculation of Λ^{corr} are

$$X_{\text{SiO}_2} = 0.5, X_{\text{Al}_2\text{O}_3} = 0.15, X_{\text{CaO}} = 0.1, X_{\text{MgO}} = 0.1 \text{ and } X_{\text{K}_2\text{O}} = 0$$

After correction of Λ the viscosity can be calculated via equations 21-23.

Mills and Sridhar^[25] derived the following empirical equations from various experimental data:

$$\ln\left(\frac{B}{1000}\right) = -1.77 + \frac{2.88}{\Lambda^{\text{corr}}} \quad (21)$$

$$\ln A = -232.69 \cdot (\Lambda^{\text{corr}})^2 + 357.32 \cdot \Lambda^{\text{corr}} - 144.17 \quad (22)$$

The viscosity can be calculated via equation 23:

$$\eta(\text{Pa} \cdot \text{s}) = A \cdot e^{\left(\frac{B}{T}\right)} \quad (23)$$

Ray and Pal^[26] applied the optical basicity concept to the Weymann-Frenkel type of equation:

$$\eta(P) = AT \cdot e^{\left(\frac{1000B}{T}\right)} \quad (24)$$

where A and B are linearly related, and B is a function of optical basicity:

$$-\ln A = 0.2056B + 12.492 \quad (25)$$

$$B = 297.14\Lambda^2 - 466.69\Lambda + 196.22 \quad (26)$$

The model is said to accurately predict viscosities of standard glasses, but is less accurate for slags^[27].

3.4 Iida Model

Iida's viscosity model ^[28] is based on the Arrhenius type of equation, where network structure of the slag is taken into account by using basicity index B_i .

$$\eta(\text{Pa} \cdot \text{s}) = A \cdot \eta_0 \cdot \exp\left(\frac{E}{B_i}\right) \quad (27)$$

where A is pre-exponential term, E is activation energy and η_0 is hypothetical viscosity for each slag constituent (i).

The parameters A , E and η_o are all given as functions of temperature.

$$A = 1.029 - 2.078 \times 10^{-3} T + 1.050 \times 10^{-6} T^2 \quad (28)$$

$$E = 28.46 - 2.884 \times 10^{-2} T + 4.000 \times 10^{-6} T^2 \quad (29)$$

$$\eta_o = \sum \eta_{oi} X_i \quad (30)$$

η_{oi} values can be approximately calculated using the following expression:

$$\eta_{oi} = 1.8 \times 10^{-7} \frac{[M_i(T_m)_i]^{1/2} \exp(H_i/RT)}{(V_m)_i^{2/3} \exp[H_i/R(T_m)_i]} \quad (31)$$

where M_i - formula weight, V_{mi} - molar volume, T_{mi} - melting temperature, R - gas constant, X - mole fraction, H_i - melting enthalpy of individual component i . H_i can be calculated from a simplified formula:

$$H_i = 5.1 \cdot T_{mi}^{1.2} \quad (32)$$

The various constituents are divided into the following categories [20]:

- (1) acidic (SiO_2 , ZrO_2 , TiO_2) denoted by subscript A,
- (2) basic (CaO , MgO , Na_2O , K_2O , Li_2O , FeO , MnO , CrO , CaF_2 , etc.) denoted by subscript B, and
- (3) amphoteric (Al_2O_3 , B_2O_3 , Fe_2O_3 , Cr_2O_3).

In the **original Iida model** the basicity index B_i is calculated by [20]:

$$B_i = \frac{\sum (\alpha_i W_i)_B}{\sum (\alpha_i W_i)_A} \quad (33)$$

where α_i is specific coefficient, W_i mass percentage for component i and the subscripts A and B represent acidic oxide and basic oxide or fluoride, respectively.

The Iida model was later modified [28] to account for the amphoteric oxides where their basicity changed according to the temperature. This was done through the **modified basicity index** (Eq. 34). It was concluded that Fe_2O_3 and Cr_2O_3 worked basically as basic oxides so they appear on numerator.

$$Bi^* = \frac{\Sigma(\alpha_i W_i)_B + \alpha_{Fe_2O_3}^* W_{Fe_2O_3} + \alpha_{Cr_2O_3}^* W_{Cr_2O_3}}{\Sigma(\alpha_i W_i)_A + \alpha_{Al_2O_3}^* W_{Al_2O_3}} \quad (34)$$

α_i^* is the modified specific coefficient indicating the interaction of the amphoteric oxide with other components in slag. If we assume that value of α^* is independent of slag composition and temperature $\alpha_i^* = \alpha_i$.

The model gets exceedingly complicated because the modified α (denoted α^* in Eq. 34) for Al_2O_3 is obtained from experimental viscosity data for certain systems, e.g. $CaO+MgO+Al_2O_3+SiO_2$ and then expressed by equation (35)^[20]:

$$\alpha_{Al_2O_3}^* = aBi + bW_{Al_2O_3} + c \quad (35)$$

Iida et al.^[28] defined the a , b and c equations for $CaO+MgO+Al_2O_3+SiO_2$ system to be:

$$a = 1.20 \cdot 10^{-5} T^2 - 4.3552 \cdot 10^{-2} T + 41.16 \quad (36)$$

$$b = 1.40 \cdot 10^{-7} T^2 - 3.4944 \cdot 10^{-4} T + 0.2062 \quad (37)$$

$$c = -8.00 \cdot 10^{-6} T^2 + 2.5568 \cdot 10^{-2} T - 22.16 \quad (38)$$

Values for the coefficients a , b and c for the same system determined by **Forsbacka et al.**^[29] are shown in Table 8.

Table 8. Values for the coefficients a , b and c in eq. 35 by Forsbacka et al.^[29]

Temperature, °C	a	b	c
1580	1.057	0.0022	-1.019
1600	1.056	0.0058	-1.115
1650	1.038	0.0157	-1.379
1700	0.991	0.0243	-1.587
1750	0.863	0.0186	-1.249

Forsbacka et al.^[30] reported also that Cr_2O_3 was found to have much stronger basic characteristics with the parameter $\alpha_{Cr_2O_3}$ as large as 0.71. The parameter $\alpha_{Cr_2O_3}$ has been reported earlier to have a value of 0.13 (see Table 9).

It is difficult to apply the Iida model to systems where there is no experimental data since $\alpha_{Al_2O_3}^*$ values are determined for each system/family and there is no general overall value for $\alpha_{Al_2O_3}^*$. The high accuracy claimed with this model comes from its calibration with experimental data for each family of slags.^[15]

The values for calculation of slag viscosities using Iida model are listed in Table 9.

Table 9. Values for melting temperature (T_m), density (ρ_m), formula weight (M_i), molar volume (V_m) at T_m , hypothetical viscosity (η_{oi}) and specific coefficient α_i for slag components i . [31]

Component		$(T_m)_i$ (K)	Ref.	$(\rho_m)_i$ (10^3 kg/m^3)	Ref.	M_i (10^{-3} kg/mol)	$(V_m)_i$ ($10^{-6} \text{ m}^3/\text{mol}$)	Ref.	μ_{oi} ($\text{mPa}\cdot\text{s}$)	α_i
Acidic oxide	SiO ₂	2001	1	2.20	—	60.08	27.29	2	$0.13170 \exp(5613.5/T)$	1.48
	ZrO ₂	2950	1, 3	5.68	4	123.22	21.69	—	$0.21281 \exp(8943.9/T)$	0.08
	MoO ₃	1068	1, 5	3.25	6	143.94	44.29	—	$0.15016 \exp(2642.5/T)$	0.96
	B ₂ O ₃	723	1, 3, 5, 7	1.67	7	69.62	41.69	—	$0.10772 \exp(1654.6/T)$	1.12
	P ₂ O ₅	845	1	2.30	4	141.94	61.71	—	$0.11907 \exp(1995.1/T)$	1.23
	GeO ₂	1389	1, 3, 5	3.39	6	104.61	30.86	—	$0.16253 \exp(3622.2/T)$	0.56
	V ₂ O ₅	943	6	2.32	6	181.88	78.40	—	$0.11518 \exp(2275.9/T)$	0.53
Amphoteric oxide	Al ₂ O ₃	2313	1	3.04	2	101.96	33.58	2	$0.14792 \exp(6679.5/T)$	0.10
	Fe ₂ O ₃	1838	4	4.24	6-1	159.69	37.66	—	$0.17405 \exp(5069.3/T)$	0.08
	TiO ₂	2108	1	3.65	6	79.87	21.88	—	$0.17536 \exp(5975.6/T)$	0.36
Basic oxide	BaO	2190	1	4.82	—	158.33	31.79	2	$0.18891 \exp(6255.6/T)$	0.67
	CaO	2873	1	2.39	—	56.08	23.49	2	$0.13651 \exp(8664.4/T)$	1.53
	MgO	3073	1, 5	2.49	—	40.30	16.16	2	$0.14743 \exp(9393.1/T)$	1.51
	K ₂ O	980	1, 5	2.30	—	94.20	40.96	2	$0.12787 \exp(2383.4/T)$	1.37
	Na ₂ O	1193	1, 5	2.27	—	61.98	27.25	2	$0.13621 \exp(3017.9/T)$	1.94
	Li ₂ O	2000	1, 5	1.49	—	29.88	20.07	2	$0.11400 \exp(5610.1/T)$	3.55
	MnO	2053	1	4.18	6-2	70.94	16.97	—	$0.19612 \exp(5789.0/T)$	1.03
	FeO	1642	1	4.62	6	71.84	15.55	—	$0.21163 \exp(4427.7/T)$	0.96
	Cr ₂ O ₃	2538	1	5.22	4	151.99	29.12	—	$0.19708 \exp(7466.6/T)$	0.13
	PbO	1159	1, 3, 5	8.52	6-3	223.20	26.20	—	$0.26535 \exp(2915.0/T)$	0.43
CaF ₂	1691	1, 3	2.55	—	78.07	30.62	2	$0.14025 \exp(4586.8/T)$	1.53	

3.5 KTH Model

The KTH viscosity model is based on the Eyring equation which is similar to the Weymann-Frenkel formalism. The viscosity, η , can be expressed by the following equation [3]:

$$\eta(\text{Pa}\cdot\text{s}) = \frac{hN_A\rho}{M} \exp\left(\frac{\Delta G^*}{RT}\right) \quad (39)$$

where h is the Planck's constant; N_A is Avogadro's numbers; ρ and M are the density and molecular weight of the melt, respectively; R is the gas constant; T is temperature in Kelvin. ΔG^* is the Gibbs energy of activation for viscosity, which is considered to be a function of both temperature and composition of the melt.

In the case of multicomponent systems, the use of Eq. (39) requires the molecular weight and density of the melt. The molecular weight can be calculated by:

$$M = \sum_{i=1}^m X_i M_i \quad (40)$$

where X_i and M_i represent the mole fraction and the molecular weight of component i in the solution, respectively.

The density can be approximated as:

$$\rho = \sum_{i=1}^m X_i \rho_i \quad (41)$$

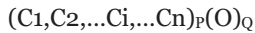
where ρ_i is the density of pure component i in the liquid state.

The Gibbs activation energy for viscosity in Eq. (39) can be expressed as:

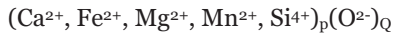
$$\Delta G^* = \sum_{i=1}^m X_i \Delta G_i^* + \Delta G_{\text{mix}}^* \quad (42)$$

where ΔG_i^* represents the Gibbs activation energy of pure component i in the liquid state and is usually a linear function of temperature. The term ΔG_{mix}^* is due to mutual interactions between different species and is expected to be a function of composition.^[3] In the case of oxide systems, only the interactions of different cations in the presence of O^{2-} ions are taken into account.^[32]

In the case of ionic solutions, the Temkin description is adopted. It classifies the cations and anions in different subgroupings. An oxide ionic solution can be represented by the formula^[3]:



For example, a silicate solution, $\text{CaO-Fe}_n\text{O-MgO-MnO-SiO}_2$ can be represented by: ^[32]



where P and Q are the stoichiometric coefficients

The ionic fraction of cation C_i within the cation grouping is defined as:

$$y_{C_i} = \frac{N_{C_i}}{\sum N_C} \quad (43)$$

N_{C_i} represents the number of the C_i cations, and $\sum N_C$ the total number of cations in the system.

The Gibbs free energy expression contains many adjustable parameters, which are used to obtain agreement with experimental results. The expression of the Gibbs activation energy for the viscosity in the CaO-Fe_nO-MgO-MnO-SiO₂ system is given in Eq. (44). In view of the similarity of the cations, Ca²⁺, Fe²⁺, Mg²⁺ and Mn²⁺, the binary interactions between these ions are not considered in the model calculations. [32]

$$\begin{aligned} \Delta G^*(\text{CaO} - \text{Fe}_n\text{O} - \text{MgO} - \text{MnO} - \text{SiO}_2) = & \\ \left[X_{\text{CaO}} \Delta G_{\text{CaO}}^* + X_{\text{Fe}_n\text{O}} \Delta G_{\text{Fe}_n\text{O}}^* + X_{\text{MgO}} \Delta G_{\text{MgO}}^* + X_{\text{MnO}} \Delta G_{\text{MnO}}^* + X_{\text{SiO}_2} \Delta G_{\text{SiO}_2}^* \right] + & \quad (44) \\ \Delta G_{\text{Mix}}^*(\text{CaO} - \text{SiO}_2) + \Delta G_{\text{Mix}}^*(\text{Fe}_n\text{O} - \text{SiO}_2) + \Delta G_{\text{Mix}}^*(\text{MgO} - \text{SiO}_2) + \Delta G_{\text{Mix}}^*(\text{MnO} - \text{SiO}_2) + & \\ \text{GCAFESI} + \text{GCAMGSI} + \text{GCAMNSI} + \text{GFEMGSI} + \text{GFEMNSI} & \end{aligned}$$

Model parameters predicting viscosity of slag system consisting of CaO-Fe_nO-MgO-MnO-SiO₂ are shown in Table 10.

Table 10. Optimised model parameters.[32]

Component <i>i</i>	Density (g · cm ⁻³)	Molar weight (g · mol ⁻¹)	ΔG_i^* (J · mol ⁻¹)
CaO	3.3	56.079	1.85327311×10^5
Fe _n O	4.7	71.846	$1.33749591 \times 10^5 - 18.0328243T$
MgO	3.58	40.311	1.86541828×10^5
MnO	5.43	70.937	1.32713886×10^5
SiO ₂	2.3	60.085	$5.33067968 \times 10^5 - 53.2975311T$
ΔG_{Mix}^* (J · mol ⁻¹)			
Binary interaction			
CaO-SiO ₂	$\Delta G_{\text{Mix}}^*(\text{CaO} - \text{SiO}_2) = y_{\text{Ca}}^{2+} y_{\text{Si}}^{4+} [-8.56218889 \times 10^5 + 103.7330927T + 2.64594343 \times 10^5 (y_{\text{Ca}}^{2+} - y_{\text{Si}}^{4+})]$		
Fe _n O-SiO ₂	$\Delta G_{\text{Mix}}^*(\text{Fe}_n\text{O} - \text{SiO}_2) = y_{\text{Fe}}^{2+} y_{\text{Si}}^{4+} [-9.70281422 \times 10^5 + 242.4809307T + 1.90586769 \times 10^5 (y_{\text{Fe}}^{2+} - y_{\text{Si}}^{4+})]$		
MgO-SiO ₂	$\Delta G_{\text{Mix}}^*(\text{MgO} - \text{SiO}_2) = y_{\text{Mg}}^{2+} y_{\text{Si}}^{4+} [-8.18430330 \times 10^5 + 91.36380277T + 1.35009560 \times 10^5 (y_{\text{Mg}}^{2+} - y_{\text{Si}}^{4+})]$		
MnO-SiO ₂	$\Delta G_{\text{Mix}}^*(\text{MnO} - \text{SiO}_2) = y_{\text{Mn}}^{2+} y_{\text{Si}}^{4+} [-7.30955356 \times 10^5 + 85.84158067T - 7.47554681 \times 10^4 (y_{\text{Mn}}^{2+} - y_{\text{Si}}^{4+})]$		
Ternary interaction			
CaO-Fe _n O-SiO ₂	$\Delta G_{\text{Mix}}^*(\text{CaO} - \text{Fe}_n\text{O} - \text{SiO}_2) = \Delta G_{\text{Mix}}^*(\text{CaO} - \text{SiO}_2) + \Delta G_{\text{Mix}}^*(\text{Fe}_n\text{O} - \text{SiO}_2) + \text{GCAFESI}$ $\text{GCAFESI} = y_{\text{Ca}}^{2+} y_{\text{Fe}}^{2+} y_{\text{Si}}^{4+} (1.14932406 \times 10^6 - 139.466890T - 1.05268958 \times 10^6 y_{\text{Ca}}^{2+} - 1.18703224 \times 10^6 y_{\text{Fe}}^{2+})$		
CaO-MgO-SiO ₂	$\Delta G_{\text{Mix}}^*(\text{CaO} - \text{MgO} - \text{SiO}_2) = \Delta G_{\text{Mix}}^*(\text{CaO} - \text{SiO}_2) + \Delta G_{\text{Mix}}^*(\text{MgO} - \text{SiO}_2) + \text{GCAMGSI}$ $\text{GCAMGSI} = y_{\text{Ca}}^{2+} y_{\text{Mg}}^{2+} y_{\text{Si}}^{4+} (1.07014539 \times 10^6 - 324.5018097T)$		
CaO-MnO-SiO ₂	$\Delta G_{\text{Mix}}^*(\text{CaO} - \text{MnO} - \text{SiO}_2) = \Delta G_{\text{Mix}}^*(\text{CaO} - \text{SiO}_2) + \Delta G_{\text{Mix}}^*(\text{MnO} - \text{SiO}_2) + \text{GCAMNSI}$ $\text{GCAMNSI} = y_{\text{Ca}}^{2+} y_{\text{Mn}}^{2+} y_{\text{Si}}^{4+} (-6.75779022 \times 10^5 + 504.1617637T)$		
Fe _n O-MgO-SiO ₂	$\Delta G_{\text{Mix}}^*(\text{Fe}_n\text{O} - \text{MgO} - \text{SiO}_2) = \Delta G_{\text{Mix}}^*(\text{Fe}_n\text{O} - \text{SiO}_2) + \Delta G_{\text{Mix}}^*(\text{MgO} - \text{SiO}_2) + \text{GFEMGSI}$ $\text{GFEMGSI} = y_{\text{Fe}}^{2+} y_{\text{Mg}}^{2+} y_{\text{Si}}^{4+} (7.83484279 \times 10^5 - 271.0897927T)$		
Fe _n O-MnO-SiO ₂	$\Delta G_{\text{Mix}}^*(\text{Fe}_n\text{O} - \text{MnO} - \text{SiO}_2) = \Delta G_{\text{Mix}}^*(\text{Fe}_n\text{O} - \text{SiO}_2) + \Delta G_{\text{Mix}}^*(\text{MnO} - \text{SiO}_2) + \text{GFEMNSI}$ $\text{GFEMNSI} = y_{\text{Fe}}^{2+} y_{\text{Mn}}^{2+} y_{\text{Si}}^{4+} (1.66129998 \times 10^6 - 891.7154297T)$		

The model is reported to be applicable to a wide range of systems, from liquid metals to molten slags. The KTH model is now commercially available as a software, ‘THERMOSLAG’ [11].

4 Performance of models in predicting viscosities of industrial slags

As shown in chapter 3 various viscosity models have been developed to estimate the viscosity of fully molten oxide slags. In this chapter the viscosities of converter slags (Basic Oxygen Furnace, Argon-Oxygen Decarburization furnace) predicted with different models are compared.

4.1 BOF slag

The purpose of the Basic Oxygen Steelmaking (BOS) process is to refine the hot metal produced in the blast furnace into raw liquid steel, which may be subsequently refined in the secondary steelmaking shop.

The main functions of the Basic Oxygen Furnace (BOF) are to decarburise and remove phosphorus and other impurities from the hot metal, and to optimise the steel temperature so that any further treatments prior to casting can be performed with minimal reheating or cooling of the steel. The exothermic oxidation reactions that occur during BOS generate a lot of heat energy - more than is necessary to attain the target steel temperature. This extra heat is used to melt scrap and/or iron ore additions.

BOF slag is generated at a rate of 60 to 100 kg per tonne of steel. The BOF-slag contains oxides arising from some oxidation reactions (SiO_2 , MnO , FeO , V_2O_5 , P_2O_5 and TiO_2), added fluxes (CaO , MgO) and refractory wear (MgO). Typical composition of the BOF-slag is shown in Table 11.

Table 11. Typical composition of BOF-slag (wt-%).^[33]

CaO	SiO ₂	MgO	Al ₂ O ₃	MnO	FeO	V ₂ O ₅	P ₂ O ₅	TiO ₂	Cr ₂ O ₃
54.6	11.4	1.6	1.2	3.5	21.7	3.1	0.8	1.8	0.3

Figure 4 shows comparison of estimated viscosity values calculated using different models for BOF-slag as a function of temperature.

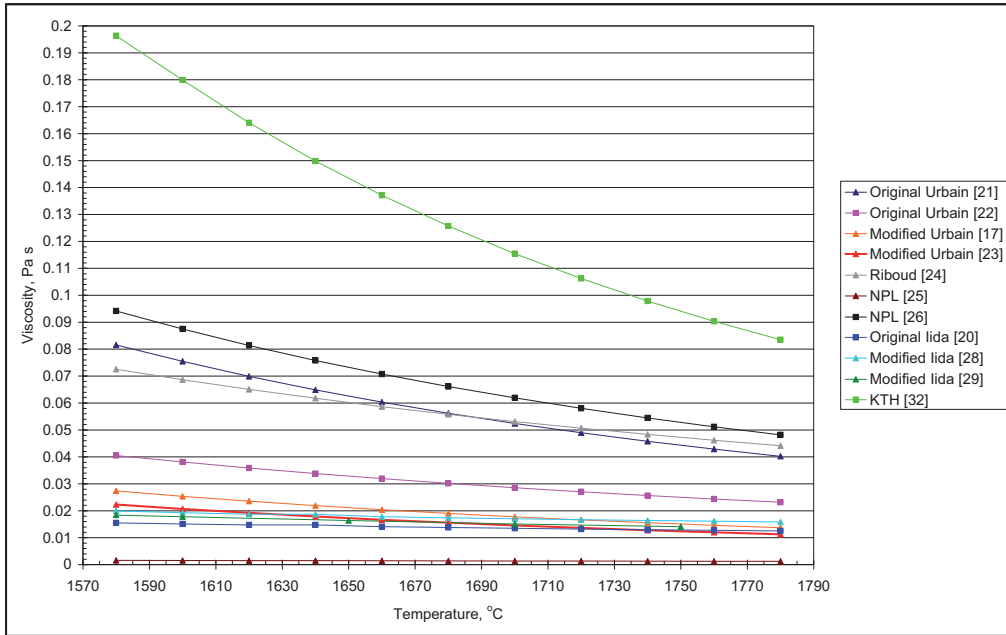


Figure 4. Calculated viscosity values of BOF-slag.

The viscosity values calculated by the Iida^[20, 28, 29] and modified Urbain models^[17, 23] are almost equal through the whole temperature range. The values changes from ~ 0.021 Pa·s at 1580°C to ~ 0.013 Pa·s at 1780°C. The use of the original Urbain model^[21] resulted higher viscosity values compared to the other Urbain models^[17, 22, 23]. The major advantage of the modified Urbain models is that they enables the differences in chemistry of individual components to be taken into account and thus these models should be more accurate in predicting slag viscosities than the original Urbain model.

In addition to the original Urbain model^[21], the Riboud model^[24] fails to differentiate between the various cations, e.g. MgO on a mole fraction basis is treated as if it was CaO etc. Thus similar viscosity values were obtained by both of these models.

The values calculated by KTH model^[32] seems to be too high for this high basic slag whereas the NPL model by Mills and Sridhar^[25] show too low viscosity values. In the NPL model by Ray and Pal^[26] the temperature dependence of the viscosity is expressed in the forms of the Weymann-Frenkel equation instead of Arrhenius equation which is used in the model by Mills and Sridhar thus different viscosity values were obtained. According to the literature^[25] the slag compositions, which have corrected optical basicity above 0.73 are unlikely to receive very accurate viscosity prediction by using the NPL model. Since the corrected optical basicity of the BOF-slag is 0.86, the slag composition is outside of the working range of the NPL model.

Although the Iida^[20, 28, 29] and the modified Urbain models^[17, 23] seems to be more reliable than the other models, it is not possible to evaluate their performance in predicting viscosities of BOF-slag since no measured viscosity values corresponding to the slag composition shown in Table 11 were found in the literature.

4.2 AOD slag

In the AOD-converter (Argon Oxygen Decarbonization), decarburisation of stainless steel is carried out with an oxygen – inert-gas mixture. The AOD process uses the dilution principle to minimise chromium oxidation. The molten metal is initially blown with a high ratio of oxygen to inert gas. As the carbon content of the bath decreases, the oxygen-to-inert gas ratio lowers. Dilution of the oxygen by the inert gas lowers the partial pressure of carbon monoxide in the bath, which favors carbon removal. As a result, carbon removal is increased, while metallic chromium oxidation is diminished. During the reduction period, oxidised chromium is returned from the slag to the metal phase simultaneously with desulphurisation. Typical AOD-slag compositions after oxidation and reduction periods are shown in Tables 12 and 13, respectively.

Table 12. Typical composition of AOD-slag after oxidation period (wt-%).^[34]

CaO	SiO ₂	MgO	Al ₂ O ₃	MnO	FeO	Cr ₂ O ₃
42.1	5.3	4.2	1.1	10.5	10.5	26.3

Table 13. Typical composition of AOD-slag after reduction period (wt-%).^[34]

CaO	SiO ₂	MgO	Al ₂ O ₃	MnO	FeO	Cr ₂ O ₃
57.0	31.1	9.3	1.1	0.5	0.5	0.5

Comparison of estimated viscosity values calculated using different models for AOD-slag as a function of temperature after oxidation and reduction periods are shown in Figures 5 and 6, respectively.

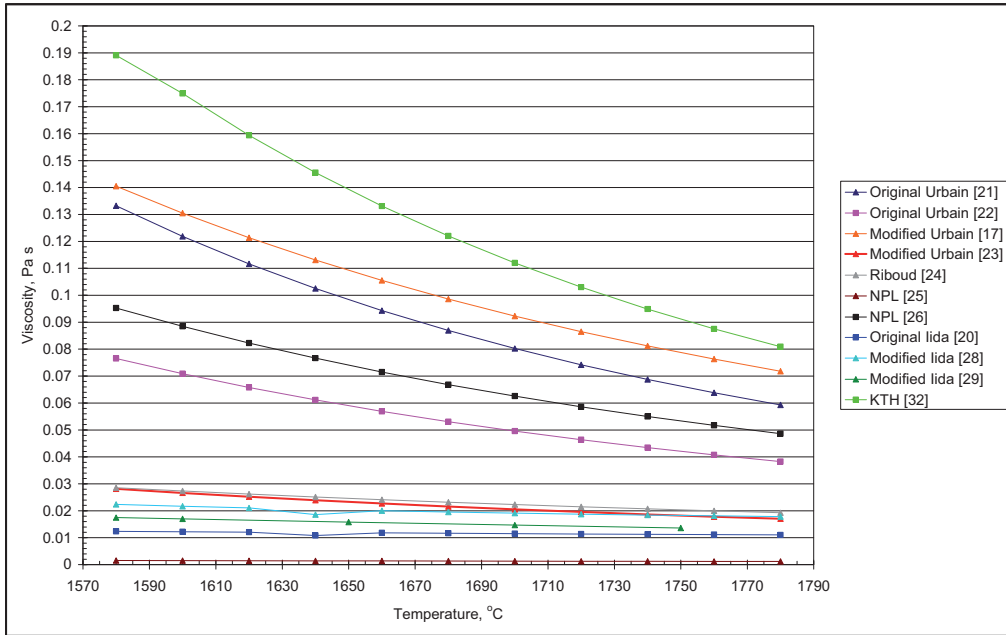


Figure 5. Calculated viscosities of AOD-slag after oxidation period.

The viscosity values calculated by the Iida^[20, 28, 29], modified Urbain^[23] and Riboud^[24] models are quite close to each other through the whole temperature range. The other values are divergent. Also in this case the highest viscosity values were obtained by KTH model^[32] and the lowest values by NPL model^[25]. Forsbacka et al.^[23] extended the modified Urbain model by Kondratiev and Jak^[17] to include parameters for chromium oxides as well as for magnesia in addition to existing Al_2O_3 , CaO , FeO and SiO_2 and thus the calculated viscosity values between these models are quite different.

Like in the case of BOF-slag, no measured viscosity values corresponding to the slag composition shown in Table 12 were found in the literature. This is due to chromium-containing slags are one of the most difficult slags to be measured. They have very high melting points and the chromium appears in two oxidation stages in metallurgical slags: Cr^{2+} and Cr^{3+} , with corresponding oxides CrO and Cr_2O_3 ($\text{CrO}_{1.5}$). Both of these oxides have a different effect on viscosity and it is therefore necessary to know how much CrO and Cr_2O_3 there are in the slag.^[35] In the model calculations all the chromium was assumed to be in Cr_2O_3 form.

Due the facts mentioned above it is not possible to say which of the models (if any) are suitable in predicting viscosity of AOD-slag during oxidation period. However the Urbain model modified by Forsbacka et al.^[23] as well as the modified Iida models^[28, 29] takes account of chromium oxide and are thus assumed to be more reliable than the other models in predicting viscosities of chromium containing slags.

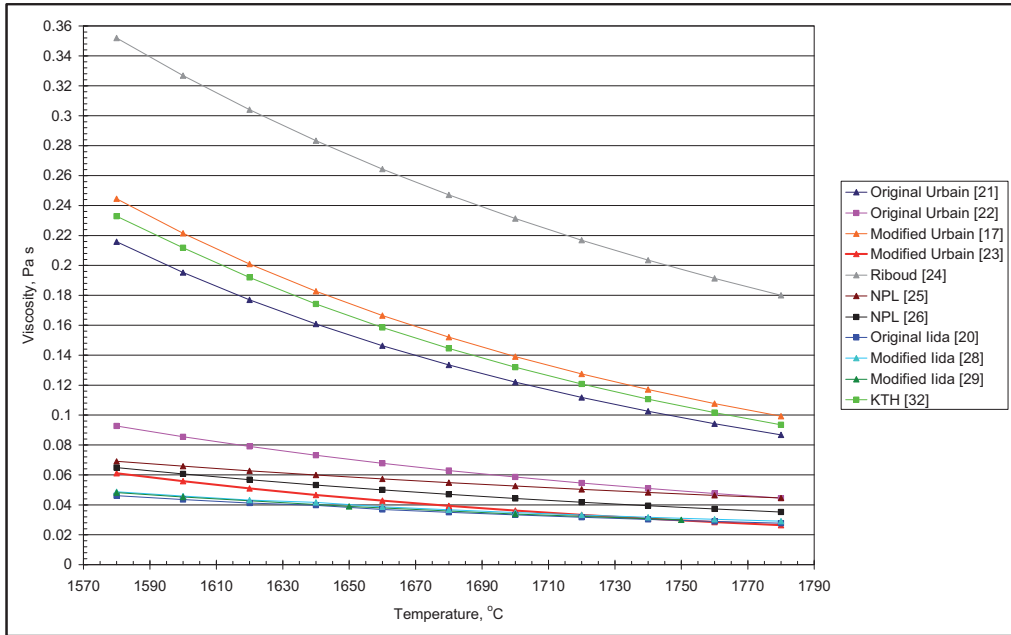


Figure 6. Calculated viscosities of AOD-slag after reduction period.

In this case the NPL-models^[25, 26] gives almost equal viscosity values through the whole temperature range than the Iida models^[20, 28, 29]. The corrected optical basicity value of the investigated slag is 0.74 so the slag composition is assumed to be inside the working range of the NPL model. In addition to these models the Urbain model modified by Forsbacka et al.^[23] is assumed to be reliable. The model by Forsbacka et al.^[23] includes separate parameters for MgO unlike the other Urbain models. This is important since the slag contains almost 10% MgO. The calculated viscosity values by this model are close to values obtained by Iida and NPL models.

Unfortunately no measured viscosity values corresponding to the slag composition shown in Table 13 were found in the literature.

5 Discussion and Conclusions

Viscosity is a physical property which is related to the structural and physical properties of the melt. In slags, viscosity is dominated by the silicate structure; an acid slag with large polymerized silicate ions is highly viscous whereas a basic slag with small de-polymerized silicates is much more fluid. Except the presence of net-forming and non-net-forming oxides in the slag, complicated interactions between the cations and anions make the predicting and modeling of slag viscosity often quite problematic.

Although viscosity of slags can be measured experimentally, the high cost and low accuracy of high temperature experiments impede the acquirement of reliable data. The uncertainty in the measurements for many slags is ca. $\pm 20\%$. Variations in reported viscosity values for laboratories using good practice are $<10\%$.^[11, 15] Experimentally measured viscosity data are available for ternary systems which consists of most oxide components for metallurgical interest, such as MgO, CaO, SiO₂, Al₂O₃, FeO. As the order of the system gets higher, less data in limited ranges are available.

Several models have been reported for calculating the viscosity of melts from their chemical composition. Among these the Iida^[20, 28, 29] and the modified Urbain models^[17, 23] seems to be more reliable than the other models in predicting the viscosities of BOF-slag. As mentioned earlier no measured viscosity values corresponding to investigated BOF-slag compositions were found in the literature. However Ji^[12] reported that steelmaking slag has a viscosity value about 0.05 Pa·s at 1873K. This is bit higher compared to the calculated values using the above mentioned models (~ 0.02 Pa·s at 1873K). Assuming that the basicity of the slag used in the calculations ($\text{CaO/SiO}_2 = 4.8$) is higher compared to 'normal' slag practice ($\text{CaO/SiO}_2 = 3.5-4.5$), lower viscosity value is expected to be received with this slag compared to 'normal' slag composition.

Urbain model modified by Forsbacka et al.^[23] as well as the modified Iida models^[28, 29] takes account of chromium oxide and are thus assumed to be more reliable than the other models in predicting viscosities of chromium containing slags e.g. AOD-slag after oxidising period. However the solubility of Cr₂O₃ to this type of slag is about 5%^[34]. Since the Cr₂O₃ content of slag after the oxidation period is about 25% (see Table 12) the slag contains solid phases which have influence on slag viscosity. The viscosity models used in the calculations are only valid for homogenous Newtonian liquids. When the solid phase starts to precipitate out of slag, the viscosity quickly becomes non-Newtonian. The limit of the Newtonian/non-Newtonian transition has been reported to be from 10 to 40 vol% solid fraction of melt depending on the shape and size of solid particles^[8].

Finally NPL^[25,26], Iida^[20,28,29] and the Urbain model modified by Forsbacka et al.^[23] is assumed to be reliable to predict viscosity of slag composition corresponding the AOD-slag after reduction period.

As mentioned earlier no measured viscosity values corresponding to investigated slag compositions were found in the literature. This is caused by difficulties encountered in experimental studies. These are mainly chemical attack of the containing materials by slags and difficulty in controlling the oxidation states of Fe and Cr in melts^[36]. Due to lack of experimental data the performance of the models in predicting viscosities of converter slags was not able to evaluate. Most of the available models employ parameters extracted from experimental data of viscosity, which ensure the validity of the models in viscosity estimation. Thus more experimental work is necessary to provide the data to test and optimise the models for these very complex compositions. As a final comment, it should be pointed out that the accuracies of the viscosity models that are available can only be as good as the original experimental data.

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