ice | science

Institution of Civil Engineers

publishing

Structural aspects of blast furnace slag

[1] **J. N. Tiwary** BTech
National Institute of Technology, Rourkela, Orissa, India

[2] **S. Sarkar** PhD
National Institute of Technology, Rourkela, Orissa, India

[3] **B. Mishra** PhD
Dalmia Institute of Scientific and Industrial Research, Rajgangpur,
Orissa, India

[4] **U. K. Mohanty** PhD*
National Institute of Technology, Rourkela, Orissa, India

Interdependence of structure and viscosity of blast furnace slag is discussed based on the available literature. Emphasis is given to both, bridging tendency and network breaking/modifying tendency of the constituents. It is clearly pointed out that slag viscosity cannot be explained only by depolymerization through an increase in basicity, despite the fact that an increase in basicity of the slag, in general, lowers the viscosity of the slag by a process of generation of discrete anions containing simple chains and/or rings by causing depolymerization of the 3D silicate network.

1. Introduction

In a blast furnace, the flow phenomenon of the slag, as dictated by its viscosity, greatly influences the heat transfer, mass transfer and chemical reactions between the slag and the metal. The blast furnace slag should be a free-flowing one at the operating temperatures to ensure efficient slag–metal separation. It must have appreciable affinity for the gangue constituents to facilitate the production of metal of choice. Yet from the available heat (in the hearth) point of view,[1] the blast furnace slag should be neither very viscous nor very fluid. In addition, a viscous slag is less damaging to the refractory in the furnace. Thus, it is rightly said 'History of slag making is the history of iron making.' This saying emphasizes on the fact that the quality of metal produced cannot be better than the quality of the slag produced; one of the most important factors influencing the quality of the slag being its viscosity. The viscosity of the blast furnace slag governs the reaction rates in the furnace by its effect on the diffusion of ions through the liquid slag to and from the slag–metal interface. It also affects the operational efficiency of the blast furnace by its influence on the aerodynamics of the furnace since the flow pattern of the molten slag significantly influences the gas permeability and heat transfer in the furnace.

Highly viscous molten covalent oxides, such as silica, and relatively low viscous ionic melts in an oxide slag influence the viscosity of the molten oxide slag. The viscosity of the silicate melts is affected by the nature of network-breaking cations (e.g. Ca^{2+}, Mg^{2+}), the fitting of certain cations (e.g. Al^{3+}, Ti^{4+}) into the silicate network and the degree of polymerization of the silicate network. Alumina, an amphoteric oxide, plays a peculiar role in influencing the viscosity of blast furnace slag. In a basic slag, both alumina and silica behave similarly; both Al and Si occupy similar sites in the lattice; the total network forming ions being Al + Si. On the other hand, in acid slag, that is, when the Al_2O_3/CaO ratio is high and SiO_2 content is also high, Al_2O_3 would act as a network breaker and would decrease the viscosity of the slag. Thus, it is rightly concluded that the viscosity of the blast furnace slag is structure oriented and that it strongly depends on its composition at the operating temperatures.

A process of depolymerization lowers the viscosity of the slag. An increase in basicity decreases the viscosity of the blast furnace slag, breaking the 3D silicate network into discrete anionic groups thereby causing depolymerization. However, the blast furnace slag viscosity cannot be described only by the enhanced degree of depolymerization. Beyond certain levels of basicity, the viscosity actually increases, despite the enhanced degree of depolymerization, as such an increase in the basicity may also result in an increase in the chemical potential of some primary solid phases.

It is in this context that the present article makes an attempt at analyzing the diversities pertaining to the structure and related viscosity of oxide melts under the blast furnace conditions. An attempt is made to analyze the findings of several workers on the basis of their conclusive remarks and to make it available

*Corresponding author e-mail address: u_k_mohanty@rediffmail.com

in one place. This will help to analyze data generated by future experimenters.

2. Structure and viscosity of molten silica

Pure solid silica has a 3D continuous network of SiO_4 tetrahedron. Each silicon ion is coordinated with four oxygen ions, while each oxygen is linked to two Si^{4+} ions. Though there may be a change from long- to short-range ordering during melting, the structure of pure liquid silica is very similar to that of pure solid silica. The very high viscosity of pure fused silica attributed to the associated high activation energy of viscous flow, indicate that the movement of flow units involves breaking of Si-O bonds (heat of dissociation = 104 Kcal/mole).[2]

The flow unit is that which requires the least energy of transfer from the initial to the transition state. It is suggested that this is a SiO_2 molecule since any larger unit would involve a greater number of Si-O bonds during the formation of the activated complex.[3]

The high value of viscosity and activation energy of viscous flow of pure molten silica indicate that, at any instant only, a small fraction of the melt may exist in the form of SiO_2 molecules and that these molecules that take part in the flow process must be formed from the three dimensionally bonded lattice.

3. Structure and viscosity of binary silicate melts

On addition of a basic metal oxide to molten silica, the added oxygen ion enters the network and separates the corners of two tetrahedra, while the added cation remains adjacent to the negative charges breaking the oxygen bridges between groups (Equations 1 and 2).

$$1. \quad -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-M^{++} \rightarrow \quad -\overset{|}{\underset{|}{Si}}-O^-M^{++}O^--\overset{|}{\underset{|}{Si}}-$$

$$2. \quad -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-2M^+ \rightarrow \quad -\overset{|}{\underset{|}{Si}}-O^-\underset{M^+}{M^+}O^--\overset{|}{\underset{|}{Si}}-$$
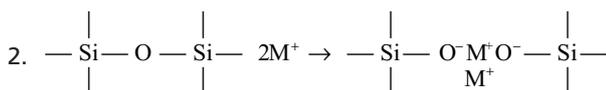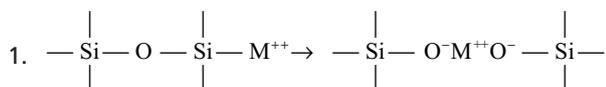
(Addition of divalent and monovalent basic metal oxide to the silicate network)

The type of metal oxide added governs the degree of breakdown; while divalent metal cations tend to link the network by bridging two oxygen, monovalent ones do not.[4] Furthermore, a gradual addition of cations (e.g. Na^+, Ca^{++}) brings in progressive breaking of the oxygen bonds with the formation of nonbridging oxygen (NBO), denoted by O^- and eventually the formation of free oxygen, O^{2-} ions.

The breaking down of the silicate network results in smaller and smaller silicate groups known as anionic units or flow units. Since smaller and smaller flow units require relatively higher oxygen, the progressive addition of metal oxides is less and less effective in reducing the flow unit size. This explains the decrease in viscosity at a slower rate with the increase in metal oxide percentage.

E_μ, the activation energy of viscous flow, is related to the energy required to move one silicate group or a major part thereof, with respect to the other, enabling the group to move. The effects of monovalent and divalent metal oxides on E_μ are different. Unlike the Group I metal oxide systems, where E_μ is independent of the cationic species at all compositions up to about 35 mole %, in case of Group II metal oxides, the independence is retained till about 55 mole percentage of metal oxide, indicating that the effect of monovalent metal oxide on E_μ is more pronounced than the divalent ones. This is because, at equimolar compositions, there are twice as many monovalent cations as divalent ones and as pointed out earlier, the divalent cations maintain the continuous bonding of the lattice by bridging the oxygen atoms. Hence, by addition of Group II metal oxides, the decrease in E_μ will be more gradual. This leads to the fact that in case of the Group II metal oxides, collapse of the SiO_2 network will occur only when comparatively more metal oxides have been added.

Metal oxides with smaller cations are less efficient in reducing the viscosity by bringing down the E_μ. In the case of the smaller cations, due to spatial arrangement of atoms in the molecule, the columbic interactions between metal cations and singly bonded oxygen will be relatively smaller. The tendency to form more extreme depolymerized (e.g. SiO_4^{4-}) and polymerized (e.g. SiO_2) anionic units can be ranked in terms of the parameter, Z/r^2, where 'r' is the radii and 'Z' is the valency; the higher the ratio, the higher is the tendency. This tendency of the metal oxides can thus, given in the order $Mg^{2+} > Ce^{2+} > Sr^{2+} > Pb^{2+} > Ba^{2+} > Li^+ > Na^+ > K^+$.

Again, the addition of x moles of Na_2O to a given amount of a given silicate slag should result in greater lowering in viscosity in comparison with the lowering observed due to the addition of x moles of CaO to the same amount of the same silicate slag. This is because the alkaline earth cations having a bridging tendency would not permit the O^-–O^- interactions to be as effective as the case when only alkali metal cations are involved.

The cations, randomly distributed throughout the lattice of the silicate network introduce weak points into the network and also weaken the Si-O bonds near the metal ion due to a polarization effect. This causes a general loosening effect in the lattice. This is represented in Figure 1 in a simplified, 2D figure.

The discrete anion and the chain formation concept, proposed by[3–5] is probably the most accepted structural model of silicate melts that explain the change in various physical properties such as expansivity and miscibility gaps in silicate melts. They propose that the structure, consistent with the behavior of the energy of activation–composition relationship, contains discrete silicate ions. As an example, the formulae for these ions at Si/O ratio of 0·25–0·33, that is, at molar percentage of metal oxides from 66% to 50% are presented[3] in Table 1. The composition dependence of the structure is clearly explained by analyzing the data in the table. It is evident that discrete silicate chain ions of higher order are formed by the addition of SiO_2 to the ortho silicate (66 mole % MO) composition. This increases the size of the flow unit until the meta silicate composition (50 mole % MO) is approached with the consequent increase in the heat of activation.

These authors proposed that the different structures existing between 33 and 50 mole % CaO are $Si_3O_9^{6-}$ planar rings and $Si_4O_{10}^{4-}$ tetrahedra. Further increase in SiO_2 causes polymerization

∘   Si

○   Cation

‑ ‑ ‑ ‑   Direction of crack
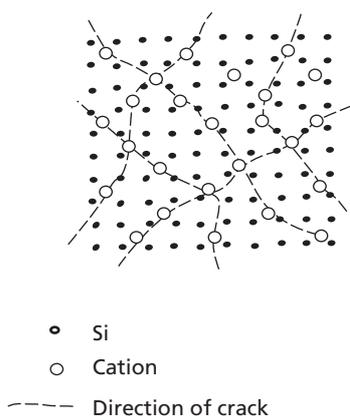
Figure 1. Mechanism of collapse of silicate lattice.

Si/O	CaO/SiO$_2$	Percentage of molar oxide	Length of chain (Å)	Empirical formula
0·250	$2CaO.SiO_2$	66	1	SiO_4^{4-}
0·286	$3CaO.2SiO_2$	60	2	$Si_2O_7^{6-}$
0·300	$4CaO.3SiO_2$	57	3	$Si_3O_{10}^{8-}$
0·307	$5CaO.4SiO_2$	55	4	$Si_4O_{13}^{10-}$
0·312	$6CaO.6SiO_2$	54	6	$Si_5O_{16}^{12-}$
0·322	$11CaO.10SiO_2$	52	10	$Si_{10}O_{31}^{22-}$
0·333	$CaO.SiO_2$	50	∞	$Si_nO_{3n}^{2n-}$

Table 1. Empirical formulae of anions in the range Si/O = 0·25–0·33 (66–50% MO).

of the rings, and bigger anions of the general formula $Si_nO_{2n+3}^{6-}$ or $Si_nO_{2n+4}^{8-}$ may result. On further addition of SiO_2, the size of the discrete anions further increases. The formation of these larger anions, on addition of SiO_2, can be presented, as below, in Equations 3 and 4:

3.
$$Si_3O_9^{6-} + 3SiO_2 \rightarrow Si_6O_{15}^{6-}$$

4.
$$Si_6O_{15}^{6-} + 3SiO_2 \rightarrow Si_9O_{21}^{6-}$$
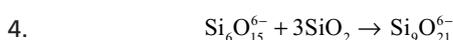
This continues and the idealized silicate ion, at 33 mole% MO, is $Si_6O_{15}^{6-}$, which is essentially formed by the linking two $Si_3O_9^{6-}$ rings. Behera et al.[6] have discussed the discrete anion theory in detail.

The limitation of the discrete anionic theory is that the theory completely ignores the formation of the free oxygen ions (O^{2-}), which increase with the increase in the metal oxide content. However, the shortcomings of the discrete anionic theory are more than explained by a model suggested[7–9] by Toop and Semis. They propose the following reactions to explain the association or polymerization of two silicate anions (Equations 5 and 6):

5.
$$2SiO_4^{4-} \rightarrow Si_2O_7^{6-} + O^{2-}$$
$$8O^- \rightarrow O^0 + 6O + O^{2-}$$
$$2O^- \rightarrow O^0 + O^{2-}$$

6.
$$SiO_4^{4-} + Si_2O_7^{6-} \rightarrow Si_3 + O_{10}^{8-} + O^{2-}$$
$$10O^- + O^0 \rightarrow 8O^- + 2O^0 + O^{2-}$$
$$2O^- \rightarrow O^0 + O^{2-}$$
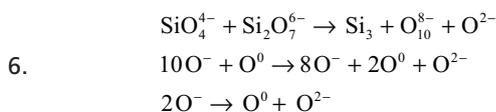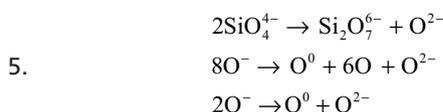
On the basis of the above, it is clearly shown that when the two silicate anions polymerize, the resultant reaction reduces to the following reaction (Equation 7):

7.
$$2O^- = O^0 + O^{2-}$$

The equilibrium constant 'k' is as follows:

8.
$$k = (O^0)(O^{2-})/(O^-)^2$$
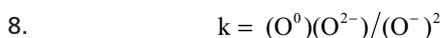
They proposed that by simple mass-balance and charge-balance considerations, it is possible to express (O^0) and (O^{2-}) in terms of (O^-) and N_{SiO_2}, where N_{SiO_2}, is the number of moles of SiO_2.

Thus, a quadratic equation would be generated that can be solved for various values of N_{SiO_2} and k. However, 'k' cannot be easily found out for a given melt at a given temperature. The value of 'k' has to be estimated, and it has to be seen if the calculated (O^{2-}) values coincide with the observed activity values for metal oxide over the entire composition range using Temkin model.[10] This is given below in Equation 9:

9. $$a_{MO} = N_{O^{2-}}$$

Thus, once (O^-) and (O^0) are known, it is possible to calculate the most probable number of silicate anions in the melt.

Different structure-based thermodynamic models of binary silicate melts have been proposed,[8,9,11–14] and these models have been exhaustively reviewed by Gaskel.[15]

These models provide a direct link between the properties and the structure of binary silicate melts. Different thermodynamic properties measured by various groups agree considerably with the theoretically calculated values using the different models as aforementioned.

Structure of silicate melts are affected by the nature of network-breaking cation (e.g. Ca^{2+}, Mg^{2+}), the fitting of certain cations (e.g. Al^{3+}, Ti^{4+}) into the silicate network and the degree of polymerization of the silicate melt, as proposed by Mysen.[16]

Investigations are conducted on the structure of molten binary $CaO-SiO_2$ and $MgO-SiO_2$ melts by means of high-temperature X-ray diffraction technique.[17] The results show that these molten silicate melts consist mainly of SiO_4 tetrahedra units up to 57 mole % alkaline earth metal oxides. Furthermore, the number of oxygen that surrounds Ca^{++} and Mg^{++} ions at the monosilicate composition is seven and five, respectively. The investigations further show that the structure of molten silicate is insensitive to temperature within the experimental temperature range.

4. Structure and viscosity of poly component and complex silicate melts

A ternary melt-containing cations of different groups may be viewed as an ideal mixture of two binary melts, provided that the total molar concentration of metal oxides remains the same.[18] On this basis, E_μ can be determined from the relationship as presented in Equation 10.

10. $$E_\mu = n_A(E_A)_x + n_B(E_B)_x$$

where, n_A and n_B are the mole fractions of the two oxides, and $(E_A)_x$ and $(E_B)_x$ are the activation energies for the two groups at the total metal oxide concentrations.

E_μ, calculated using Equation 10, agrees with the E_μ value experimentally evaluated for poly component systems. Therefore, it can be concluded that the discrete ion theory, based on binary systems, is also applicable to poly component melts. Thus, it can be further concluded that the mechanism of flow in binary and poly component silicate melts is identical at the same molar concentration of SiO_2.

In line with Equation 10, Mackenzie[18] proposed Equation 11, to calculate the viscosity of poly component systems. The calculated and experimentally evaluated viscosity values are seen to be in good agreement.

11. $$\mu = n_A(\mu_A)_C + n_B(\mu_B)_C$$

$(\mu_A)_C$ and $(\mu_B)_C$ are calculated using the empirical relationship as given in Equation 12.

12. $$\log\mu = (\alpha + \beta c) + \frac{\gamma + \delta c}{2\cdot303\,RT}$$

α, β, γ and δ are constants and 'c' is the total molar concentration of metal oxides.

Values of these constants for Group I and Group II metal oxides are determined directly from measured viscosity values of all available binary systems. These values of the constants as determined by Mackenzie[18] are listed in Table 2.

The industrial slags, involved in actual extraction process, are complex in nature. They contain oxides such as Al_2O_3, CaO, MgO and many other minor oxides. It is worthwhile to review the effect of these oxides on the viscosity of the slag.

Al_2O_3 in silicate melts acts both as network former and network modifier adopting a fourfold (AlO_4) or sixfold (AlO_6) coordinations.[19] This depends on the presence of other cations in the melt that determines whether four or six oxygen ions are required for screening the Al^{3+} ion. For instance, the presence of ions such as K^+, Na^+, having weaker potential fields, allow the polarization of O^{2-} ions and thus encourage the formation of AlO_4 groups where as lithium, with a stronger potential field, tightens the O^- ions to such an extent that more than four O^- ions are required to screen the potential field of Al^{3+} ions, and AlO_6 group formation is favored.

Group	α	β	γ	δ
I	−4·02	0·0210	60·52 × 10³	−0·752 × 10³
II	−4·99	0·0195	71·04 × 10³	−0·675 × 10³

Table 2. Constants for the calculation of viscosity.

Machin and Hanna[20] suggested that when sufficient basic oxide is present in the melt (molar ratio of Al_2O_3/CaO is less than one), Al adopts a fourfold coordination, and the melt contains SiO_4^{4-} and AlO_4^{5-} ions. However, when sufficient oxygen is not available for the formation of the Al and Si tetrahedra as aforementioned, Al adopts a sixfold coordination with oxygen and enters the interstices in the structure.[21] Thus, when basic oxides present are less than enough to provide for the required oxygen, polymeric ions as in Equations 13 and 14 will be formed.

13.

$$\left\{ O - \underset{|}{\overset{|}{Si}} - O - \underset{|}{\overset{|}{Si}} - O \right\}$$

14.

$$\left\{ O - \underset{|}{\overset{|}{Al}} - O - \underset{|}{\overset{|}{Al}} - O \right\}$$
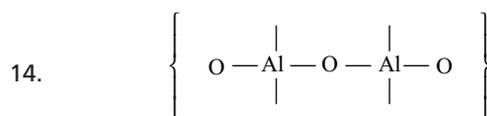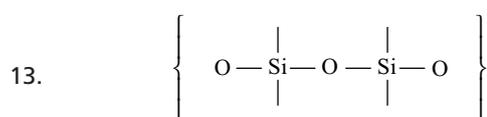
Increase in percentages of CaO and/or MgO increases the percentage of these polymeric ions in the melt, while increase in Al_2O_3 or SiO_2 decreases the same.

The degree of polymerization is represented in Equation 15.

15.
$$R = (4 - N)/2(N - 2)$$

'R' is the degree of polymerization, 'N' is the O/Si ratio (the number of oxygen atoms/the number of Al or Si atoms present in the unit).

In neutral and basic slags (Al_2O_3/CaO is less than or equal to unity), both Al_2O_3 and SiO_2 behave similarly. This means, in such slags, both Al and Si will occupy similar sites in the lattice, and the total network forming ions will be (Al + Si). However, at high Al_2O_3/CaO ratios and high silica contents, Al_2O_3 would decrease the viscosity acting as network breaker. This is consistent with the generally accepted view that alumina is amphoteric in nature.

Al-nuclear resonance studies on CaO-SiO_2-Al_2O_3 glasses[22] indicate that the oxygen coordination sphere of Al is more or less distorted. This supports the prediction of a variable coordination number of Al^{3+} ions in the melt. It can thus be appreciated that, in melts containing Al-Si, Al^{3+}-O^--type interactions are also present, besides Ca^{2+}-O^- and O^-–O^--type interactions. This Al^{3+}-O^- interactions in the melt may be high or low depending on the Al_2O_3/SiO_2 ratio, that is, the Al/(Al + Si) ratio and would increase the activation energy of viscous flow, increasing the viscosity of silicate melt.

Therefore, flow unit size alone cannot be considered as a measure of viscosity; for constant average flow, unit mass viscosity would

rise with increase in Al/(Al + Si) ratio; for the same, Al/(Al + Si) ratio, viscosity would rise with the increase in average flow unit mass.

Turkdogan and Bills[23] suggest that, at a given temperature and viscosity, the silica equivalence of alumina (N_a) is given by Equation 16:

16.
$$N_a = N_{SiO_2}(\text{binary}) - N_{SiO_4}(\text{Ternary})$$

N_{SiO_2} and N_{SiO_4} are the silica concentrations in the binary (CaO-SiO_2) and ternary (CaO-SiO_2-Al_2O_3) melts. This equation is valid when Al_2O_3/CaO ratio and SiO_2 concentrations are high. The calculated values of mole fractions of alumina is plotted against N_a for several Al_2O_3/CaO ratios in silicate melts from the respective viscosity data in Figure 2.

Poe and MacMillan[24] suggest that an oxygen-exchange mechanism involving the formation of five coordinated Al-intermediate species may play an important role in oxygen diffusion and viscosity in the calcium-aluminate liquids. They suggest that the average aluminium coordination increases as a function of increasing Al_2O_3 content in the CaO-Al_2O_3 liquids and that both five and six coordinated aluminium species become more abundant with increased Al_2O_3 content in the CaO-Al_2O_3 melts.

Data pertaining to viscosity measurement of Fe-O-SiO_2, Fe-O-CaO-SiO_2 and Fe-O-MgO-SiO_2 show that[25] the addition of MgO or CaO results in a small decrease in the viscosity where as replacing MgO or CaO by FeO, the viscosity can be decreased substantially (Figure 3). The experimenters explained that CaO, in these slags, acts primarily as a diluent for silicate anions and less
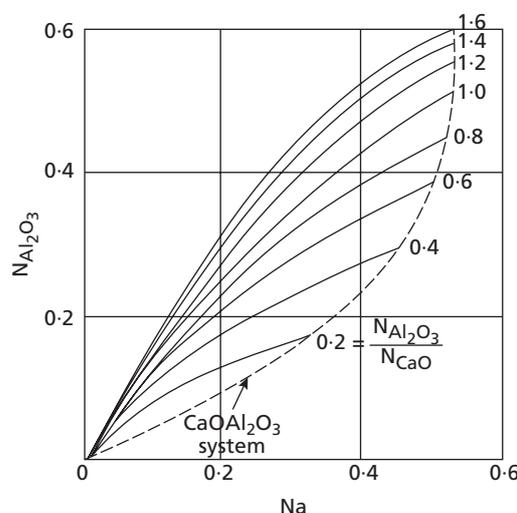
Figure 2. Silica equivalence of alumina related to molar alumina concentrations and molar Al_2O_3/CaO ratio in CaO-SiO_2-Al_2O.

as a -Si-O-Si- bridge breaker. Furthermore, they suggested that, even when CaO breaks the -Si-O-Si- bridge, the Ca^{2+} cations raise the potential barriers of the silicate anions and thus increase their contributions to the viscosity. The net result is a small decrease in viscosity with CaO addition. As is clear from the diagram (Figure 3), MgO additions lower the viscosity, but as the addition raises the liquidus temperature of the slag, the viscosity measurements are limited to N_{MgO} / N_{SiO_2} ratio of 0·2 only.

Waseda *et al.*[26] opine that, at a constant Fe/Si ratio and temperature, the slag system Fe-O-SiO_2, show a slight rise in viscosity in the region close to the faylite composition. This rise in viscosity is attributed to the bridging of Fe^{2+} cation to SiO^{4-} tetrahedra as presented in Equation 17:

17.
$$-\,\overset{|}{\underset{|}{Si}}\!-\!O^-\!-\!Fe^{2+}\!-\!O^-\!-\!\overset{|}{\underset{|}{Si}}\!-$$
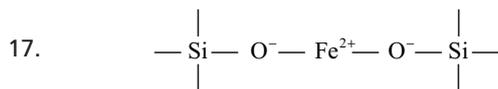
However, at higher temperatures, this structure is easily broken and viscosity is lowered as the ions acquire more energy. This finding leads to the conclusion that, within the range of compositions examined, MgO and CaO act primarily as diluents and less as slag modifiers, whereas FeO acts as a stronger modifier compared with both CaO and MgO.

Dietzel[27] suggests that the cation–oxygen attraction is in the order $Si^{4+} > Mg^{2+} > Fe^{2+} > Ca^{2+}$, on the basis that the effect of a particular cation on silicate anions depends on its attraction for oxygen. This is not in line with the suggestions made by Kucharski *et al.*[25] They suggested the order to be $Si^{4+} > Mg^{2+} > Ca^{2+} > Fe^{2+}$. This difference in opinion is probably due to the fact that these experimenters
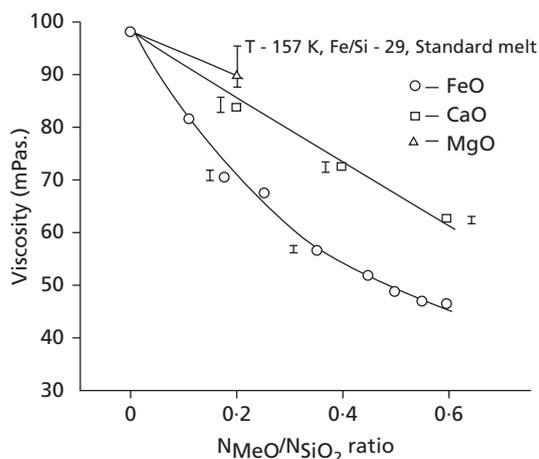
Figure 3. Viscosity results as a function of various oxide additions to Fe-O-SiO_2 melts.

did not consider the fact that the cation–oxygen interactions also depend on their surrounding neighbors.

Ferric ion, Fe^{3+}, can adopt both fourfold and sixfold coordination.[16,28] For slags containing 10% Fe_2O_3, Fe^{3+} adopts a fourfold coordination and works as a network former when the $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ ratio is greater than 0·5; the reverse happens when the ratio is less than 0·3.

According to the reactions given in Equations 18 and 19, iron oxide added to silicate melts can break the silicate anions by providing free oxygen ions.[29]

18.
$$FeO = Fe^{2+} + O^{2-}$$

19.
$$Fe_2O_3 = 2FeO^{2+} + O^{2-}$$

The iron oxide decreases the viscosity of acid slags to a greater extent compared with that in basic slags. This is because, in basic slags, the trivalent ion exists in the form of ferrite anions to a greater extent, and these ions are not able to provide free oxygen ions. Moreover, in basic slags, though the iron oxide content is low, the silicate anion is of smaller size, and hence the viscosity is already low. Consequently, in basic slags, addition of iron oxide has little effect in lowering the viscosity.

5. Parameters used to represent structure

Viscosity of the slag is one of its most sought-after characteristic structure-dependent properties. The factors 'NBO/T', 'Λ' and 'Q', as discussed below, provide a measure of depolymerization/polymerization of the slag that have a direct influence on the structure of the slag. Thus, a measure of these factors help one to analyze the viscosity of the slag on the basis of its structure and the structure of the slag on the basis of its viscosity.

The overall structure of the slag can be represented by a measure of its depolymerization and polymerization. Optical basicity of the slag is also a measure of the structure.[30]

$(NBO/T)_{corr.}$ is a measure of the depolymerization of the slag. NBO/T is the number of NBO per tetragonally bonded oxygen. $(NBO/T)_{corr.}$ can be calculated as follows:

(*i*) $\quad Y_{NB} = \sum 2[X_{CaO} + X_{MgO} + X_{FeO} + X_{MnO} + X_{CaO} + 2X_{TiO_2}$
$\qquad\qquad + X_{Na_2O} + X_{K_2O} + 3fX_{Fe_2O_3} - 2X_{Al_2O_3} - 2(1-f)X_{Fe_2O_3}],$
where, X stands for the mole fraction of respective oxides and f is the fraction of Fe^{3+} ions that act as a network breaker.

(*ii*) $\quad X_T = \sum X_{SiO_2} + 2X_{Al_2O_3} + 2fX_{Fe_2O_3} + \ldots$

(*iii*) $\quad (NBO/T)_{corr.} = Y_{NB}/X_T$

'Q' is a measure of the polymerization of the slag.

$Q = 4 - (NBO/T)$, that is, when $(NBO/T) = 0$, $Q = 4$ and when (NBO/T) assumes the value 1,2,3,4, then Q becomes 3,2,1,0, respectively.

Optical basicity (Λ) is often used as a measure of structure of the slag since both (NBO/T) and 'Q' does not differentiate between the effects of different cations on the silicate structure. Optical basicity can be measured as follows:

$\Lambda = \Sigma(X_1 n_1 \Lambda_1 + X_2 n_2 \Lambda_2 + X_3 n_3 \Lambda_3 + \ldots) / \Sigma(X_1 n_1 + X_2 n_2 + X_3 n_3 + \ldots)$

where X_1, X_2, X_3 ... = represent the respective mole fractions.

n_1, n_2, n_3 ... = number of oxygen in respective oxides, for example $n = 2$ for SiO_2, $n = 3$ for Al_2O_3.

Λ_1, Λ_2, Λ_3 ... = the recommended optical basicity values of the respective oxides.

(Some recommended optical basicity values are as follows: $Al_2O_3 = 0.60$, $CaO = 1.0$, $FeO = 1.0$, $MgO = 0.78$, $SiO_2 = 0.48$, $TiO_2 = 0.60$).

6. Viscosity of slags

The ionic structure of liquid slags affects their viscosity and thus a measurement of their viscosity helps to predict the structure of the slag.

Viscosity of silicate and oxide melts is governed by the Arrhenius equation (Equation 20).

20.
$$\mu = A \exp(E_\mu / RT)$$

However, a change in the structure may break the straight line relationship. If rise in temperature causes a general weakening of the cation and discrete anion bond, then E_μ remains constant within the temperature range. On the other hand, if the rise in temperature causes a decrease in the viscosity due to gradual breakdown of the discrete anions into small flow units, the E_μ value changes with the change in temperature.

According to transition state theory, viscosity can be expressed by Equation 21:

21.
$$\mu = (Nh/V) \exp(-\Delta S^* / R) \exp(\Delta H^* / RT)$$

where, N = Avogadro's number; h = Plank's constant; V = molar volume of flow units, ΔS^* = entropy of activation = $S^* - S_i$, where

S^* = entropy of flow unit in the activated state, S^i = entropy of flow units in the normal state; ΔH^* = activation energy of viscous flow (heat of activation) = $(H^* - H_i)$, where H^* = heat of activation of the flow unit in the activated state, H_i = heat of activation of the flow unit in the normal state

It must be recorded that ΔH^* depends on two factors:

(*i*) The average flow unit size (increases with the size of the flow unit).
(*ii*) The strength and number of various columbic interactions between the flow units and the surrounding species.

In binary silicate melts, the columbic interactions may be attractive in nature, such as M^{++}–O^- interactions (singly bonded oxygens of the flow units and the metallic ions) or repulsive, such as O^-–O^- interactions (between two singly bonded oxygen of two different flow units). Greater the number of M^{++}–O^- interactions, higher is ΔH^* and greater the O^-–O^-, lesser is the ΔH^* value. This clearly illustrates that the greater the former is, the lesser is the entropy S^i and hence higher will be the ΔH^*, and that, for similar reasons, repulsive interactions would tend to decrease the ΔH^* value.

From Equation 20, it is clear that effect of variation of ΔS^* and V is opposite to that of ΔH^*. However, since viscosity decreases with increasing additions of metal oxide, it is obvious that the effect of variation of ΔH^* value is more dominant.

The slags of more practical interest are CaO-MgO-Al_2O_3-SiO_2-type quaternary slags. Machin *et al.*[31–33] systematically measured the viscosity of these systems over a wide range of compositions. Their findings, on the basis of composition variations, are listed below:

(*i*) When silica is below 40% or over 60%, Al_2O_3 appears to be less effective in increasing the viscosity.
(*ii*) In the range of 40–60% SiO_2, the effect of Al_2O_3 on the viscosity of the melt is as great as that of silica.
(*iii*) At constant CaO content, decrease in MgO increases the viscosity of the melt, if SiO_2 is constant.
(*iv*) When SiO_2 and Al_2O_3 are constant, increase in MgO decreases the viscosity up to 10 wt.% additions.
(*v*) When MgO is increased to 20 wt.%, the decrease in viscosity for same SiO_2 and Al_2O_3 value is more pronounced.

Similar findings have been reported by Yakushev *et al.*,[34] investigating with a synthetic slag containing of 40–48% CaO, 17.5–40% Al_2O_3, 15–30% SiO_2 and 4–12% MgO.

It is reported[4,18] that alkaline earth oxides are interchangeable in their effect on the viscosity of binary melts and that similar behavior is also expected to hold for quaternary melts. This is also illustrated graphically by Turkdogan and Bills[23] as in Figure 4. The figure

indicates that the viscosity data of binary, ternary and quaternary melts could be represented by a single curve with a small scatter. It can also be observed that lime and magnesia are replaceable on the molar basis.

Kawahara et al.[35] suggest that MgO is amphoteric in nature. They report that, in the CaO-MgO-SiO_2 system, MgO behaves like CaO, but in the Na_2O-CaO-MgO system, it acts as an acidic oxide, that is, like all amphoteric oxides, the strength of MgO as a basic oxide increases with decreasing basicity of the melt.

7.   Viscosity of blast furnace slags

The variation of viscosity of actual blast furnace slags as obtained from industry, with composition, is reported to be complicated by various workers.[36–39] However, there is a general agreement as follows:

(*i*)   The higher the MgO content of the slag, the lower is the desired CaO/SiO_2 ratio for optimum viscosity.

(*ii*)   A high MgO combined with a high CaO/SiO_2 ratio results in a short slag (difference between flow temperature and liquidus temperature is low).

(*iii*)   High-alumina blast furnace slags (20–34% Al_2O_3) show erratic viscosity variations. This is because, when Al_2O_3 content is constant, higher CaO/SiO_2 ratio results in an increase in the Al/Si ratio; while high CaO/SiO_2 ratio tends to decrease the viscosity of the slag, an increased Al/Si ratio tends to increase the viscosity.

Titaniferrous ores smelted in the blast furnace are found to cause problems, such as accretions, scaffolds, hearth clogging and high fuel consumption.[40] Experimenters[41–45] have reported the effect of different titanium oxides (TiO, TiO_2, Ti_2O_3) on the viscosity and

Figure 4. Variation of viscosity with composition of CaO-MgO-Al_2O_3-SiO_2 melts at 1500°C.

liquidus temperature of resulting slags. The findings, in general, agree that, all oxides of titanium, up to a total amount of 10 wt.%, are effective in reducing the viscosity when the slag is slightly acidic so long as titanium carbide is not formed. Handfield and Charette[44] further suggested that Ti_2O_3 is a much more effective network modifier than TiO_2. These workers also report that, in titania bearing slags, when Al_2O_3 exceeds 23% and MgO exceeds 10 wt.% with $(CaO + MgO)/(SiO_2 + Al_2O_3)$ exceeding 0·95, the slag tends to achieve shortness.

Athappan[46] measured and reported viscosity data of blast furnace slag at 20% Al_2O_3 for varying MgO content. He concludes that, at 1450°C, the viscosity decreases with increase in MgO content. However, after MgO additions exceed 10%, further addition has no impact on viscosity. Gupta and Chatterjee[1] reported viscosity data of blast furnace slag with high FeO content (bosh slag when burden contains iron ore). They concluded that blast furnace–burden composition should be such that initial slag formation should start at a temperature higher than 1300°C.

Lee et al.[47] reported the viscous behavior of CaO-SiO_2-Al_2O_3-MgO-FeO slag. Under the compositions studied, they observed that the viscosity of blast furnace–type slag decreased with increased FeO content[48] at a fixed CaO/SiO_2 ratio (basicity) of slags. Slag viscosity showed a minimum value with increasing MgO content of slag when FeO is low (<7·5%). From the data obtained, it is concluded that the addition of MgO does not affect the viscosity at FeO ≥7·5%. A minimum value is obtained at about 7% MgO with 5% FeO.

In line with Bockris and Lowe[3] and Toop and Semis,[9] they reported that slag viscosity decreases continuously with basicity up to about 1·3 CaO/SiO_2 ratio, and the viscosity actually increases as the basicity increases from 1·3 to 1·5. In line with the findings of Zhang and Jahansahi,[49] they proposed that the driving force for decrease in viscosity with increase in basicity is an increase in the degree of depolymerization of the silicate network as a consequence of which the silicate structure changes from the 3D network to discrete anionic groups containing simple chains and/or rings. They also proposed that the driving force for increase in viscosity beyond CaO/SiO_2 ratio >1·3, is an increase in the chemical potential of the primary solid phase $2CaO.SiO_2$ (dicalcium silicate) derived from the fact that the viscosity isotherms with composition are similar to phase diagrams of the alloy and slag systems.[50]

Lee et al.[51] furthered their investigations to explain the disagreement of the viscosity data with the degree of depolymerization using infrared spectra and measuring the liquidus temperature using differential thermal analysis for the samples. On the basis of their studies, they proposed the following:

(*i*)   A depolymerization and the liquidus temperature of the slag affect its viscosity.
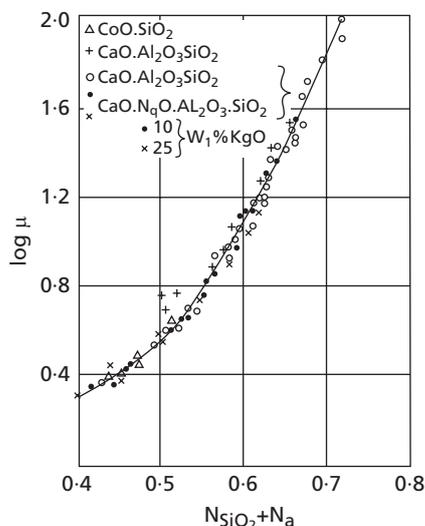
(*ii*) Degree of depolymerization affects the viscosity more when the difference between the prevailing temperature and the liquidus temperature is high.

(*iii*) Liquidus temperature affects the viscosity more when the difference between the two temperature is low, that is, when the prevailing experimental temperature approaches the liquidus temperature.

The effect of MgO content on the viscosity of blast furnace slag is reported by Jia and Shih- Hsien.[52] For the semisynthetic slag containing SiO_2-MgO-CaO-Al_2O_3, they predicted a better stability in viscosity data when MgO = 5·4 mass %, Al_2O_3 = 10–15 mass % and CaO/SiO_2 = 1·2. They found out that the slag viscosity, within the range of compositions studied, is independent of MgO content when MgO = 5–9 mass %, Al_2O_3 = 15 mass % and CaO/SiO_2 = 1·0–1·2.

In a novel attempt Togobitskaya *et al.*[53] conducted an exclusive study of the blast furnace operations in transient conditions. Under the experimental conditions, they proposed the following for smooth operation of the blast furnace:

(*i*) The early slag at 1350°C, during blowing in, should have a viscosity varying from 0·4 to 2·0 Pa.s.

(*ii*) In the working mode, viscosity of the slag is optimum at 1450–1500°C and should be less than 0·25–0·2 Pa.s.

(*iii*) During blowing out, the slag must have good flowability, and its viscosity should not exceed 0·2–0·3 Pa.s at 1450–1550°C.

Muller and Erwee[54] developed models for predicting viscosities and liquidus temperatures of blast furnace slags. The viscosity data generated by several workers[55,56] are used to validate the models. It is observed that the typical blast furnace slag containing SiO_2, Al_2O_3, MgO and CaO as major constituents and FeO, MnO, TiO_2,
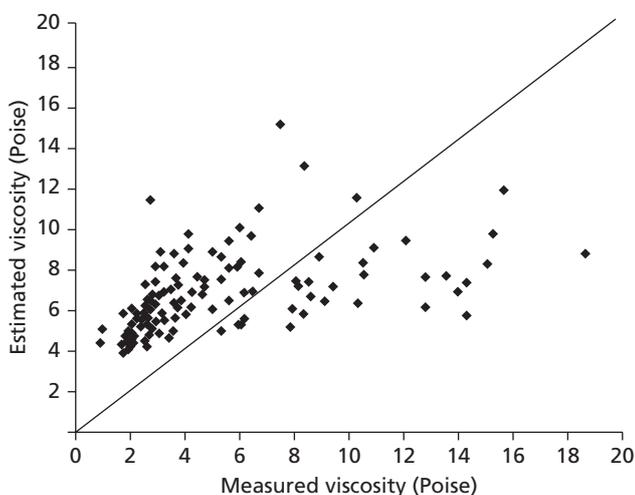
Figure 5. Correlation plot of the predicted effective viscosities versus the measured viscosities from literature.

Na_2O, K_2O and S as minor constituents exhibit a general lowering of viscosity due to broken silicate bonds when the basicity is increased. However, this increase in basicity causes an increase in the viscosity of the slag due to solid precipitation. It is further observed that SiO_2 and Al_2O_3 contribute to the increase in the viscosity with their highly covalent bonds and that monoxides such as Cao and MgO exhibiting an ionic behavior, lower the viscosity destructing the silicate network. This is in line with the work of Lee *et al.*[51] However, an increase in the addition of monoxides leads to higher activities of solid phases resulting in the precipitation of the solid phase increasing the overall viscosity.

The slag atlas[57] is used to estimate the stable solid phases forming in the blast furnace slag under equilibrium conditions. The Fact Stage software is used to calculate the phase equilibrium from the thermodynamic data. The corrected (effective) viscosity is estimated; after recording, the predicted fraction of stable solid phases present using Roscoe equation[58] given below:

22. $$\eta_{eff} = \eta_{liq}(1 - 1 \cdot 35\phi)^{-2\cdot5}$$

where, η_{liq} is the liquid viscosity (Pa.s), η_{eff} is the corrected viscosity (Pa.s) and φ is the volume fraction of the solids predicted in the liquid slag.

The correlation between the effective viscosities predicted by the model and the viscosities measured[51,59] are presented in Figure 5. It is observed that the predicted and the measured values agree well at lower viscosity values relating to higher temperatures but the agreement deteriorates at higher viscosities.

8.   Conclusions
The review of literature, thus, establishes a scope for optimizing the slag composition such that the target, tappable viscosity, can be obtained, which would enable the operation to run with decreased energy requirements. Such an operation would ensure an appropriate relationship between viscosity of the blast furnace slag and the temperature coupled with the optimum composition resulting in the most effective separation of the metal from the slag enhancing the recovery of the metal of desired composition.

REFERENCES
1. Gupta, S. S.; Chatterjee, A. *Iron Making and Steel Making Theory & Practice*. Washington: SBA Publication, 1995.
2. Paul, M. *Principles of Chemical Thermodynamics*. New York: McGraw-Hill, 1951, 146.
3. Bockris, J. O. M.; Lowe, D. C. Viscosity and the structure of molten silicates. *The Royal Society* **1954**, *226*, 423–435.
4. Bockris, J. O. M.; Kitchener, J. A.; Mackenzie, J. D. Viscous flow in silica & binary liquid silicates. *Transactions of the Faraday Society* **1995**, *51*, 1735–1748.

5. Bockris, J. O. M.; Tomlinson, J. W.; White, J. L. The structure of liquid silicates: partial molar volumes & expansivity. *Transactions of the Faraday Society* **1956**, *52*, 299–310.

6. Behera, R. C.; Mohanty, U. K.; Mohanty, A. K.; Viscosity & constitution of slags associated with metallorthermic extraction of some less common metals. *High Temp Materials & Processes* **1990**, *9*, 57–75.

7. Toop, G. W. *Some New Ionic Concepts of Silicate Slags*. MASc thesis, University of British Colombia, Vancouver, Canada, 1960.

8. Toop, G. W.; Semis, C. S. Activities of ions in silicate melt. *Canadian Metallurgical Quarterly* **1962**, *1*, 129–151.

9. Toop, G. W.; Semis, C. S. Activities of ions in silicate melt. *Transactions of the Metallurgical Society* **1962**, *224*, 878–887.

10. Temkin, M. An approach to the problem of ionic distribution in liquid silicates. *Acta Physicochimica URSS* **1945**, *20*, 411–420.

11. Masson, C. R. Determination of ionic distribution of three sorts of oxygen in a few binary silicate glasses from molar refractivity. *Proceedings of the Royal Society London* **1965**, *287(A)*, 201–221.

12. Whiteway, S. G.; Smith, I. B.; Masson, C. R. Stoichiometry & thermodynamics of metallurgical process. *Canadian Journal of Chemistry* **1970**, *48*, 33–46.

13. Borgiani, C.; Granati, P. Thermodynamic properties of silicates & of alumino–silicates from montecarlo calculations. *Metallurgical Transactions B* **1977**, *8*, 147–151.

14. Lin, P. L.; Pelton, A. D. A structural model for binary silicate systems. *Metallurgical Transactions* **1979**, *10(B)*, 667–675.

15. Gaskel, D. R. A statistical model of polymerization/depolymerization relationships in silicate melts and glasses. *Canadian Metallurgical Quarterly* **1981**, *1*, 3–19.

16. Mysen, B. O. Relationship between silicate melt structure and petrologic processes. *Earth Science Review* **1990**, *27*, 281–365.

17. Waseda, Y.; Togury, J. M. The structure of molten binary silicate systems CaO–SiO$_2$ and MgO-SiO$_2$. *Canadian Metallurgical Transaction* **1977**, *8(b)*, 563–568.

18. Mackenzie, J. D. The discrete ion theory & viscous flow in liquid silicate. *Transactions of the Faraday Society* **1957**, *53*, 1488–1498.

19. Weyl, W. A. The significance of the co-ordination requirements of cations in the constitution of glass. *Society of Glass Technology* **1951**, *35*, 421–447.

20. Machin, J. S.; Hanna, D. L. Viscosity studies of system CaO-MgO-Al$_2$O$_3$-SiO$_2$: 1.40%SiO$_2$. *Journal of the American Ceramic Society* **1945**, *28*, 310–316.

21. Moore, H.; McMillan, P. W. A study of glasses consisting of the oxides of element of low atomic weight. *Society of Glass Technology* **1956**, *40*, 66–138.

22. Ditz, H.; Schulz, G. W. The spectra resemble a theoretical spectrum calculated for such broad distribution. *Glasstech Bermuda* **1969**, *42*, 83–89.

23. Turkdogan, E. T.; Bills, P. M. A critical review of viscosity of CaO-MgO-Al$_2$O$_3$-SiO melts. *Bulletin of the American Ceramic Society* **1960**, *39*, 682–687.

24. Poe, B. T.; McMillan, P. F. High coordinate Si & Al in sodium aluminosilicate glasses quenched. *Journal of the American Ceramic Society* **1994**, *77*, 1832–1838.

25. Kucharski, M.; Stubina, N. M.; Togury, J. M. Viscosity measurement of molten Fe-O-SiO$_2$,Fe-O-CaO-SiO$_2$ and Fe-O-Mgo-SiO$_2$ slags. *Canadian Metallurgical Quarterly* **1989**, *28*, 7–11.

26. Waseda, Y.; Shiraishi, Y.; Toguri, J. M. Structure of the molten FeO-Fe$_2$O$_3$-SiO$_2$ system by X-Ray diffraction. *Materials Transactions – Japan Institute of Metals* **1980**, *21*, 51–62.

27. Dietzel, A. The cation field strengths and their relationships to devitrifying processes, to compound formation, and to melting points of silicates. *Z Electrochemistry* **1942**, *48*, 9–23.

28. Morinaga, K.; Suginohara, Y.; Yanagase, T. Oxygen coordination number of Fe ions in CaO-SiO$_2$ and Na$_2$O-SiO$_2$ systems. *Japan Institute of Metals and Materials* **1976**, *40*, 480–486.

29. Seki, K.; Oeters, F. Viscosity measurements liquid slags in the system CaO-FeO-Fe$_2$O$_3$-SiO$_2$. *Transactions of Iron and Steel Institute of Japan* **1984**, *24*, 445–454.

30. Mills, K. *The Estimation of Slag Properties (short course presented as a part of Southern African Pyrometallurgy)*. **2011**.

31. Machin, J. S.; Yee, T. B. Viscosity studies of system CaO-MgO-Al$_2$O$_3$-SiO$_2$: II, CaO-Al$_2$O$_3$-SiO$_2$. *Journal of the American Ceramic Society* **1948**, *31*, 200–204.

32. Machin, J. S.; Yee, T. B.; Hanna, D. L. Viscosity studies of system CaO–MgO–Al$_2$O$_3$–SiO$_2$: III, 35, 45, and 50% SiO$_2$. *Journal of the American Ceramic Society* **1952**, *35*, 322–325.

33. Machin, J. S.; Yee, T. B. Viscosity studies of system CaO–MgO–Al$_2$O$_3$–SiO$_3$: IV, 60 and 65% SiO$_2$. *Journal of the American Ceramic Society* **1954**, *37*, 177–186.

34. Romashin, V. M. Y.; Amfiteatrov, V. A. Viscosity of CaO based slags with variable Al$_2$O$_3$, SiO$_2$, and MgO contents. *Steel in USSR* **1977**, *7*, 617–618.

35. Kawahara, M.; Morinaga, K. J.; Yanagase, T. Behavior of MgO and NiO in molten slags. *Canadian Metallurgical Quarterly* **1983**, *22*, 143–147.

36. Sukolov, G. A.; Gul'tyai, I. I. Ways of changing the composition of final blast-furnace slags. *STAL in English* **1965**, *12*, 951–955.

37. Singh, N.; Muthykrishnan, V.; Rajozinski, T. Viscosity of blast furnace slags and its effects on their applications. *MML Technology Journal* **1970**, *12*, 12–21.

38. Gupta, V. K.; Seshadri, V. Studies on viscosity of high-alumina blast furnace slags. *Transactions of the Indian Institute of Metals* **1973**, *26*, 55–64.

39. Singh, R. N. Viscosity measurements of high alumina blast furnace slags. *Steel India* **1984**, *7*, 73–83.

40. Ross, H. V. Smelting titaniferrous ores. *Journal of Metals* **1958**, *50*, 407–411.

41. Mikhailov, V. V.; Belyakova, G. B. Effect of the oxides of titanium on the fluidity of blast furnace slags. *Ural Met*. **1939**, *6*, 7–9.

42. Semik, I. P. Viscosity of titaniferrous blast furnace slags. *Bulletin of the Academy of Sciences USSR* **1941**, *4*, 55–66.

43. Handfield, G.; Charette, G. G. Viscosity and structure of industrial high TiO2 slags. *Canadian Metallurgical Quarterly* **1971**, *10*, 235–243.

44. Handfield, G.; Charette, G. G.; Lee H. Y. Viscosity of industrial titania slags. In *Light Metals*. New York: AIME, 1971, 591–601.

45. Handfield, G.; Charette, G. G.; Lee, H. Y. Viscosity of industrial titania slags. *Journal of Metals* **1972**, *17*, 1–4.

46. Athappan, R. *Refresher Course on Iron Making Under Indian Conditions*. Ranchi: RDCIS, SAIL, 1985.

47. Lee, Y. S.; Kim, J. R.; Yi, S. H.; Min, D. J. Viscous behaviour of $CaO-SiO_2-Al_2O_3-MgO-FeO$ slag. In *VII International Conference on Molten Slags, Fluxes and Salts. The South African Institute of Mining and Metallurgy*, **2004**, 225–230.

48. Tansakanen, P. A.; Huffunen, S. M.; Manila, P. H.; Harakki, J. J. Experimental simulations of primary slag formation in the blast furnace process. In *6th International Conference on Molten Slags, Fluxes and Salts*, Stockholm, Sweden, 2000.

49. Zhang, L.; Jahansahi, S. Review and modeling of viscosity of silicate melts: Part I. Viscosity of binary and ternary silicates containing CaO, MgO, and MnO. *Metallurgical and Materials Transactions* **1998**, *29B*, 177–186.

50. Seetharaman, S.; Sichen, D. Viscosities of high temperature systems: a modeling approach. *ISIJ International* **1997**, *37*, 109–118.

51. Lee, Y. S.; Min, D. J.; Jung, S. M.; Yi, S. H. Influence of basicity and FeO content on viscosity of blast furnace type slags containing FeO. *ISIJ International* **2004**, *44*, 1283–1290.

52. Shiau, J.-S.; Liu, S.-H. Effect of magnesium oxide content on final slag fluidity of blast furnace. *China Steel Technical Report* **2008**, *21*, 21–28.

53. Togobitskaya, D. N.; Mojharenko, N. M.; Belkova, A. L.; Stepanenko, D. A. Analytical evaluation of properties of blast-furnace slag providing proper operation of furnace in transient conditions. *Iron and Steel Institute of National Academy of Science of Ukrain, Metallurgical and Mining Industry* **2010**, *4*, 249–254.

54. Muller, J.; Erwee, M. Blast furnace control using slag viscosities and liquidus temperatures with phase equilibria calculations. *Southern African Institute of Mining and Metallurgy* **2011**, *111*, 309–326.

55. Mills, K. C. Viscosities of molten slags. In *Slag Atlas, 2nd edn.*. Dusseldorf: Verlag Stahleisen, 1995, 349–354.

56. Kondratiev, A.; Jak, E.; Hayes, P. C. Predicting slag viscosities in metallurgical systems. *Journal of Metals* **2002**, *54*, 41–45.

57. *Slag Atlas, 2nd edn*. Dusseldorf: Verlag Stahleisen, 1995, 167.

58. Roscoe, R. The viscosity of suspensions of rigid spheres. *British Journal of Applied Physics* **1952**, *3*, 267–269.

59. Kim, J. R.; Min, D. J.; Jung, S. M.; Yi, S. H. Influence of MgO and Al_2O_3 contents on viscosity of blast furnace type slags containing FeO. *ISIJ International* **2004**, *44*, 1290–1297.