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THE INFLUENCE OF STRUCTURE ON THE PHYSICO-CHEMICAL PROPERTIES OF SLAGS

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Synopsis: The current status of our knowledge on the structures of silicate slags is outlined and relationships are established between property values for slags and measures of the depolymerisation of the melt viz the (NBO/T) ratio and the optical basicity corrected for the cations required to charge balance any AlO_4^{5-} tetrahedra present. Values of the following properties are dependent upon the structure: viscosity, electrical and thermal conductivity, diffusion coefficient, density and thermal expansion coefficient. It has been found that the degree of depolymerisation is the primary factor affecting these properties, the nature of the cations having only a secondary effect.

Key words: Slags, silicates, structure, (NBO/T), optical basicity, physical properties, viscosity, electrical conductivity, thermal conductivity, diffusion coefficient, density, thermal expansion coefficient.

1. INTRODUCTION

The mathematical modelling of the fluid and thermal flow in high temperature processes has become an established method for improving the performance and efficiency of these processes. This approach has resulted in a demand for physical property data for the materials involved. However, the determination of reliable property values at high temperature is both difficult and time-consuming and consequently there is a need for models to predict the physical properties of slags quickly from the chemical composition, which is routinely available.

Various models have been reported for the prediction of slag properties but for the most part these are based on numerical fits of experimental data and are rarely based on the structure of slag. However the work of Bockris [1] and others has demonstrated the link between the physical properties and the structure of slags. Thus the demand for more reliable property data, (which has accompanied the development of algorithms to describe processes), will only be met by using models which are based on the structure of the slag.

Our knowledge of slag structure has improved enormously in recent years with the introduction of new techniques such as x-ray and neutron diffraction, vibrational (especially Raman) spectroscopy and nuclear magnetic resonance. Data from these sources combined with information from structural thermodynamic models, molecular dynamics calculations and physical property data has led to a rapid advance in our knowledge of the structure of silicates. Much of the recent work on slag structure has been carried out by geologists and is summarised in the excellent review of Mysen [2].

2. STRUCTURE OF SILICATES

The principal features affecting the structure of molten silicates [2] are outlined below:

(i) Silicate slags consist of 3-dimensional (3-D) interconnected networks of SiO_4^{4-} tetrahedra in which silicons are joined by bonding oxygen atoms (0^o). The gradual addition of cations (eg Na^+, Ca^{2+}) results in the progressive breaking of these oxygen bonds with the formation of non-bridging oxygens (NBO), denoted 0^- and eventually the formation of free oxygen, 0^{2-}, ions.

(ii) The melt contains various 3-D interconnected, anionic units, eg SiO_2, $Si_2O_5^{2-}$, $Si_2O_6^{4-}$, SiO_7^{6-} and SiO_4^{4-} which coexist in the melt. These anionic units probably contain 3-6 atoms and can exist in the form of chains, sheets and rings. The introduction of more network-breaking cations, eg Ca^{2+} does not alter the nature of the anionic units but does affect the amounts of the various units, ie high concentrations of more depolymerised units are formed.

(iii) For a specific mole fraction (x) of oxide (eg x(CaO)) the nature of the cation does affect the proportion of the various units, eg $Si_2O_7^{6-}$ but not the overall degree of polymerisation. The anions with smaller radii (r) and higher valence (z), eg Mg^{2+}, favour the formation of the more depolymerised (eg SiO_4^{4-}) and polymerised (eg SiO_2) anionic units. The tendency to form more extreme anionic units can be ranked in terms of the parameter (z/r^2) in the hierarchy $Mg^{2+} > Ca^{2+} > Sr^{2+} > Pb^{2+} > Ba^{2+} > Li^+ > Na^+ > K^+$.

(iv) Other cations such as Al^{3+}, Fe^{3+}, B^{3+}, Ti^{4+} and P^{5+} can form tetrahedra (eg AlO_4^{5-}) which can fit into the 3-D silicate units and enhance the overall polymerisation of the melt; thus it is customary to refer to tetrahedrally-coordinated units by T rather than Si, eg TO_2, T_2O_5 etc. However AlO_4^{5-} ions have a different charge to SiO_4^{4-} tetrahedra and thus cations are needed, to provide electrical charge balance eg $(NaAlO_4)^{4-}$ and thus the Na^+ must be sited close to the Al atoms.

(v) There is some evidence of ordering in melts with small divalent cations (eg Mg^{2+}) which results from the requirement for the Mg^{2+} to satisfy either 0^- bonds or two AlO_4^{5-} tetrahedra.

(vi) Ferric ions, Fe^{3+} can adopt both four-fold (IV) or six-fold (VI) coordination, ie act as both network former and breaker, respectively. For slags containing 10% Fe_2O_3 it has been reported [11,12] that Fe^{3+} (IV) and (VI) coordination are favoured when the $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ ratios are > 0.5 and < 0.3, respectively. In most steelmaking slags Fe^{3+} will act as a network-breaker (VI).

Measure of the degree of polymerisation

The (NBO/T) ratio ie the number of non-bridging oxygens per tetrahedrally-coordinated atom eg (Si, Al) is considered by many to provide the best measure of the global degree of depolymerisation of the melt [2]. The (NBO/T) does take into account the concentration of cations required to charge balance AlO_4^{5-}, FeO_4^{5-} etc.

In recent years, considerable attention has been devoted to the optical basicity (Λ) which represents the power of an oxide to donate negative charge. However the optical basicity has been reported to provide a global measure of the concentrations of 0^o, 0^- and 0^{2-} present in the melt [12]. Consequently, the optical basicity may be considered to provide an alternative measure of the degree of polymerisation. However the optical basicity (Λ) does not take into account the fact that some of the cations in alumino-silicates are required for charge balancing duties: The corrected optical basicity, Λ_{corr}, used here was derived by adjusting the overall composition of the slag by subtracting the concentration of oxide (eg K_2O, CaO) needed for charge-balancing, the oxides with highest Λ being selected first.

Measure of the cation effect

Various parameters have been used as a measure of the effect of different cations on the structure and physical properties; Mysen [2] preferred the parameter (z/r^2) where z and r are the valence and radius of the cation, respectively. It has been shown in this study that (z/r^2) is inversely proportional to the optical basicity of the oxide.

3. PHYSICAL PROPERTIES

Most physical properties are strongly dependent upon temperature, thus when comparing slags with different liquidus temperatures, T_{liq}, it is necessary to compare property values at some reference temperature. The value at T_{liq} was selected since the structures of the melt would be unaffected by temperature and would allow the properties to be compared on an equal basis.

The temperature dependence of most transport properties can be represented by the Arrhenius relationship (Equation 1) where P is the property E the activation energy, R the Gas Constant and T the thermodynamic temperature.

$$P = A \exp (E_p/RT) = A \exp (B_p/T) \qquad (1)$$

3.1 Viscosity (η)

Since viscosity (η) data originating from different laboratories are prone to appreciable scatter, (± 50%) it was decided to use a data base based on the extensive work of Urbain [3] since these values were regarded as both reliable and self-consistent and consequently should reveal any trends in the data.

The relationships between ln η_m and the (NBO/T) ratio and Λ_{corr} are shown in Figures 1a and b respectively.

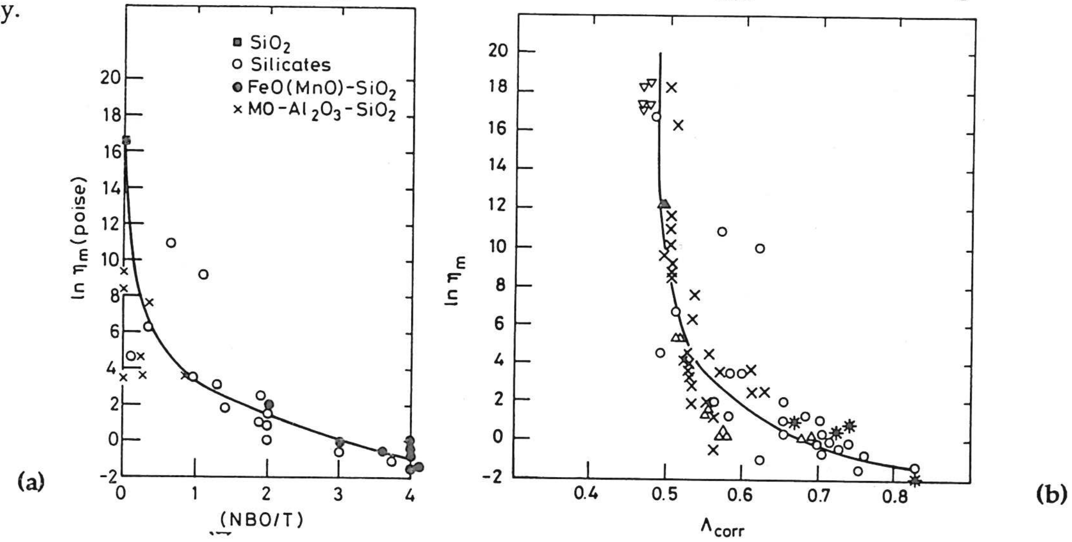

Figure 1 Viscosity as a function of (a) (NBO/T) (b) corrected optical basicity; o, ●, *, silicates; x, alumino-silicates.

It can be seen that there is a good correlation between ln η_m and the two measures of depolymerisation of the melt. However it can be seen from Figure 1a that there are appreciable differences in the ln η_m values for the alumino-silicates with (NBO/T) = 0 and the deviation was found to increase with increasing Al content. Inspection of Figure 1b indicates that Λ_{corr} provides some compensation for the effect of Al_2O_3 on ln η_m.

The activation energy (Eη) is usually regarded as the energy required to break bonds to enable viscous flow to occur. Plots of Eη as a function of (NBO/T) and Λ_{corr} revealed good correlations and also the inability of the (NBO/T) ratio to account for the effect of Al substitution on Bη (= Eη/R); this is shown in Figure 2. This behaviour results from the fact that the bond length Al-O is longer than that of Si-O (1.715 cf 1.58 Å) [2] and it was noted that Λ_{corr} provided some compensation for this effect. It can also be observed in Figure 2 that the effect of Al_2O_3 on Bη increases as (z/r^2) for the cation increases (or Λ for the oxide decreases). This may be a consequence of increased ordering produced when small, divalent cations are needed to charge balance two AlO_4^{5-} tetrahedra.

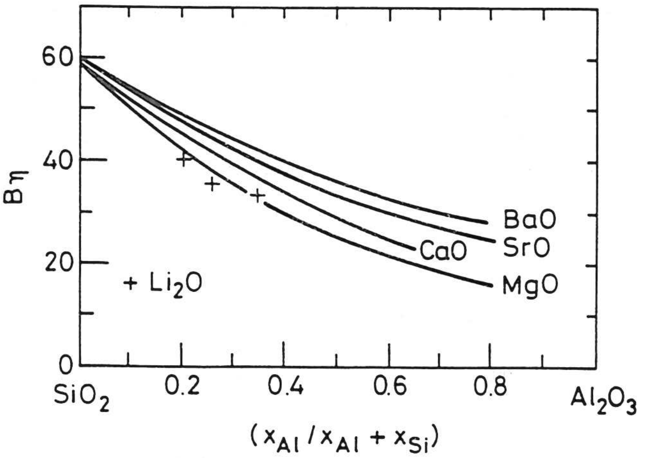

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Figure 2 The activation energy term Bη (= Eη/R) as a function of Al substitution in the silicate network for slags will (NBO/T) = 0.

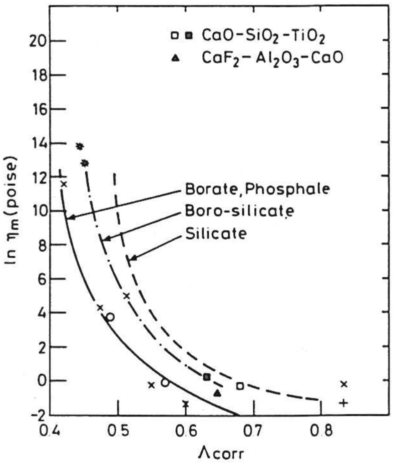

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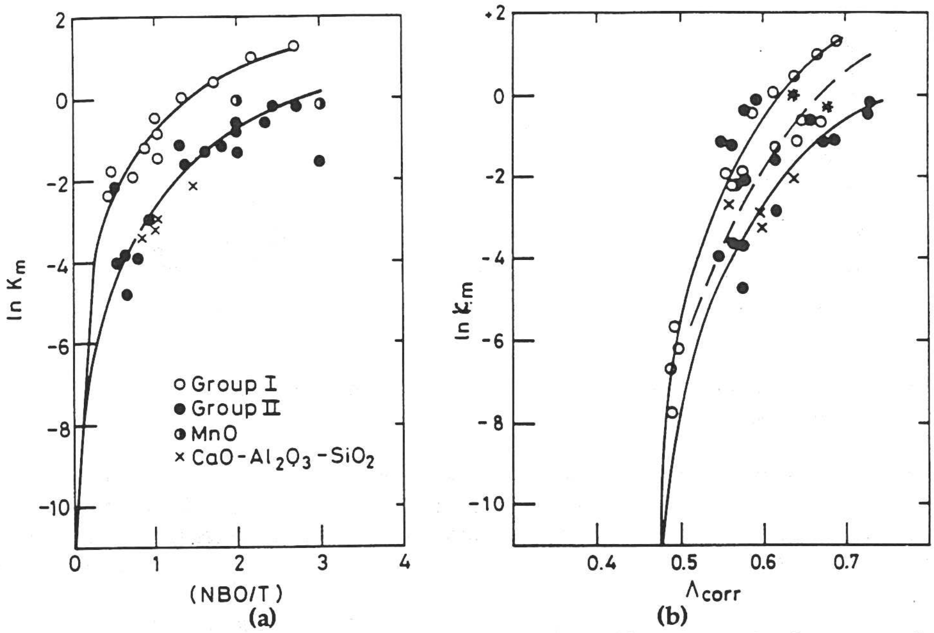
Figure 3 The ln η_m as a function of›r Λ_{corr} for borates and phosphates.

One of the attractions of the optical basicity concept is that it could be applied to other forms of slags and it can be seen from Figure 3 that the relationship for borates and phosphates have a similar form to that of silicates but the curves are moved to lower optical basicities since $\Lambda(B_2O_3)$ and $\Lambda(P_2O_5)$ are lower than $\Lambda(SiO_2)$. Recent work has shown that viscosities of glasses for temperatures between T_{liq} and the glass transition (Tg) temperature can be reliably estimated using Λ_{corr}.

3.2 Electrical Conductivity (κ)

Specific electrical conductivity (κ) data reported by Bockris et al [4] for 8 binary silicates and by Winterhager et al [5] for alumino-silicates were extrapolated to T_{liq} and the plots of ln κ_m as functions (NBO/T) and Λ_{corr} are shown in Figures 4a and b, respectively.



(a) (b)

Figure 4 Ln κ_m as functions of (a) (NBO/T) (b) corrected optical basicity o, ● silicates, x, alumino silicates.

The following observations were made:

(i) The value of ln κ_M increases markedly with increasing depolymerisation, ie increasing NBO/T and Λ_{corr} values, and thus it appears that the hinderance of catonic mobility by the silicate network is the primary factor affecting electrical conductivity and not the mobility of the cations as suggested by Bockris.

(ii) The ln κ_m values for Group I oxides were higher than those for Group II oxides; this may be due to ordering of the melt to accommodate the need for M^{2+} ions to be sited near two O^-.

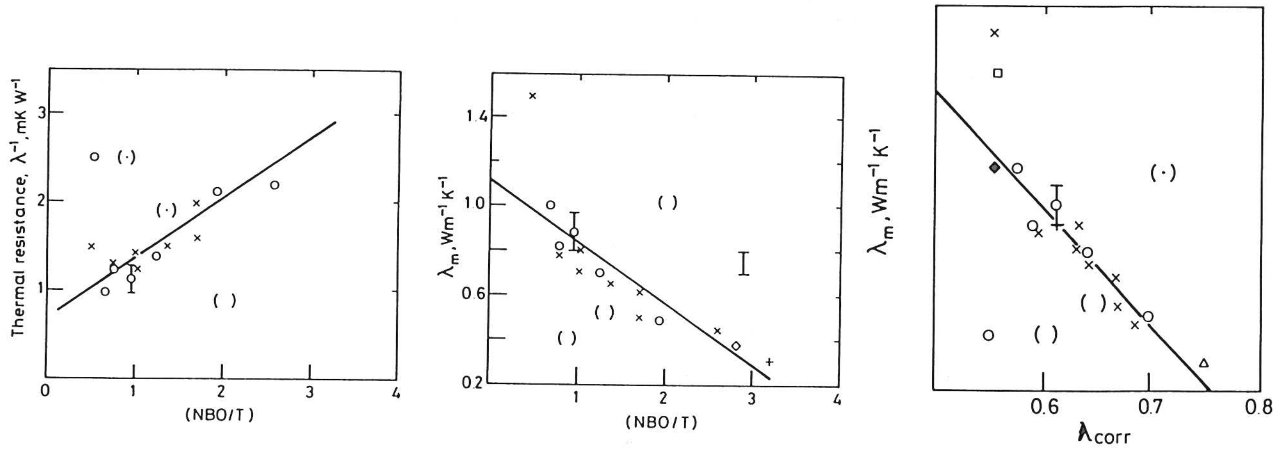
(iii) Although ln κ_m values decreased in the hierarchy $Li_2O > Na_2O > K_2O$ and $MgO > CaO >$ (SrO, BaO), ie decreasing catonic radius, however, the differences were small.

(iv) Since ln κ_m values for the alumino-silicates are in agreement with those for silicates with similar (NBO/T) or Λ_{corr}, it was concluded that the cations involved in charge balancing duties do not contribute to the electrical conductivity of the melt.

3.3 Thermal conductivity (λ)

Accurate values of the thermal conductivities of melts are notoriously difficult to obtain since the measured values can contain large contributions from both convection and radiation conduction. In order to minimise these contributions, transient techniques have been used, the values at T_{liq} obtained using these methods have been employed here [6-10].

It has been suggested [11] that the thermal resistance ($1/\lambda$) associated with the movement of phonons along the silicate chain or ring is relatively small when compared with that associated with the movement of phonons from chain to chain. Thus the thermal resistance ($1/\lambda$) would be expected to increase as the melt becomes progressively depolymerised. It can be seen from Figure 5 that the experimental data are in agreement with this proposition. Consequently, melts containing larger cations may be expected to have higher conductivities than similar melts containing small cations. Unfortunately, there are insufficient data to deduce whether the size of the cation has any effect on the thermal conductivity of the melt.



(a) (b) (c)

Figure 5 The effect of (NBO/T) on the (a) thermal resistance and (b) thermal conductivity and (c) shows the latter as a function of Λ_{corr}.

3.4 Self Diffusion Coefficients (D)

Experimental data for self diffusion coefficients, D, in liquid slags are prone to large experimental uncertainties. Nevertheless, the effect of the degree of depolymerisation of the melt on the diffusion coefficient can be clearly seen in the results obtained for the CaO-SiO_2 system [12] shown in Figure 6. The experimental uncertainties in the D(Ca) values for the CaO-Al_2O_3-SiO_2 system were considered to be too large to determine whether the cations on charge-balancing duties play a part in the diffusion processes.

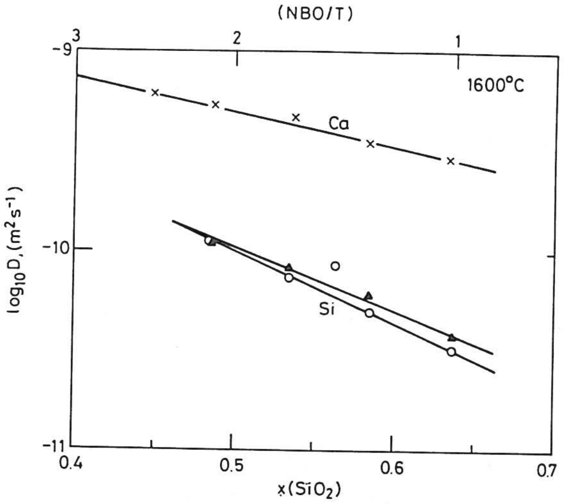


Figure 6 The self diffusion coefficients, D of Ca, Si and O at 1600 °C as a function of mole fraction SiO_2 and (NBO/T).

3.5 Molar Volume (V) Density (ρ)

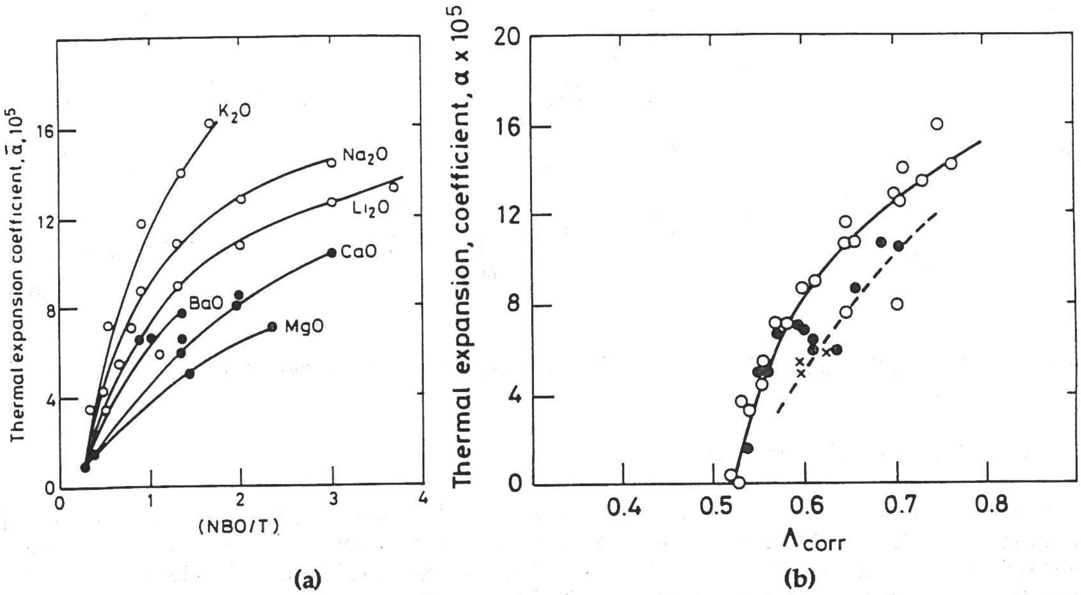
Although the molar volume is not particularly sensitive, to structural effects, it has been shown [13] that the partial molar volume $\bar{V}(SiO_2)$ versus $x(SiO_2)$ (or (NBO/T)) showed a negative departure from linearity, which could be of structural origin.

3.6 Thermal Expansion Coefficients ($\bar{\alpha}$)

Thermal expansion coefficient ($\bar{\alpha}$) data for the liquids [14,5] are shown as functions of (NBO/T) and Λ_{corr} in Figures 7(a) and (b). The thermal expansion coefficients can be seen to increase as:

(i) the melt becomes more depolymerised, ie (NBO/T) and Λ_{corr} increase;
(ii) the parameter (z/r^2) decreases for the cation or Λ(MO) increases.

It can also be seen that $\bar{\alpha}$ values for the alumino-silicates agree well with the values for silicates with equivalent (NBO/T) or Λ_{corr} and that the use of Λ_{corr} eliminates the effect of cation size and charge.



(a) (b)

Figure 7 Thermal expansion coefficients ($\bar{\alpha}$) as a function of (a) (NBO/T) and (b) the corrected optical basicity, o, ●, silicates, x, alumino-silicates.

3.7 Surface Tension (γ)

Although the surface tension (γ) of a slag is not a bulk property like those discussed above, there are indications that the surface properties may be affected by the structure of the liquid. Positive temperature coefficients ($d\gamma/dT$) has been reported [13] in slags with high SiO_2 contents and this behaviour may be associated with the presence of bridging oxygens on the surface.

3.8 Thermodynamic Properties

Plots of liquidus temperature, activity coefficient of SiO_2 and the entropy of fusion [2] all decrease progressively, with (i) increasing depolymerisation (ii) a shift from Group II to Group I oxides (iii) decreasing (z/r^2) for the cation (or increasing Λ for the oxide) within any one group.

3.9 Optical Properties

The addition of network-breaking cations into the SiO_2 network results in the destruction of 0^o bonds and the formation of O^- and O^{2-}. Under these circumstances the electron polarisability of the oxygen is increased and this results in an increase in refractive index [15]. There is also evidence to show that the absorption edge in visible/ultra-violet region is moved to higher wavelengths as a result of increased electron polarisation [16].

4 FUTURE WORK

The relationships of individual physical properties with global measures of the degree of depolymerisation, ie (NBO/T) and Λ_{corr}, will lead to development of improved mathematical models for the estimation of physical properties of slags. However, Mysen [2] has shown that it is possible to calculate the relative concentrations of various anionic units. Correlations between physical properties and the concentration of anionic units et T_2O_5 could be used to develop predictive models and this could lead to improved accuracy in the predicted values.

5. CONCLUSIONS

1) The degree of depolymerisation of the melt is the primary factor affecting most physical properties; the effect of different cations tends to be "second order" for most of the properties studied.
2) Although the (NBO/T) ratio is probably superior to Λ_{corr} as a measure of the depolymerisation of silicate melts, the latter has the advantages that it is capable of application to non-silicate systems and makes some compensation for the effect of other cations.
3) For alumino-silicates, it would appear that cations involved in charge-balancing duties do not contribute to the depolymerisation of the melt.
4) The (NBO/T) ratio does not account for the effect of the longer Al-O bond lengths on the activation energy for viscous flow in alumino-silicates, whereas Λ_{corr} provides some compensation for this effect.
5) There is some evidence of "ordering" in melts containing small, divalent cations such as Mg^{2+}. This ordering may result from the need for the Mg^{2+} cations to be sites near two O^- or two AlO_4^{5-} tetrahedra.

6. ACKNOWLEDGEMENTS

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