The factors affecting the thermophysical properties of slags and glasses

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Abstract: In this work the various factors affecting the thermo-physical properties of slags and glasses are investigated. The effects of (i) the structure of the slag, (ii) individual cations and (iii) temperature on various physical properties are explored. The parameter Q (=4-NBO/T), which is a measure of the polymerisation of the melt, was used as a measure of the structure. The various ways in which cations affect various properties are listed. This study found the following:

Liquidus temperature of slags decreased with decreasing strength of the M-O bond.

Thermal expansion coefficients increased with decreasing Q and decreasing M-O bond strength.

Viscosities increased with increasing Q, increasing cation size and with "*bridging*" due to the linking of chains by di-valent cations.

Electrical resistivities increased with increasing Q, decreasing number of available cations and increasing cation size.

The magnitude of *thermal conductivity* of solid and supercooled slags was determined by the rigidity of the silicate matrix and this decreased with decreasing Q, decreasing M-O bond strength and increasing temperature above the softening temperature.

Surface tensions decreased with increasing Q and decreasing M-O bond strength.

Key Words: Properties; Slags; Polymerisation; Cation effects; Temperature

Symbols, Abbreviations and Units

C_p= Heat capacity ($JK^{-1}kg^{-1}$)
k=Thermal conductivity ($Wm^{-1}K^{-1}$)
n= Number of cations
Q= Measure of polymerisation of melt (=4-NBO/T)
R= Electrical resistivity ($\Omega cm=10^{-2}\ \Omega\ m$)
r= Cation radius (10^{-10}m)
T= Temperature, K
T_g= Glass transition temperature
T_{liq}= Liquidus temperature
V= molar volume ()
X= Mole fraction
z= Charge on cations

α,β= Linear and volume thermal expansion coefficient (K^{-1})
γ= Surface tension (mNm^{-1})
η= Dynamic Viscosity (mPas)
κ= Electrical conductivity ($\Omega^{-1}cm^{-1}=10^{2}\ \Omega^{-1}m^{-1}$)
ρ= Density ($kg\ m^{-3}$)
NBO/T =Non-bridging oxygen/Tetragonal Oxygen
scl= supercooled liquid
%= mass %

Superscripts
m=value at T_{liq}

1. Introduction

Slags play an important role in many high temperature processes and there is a proven need for reliable thermo-physical property data to improve both process control and product quality. The use of mathematical models to achieve better process control and improve product quality has heightened the demand for reliable physical property data. There are a large number of high-temperature processes involving slags and, for any given process, the slag compositions tend to vary. Furthermore, for different processes there is a need for different property data, for instance, the most important properties of mould fluxes (affecting product quality in continuous casting) are viscosity, solidification temperature and crystallisation of the solid slag film but in Electro-slag refining electrical conductivity and viscosity are the key factors. Consequently, a large amount of property data is required. Physical property measurements are both difficult and time-consuming, so there has been a drive to develop models to estimate property data for slags from their chemical compositions. In order to derive a reliable model of a physical property of slags it is necessary to examine measured data to determine the key factors affecting that property and the relative importance of the various factors. In this paper we examine the effects of (i) the silicate network, (ii) the cations and (iii) temperature on the thermo-physical properties of slags.

1.1 Structure of silicate and alumino-silicate slags

Pure SiO_2 consists of a covalent network made up of Si^{4+} cations with 4 bonds to O^- ions arranged in the form of a tetrahedron; each O^- ion is attached to two Si^{4+} ions and this results in the formation of a 3-dimensional network. This network is broken when cations (*eg*. sodium oxide) are added to SiO_2 since a Na^+ will replace a covalent Si-O bond with a Na-O bond or a Ca^{2+} will replace 2 Si-O bonds [1, 2].

When Al_2O_3 is added to molten silicates Al^{3+} ions are integrated into the Si^{4+} chain/ring but each Al^{3+} requires a Na^+ to charge balance it ($NaAl^{4+}$) or a Ca^{2+} to charge balance two Al^{3+} ions. This reduces the number of cations available for network breaking and so the integration of Al into the silicate chain results in a more polymerised slag. Most thermo-physical properties are very dependent upon the degree of polymerisation in the silicate or alumino-silicate melt [1, 2].

1.2 Parameters to express the polymerisation of the melt

It will be seen below that the values of thermo-physical properties are greatly influenced by the polymerisation of the silicate or alumino-silicate melt. Consequently, it is necessary to quantify the degree of polymerisation in the slag. The most popular parameter is the (Non-bridging O/ Tetragonal O) ratio (NBO/T) which is a measure of the de-polymerisation of the melt. The (NBO/T) for a $CaO+Na_2O+Al_2O_3+SiO_2$ slag is given by Equation 1 where X is the mole fraction.

$$(\mathrm{NBO/T}) = 2(X_{\mathrm{CaO}} + X_{\mathrm{Na_2O}} - X_{\mathrm{Al_2O_3}})/(X_{\mathrm{SiO_2}} + 2X_{\mathrm{Al_2O_3}}) \qquad (1)$$

In this paper we prefer the parameter Q, which is a measure of the polymerisation of the melt and can be calculated from (NBO/T) using Equation 2.

$$Q = 4 - (\mathrm{NBO/T}) \qquad (2)$$

Inspection of Equations 1 and 2 show that the parameters (NBO/T) and Q do not differentiate between different cations.

1.3 Effect of cations

The nature of the cation can affect the thermo-physical properties of slags. A list of the different ways the cation can affect the properties is given below:

1.3.1 Bridging of chains

If a Ca^{2+} ion acts either as a *network breaker* or as a *charge balancer* for an Al^{3+} ion, in order to utilise its double charge, it must link to a second non-bridging oxygen (O^-) or another Al^{3+}, respectively; This link tends to restrict the movement of the silicate unit and hence tends to increase the viscosity or decrease the electrical conductivity. This is not the case for Na^+ ions so the viscosities of silicates containing Group I oxides (M_2O) tend to be lower than those containing Group 2 oxides (MO). Thus any Fe^{3+} acting as a network breaker or as a charge balancer would have to involve 3 silicate chains which would be expected to cause even more hindrance to movement than a Ca^{2+}.

1.3.2 *M-O bond strength*

The strength of the bond between a non-bridging oxygen and a cation is usually represented by the parameter (z/r^2) where z is the charge and r is the of cation radius. Other workers [3] have used bond strength values but these are not available for all slag components. Consequently, if the strength of this M-O bond is a key parameter affecting the property, for slags with equivalent compositions, property values will be in the order Mg>Ca> Sr> Ba>Li> Na> K (see Section 5) or in the reverse order. The value of r and z/r^2 are given in Table 1.

Table 1 Values of the cation radius (r)and relative values of the parameter (z/r^2) [4]; * indicates from reference [5].

	Li_2O	Na_2O	K_2O	MgO	CaO	SrO	BaO	FeO	MnO
r (10^{-10}m)	0.76	1.02	1.38	0.72	1.0	1.18	1.35	0.74*	0.80*
z/r^2	1.73	0.96	0.53	3.85	2.0	1.43	1.1	3.65	3.13

1.3.3 Covalency of M-O bond

Although the bond between a non-bridging oxygen (NBO) and a cation is largely ionic in nature it also contains some covalent contribution. Recently, Zhang *et al.* [6] showed that hierarchy of viscosities for equivalent compositions of $MO-SiO_2$ was distorted by the higher level of covalent contributions in Fe^{2+} and, to a less extent, Mn^{2+}.

1.3.4 *Cation size and hindrance*

Viscosities involve the movement of one silicate unit over another, so large cations can hinder this movement. Electrical conductivity involves the transport of cations through the silicate network and thus smaller cations will be more successful than bigger cations in passing through the network and thus will tend to have a higher electrical conductivity. This is referred to here as the *"hindrance effect"*. In these cases, the hierarchy in "resistance to movement" will correlate with values of (r^3).

1.3.5 Mixed cation effect

For systems such as $K_2O+Li_2O+SiO_2$ the replacement of Li^+ ions by K^+ results in a significant decrease in values of electrical conductivity, ionic diffusivity and T_g. This is known as the *mixed cation effect.* It occurs when there is a significant difference in the sizes of the two ions which results in defects when the mobile ions enter foreign sites [7].

1.3.6 Number of cations

For Na_2O-SiO_2 and $CaO-SiO_2$ slags with equivalent composition (*ie.* same X_{SiO2}) there are twice as many Na^+ ions as Ca^{2+} ions; the number of available cations (n) is important in properties like electrical conductivity and diffusion.

1.4 Effect of Fe_2O_3, Cr_2O_3, TiO_2 and CaF_2

1.4.1 Effect of Fe_2O_3 and Cr_2O_3

It might be expected that Fe_2O_3 and Cr_2O_3 would behave like Al_2O_3 and would be accommodated into the silicate network and thus act as a network former. However, in the case of Fe_2O_3 it would appear that it acts more as a network breaker than a network former [8]. In the case of Cr_2O_3 it would appear that it works predominantly as a network-former [8]. More work is needed to identify the roles of these additions.

1.4.2 Effect of TiO_2 structure

It might be anticipated that additions of TiO_2, like SiO_2, would increase the polymerisation of the slag but TiO_2 additions have been found to reduce viscosity [8, 9], so it would appear that TiO_2 acts more as a network breaker than a network former.

1.4.3 Effect of CaF_2 on structure

Recent work [10-12] has shown that when fluorine is added to slags the F^- combines with Ca^{2+} and thereupon stays "*out of the game*". This behaviour could be construed as F additions cause some polymerisation of the melt but in practice, any polymerisation is more than offset by the simultaneous reduction in T_{liq}.

1.5 Effect of temperature

When liquid slags are cooled they can form a crystalline slag or a glass or a mixture of the two phases. The nature of the phase formed is dependent upon several factors such as (i) the degree of polymerisation (*ie*. Q) in the slag and (ii) the cooling rate and subsequent thermal treatment (a high cooling rate promotes glass formation). If viscosities are measured in the cooling mode the appearance of the first crystallites in the melt is accompanied by an abrupt increase in viscosity (shown in Figure 1a), which is known as the "*break temperature*". In contrast, the viscosity (η) increases smoothly with decreasing temperature for more glassy melts (Figure 1b) since it forms a supercooled liquid (scl) which persists down to the glass transition temperature (T_g which corresponds to $\eta=10^{13.4}$ dPas). When a glassy slag is heated it undergoes some property changes at T_g and, in some cases, at a higher temperature, the slag starts to crystallise (which is an exothermic process). The properties of slags, between T_g and the liquidus temperature, T_{liq}, tend to vary according to whether it is glassy crystalline or a mixture of the two phases.

Increasing temperature results in a gradual breakdown in the network structure, so viscosity and electrical conductivity tend to decrease and increase, respectively, with increasing temperature.

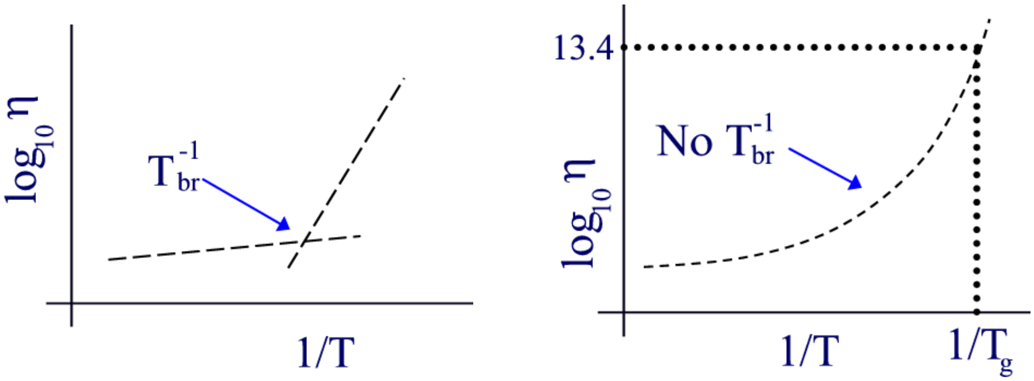


Figure 1 The dependence of $\log_{10}$ viscosity (in dPas) as a function of reciprocal temperature (K) for a silicate melt forming (a) crystalline phases and (b) a super-cooled liquid (scl)

2 Factors affecting individual properties

2.1 Liquidus Temperature (T_{liq})

Increasing temperature, like increasing cation additions, tends to break down the silicate network. Pure SiO_2 has a melting point close to 2000 K [2] and MO or M_2O additions tend to reduce T_{liq}. Inspection of the phase diagrams for M_2O-SiO_2 and MO-SiO_2 systems indicates that (i) T_{liq} values for MO-SiO_2 are significantly higher than those for the M_2O- SiO_2 system, (ii) T_{liq} within any one group, increases as (z/r^2) increases *ie.* as the M-O bond strength increases and (iii) the overall effect is T_{liq} increases as (z/r^2) increases. Consequently, T_{liq} was plotted against (z/r^2) as shown in Figure 2, and it can be seen that there is a clear trend showing T_{liq} increases as (z/r^2) increases. The scatter in Figure 2 arises from the fact that "*peaks and valleys*" in T_{liq} surface tend to occur at specific compounds (*eg.* $CaO·2SiO_2$ or $CaO·SiO_2$).

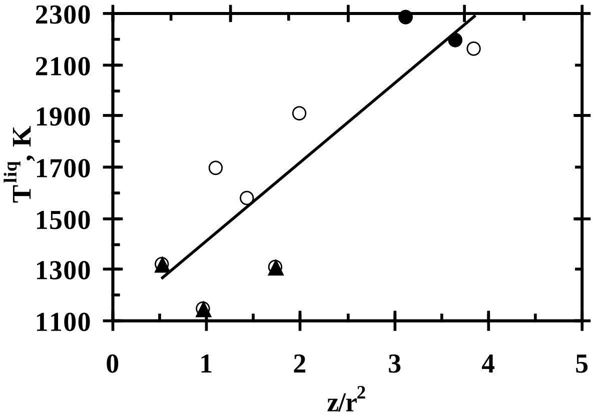


Figure 2 Liquidus temperature as a function of the M-O bond strength (represented by z/r^2) for slags with $X_{SiO_2} = 0.667$ (a plot of T_{liq} values for X_{SiO_2} =0.5 shows the same trends). ▲=M_2O-SiO_2; O=MO-SiO_2; ●= FeO(or MnO)-SiO_2.

Thus it is concluded that cation effects on T_{liq} values result principally from the M-O bond strength.

The effect of different cations on a property (*eg.* viscosity) has often been studied by comparison of viscosities at a specific temperature (T_{ref}). This is a valid practice where the T_{liq} values of the various oxides are very similar. However, this practice is invalid where there is a wide range in T_{liq} values; for instance, viscosities of low-melting silicates can be significantly reduced over the interval (T_{ref} -T_{liq}); this subsequently distorts the hierarchy of viscosities for different cations. This is referred to here as the *"T_{liq} effect"*. In such cases the hierarchy of property (P) values for slags with different cations should be compared at T_{liq} (denoted P^m).

2.2 Thermodynamic properties

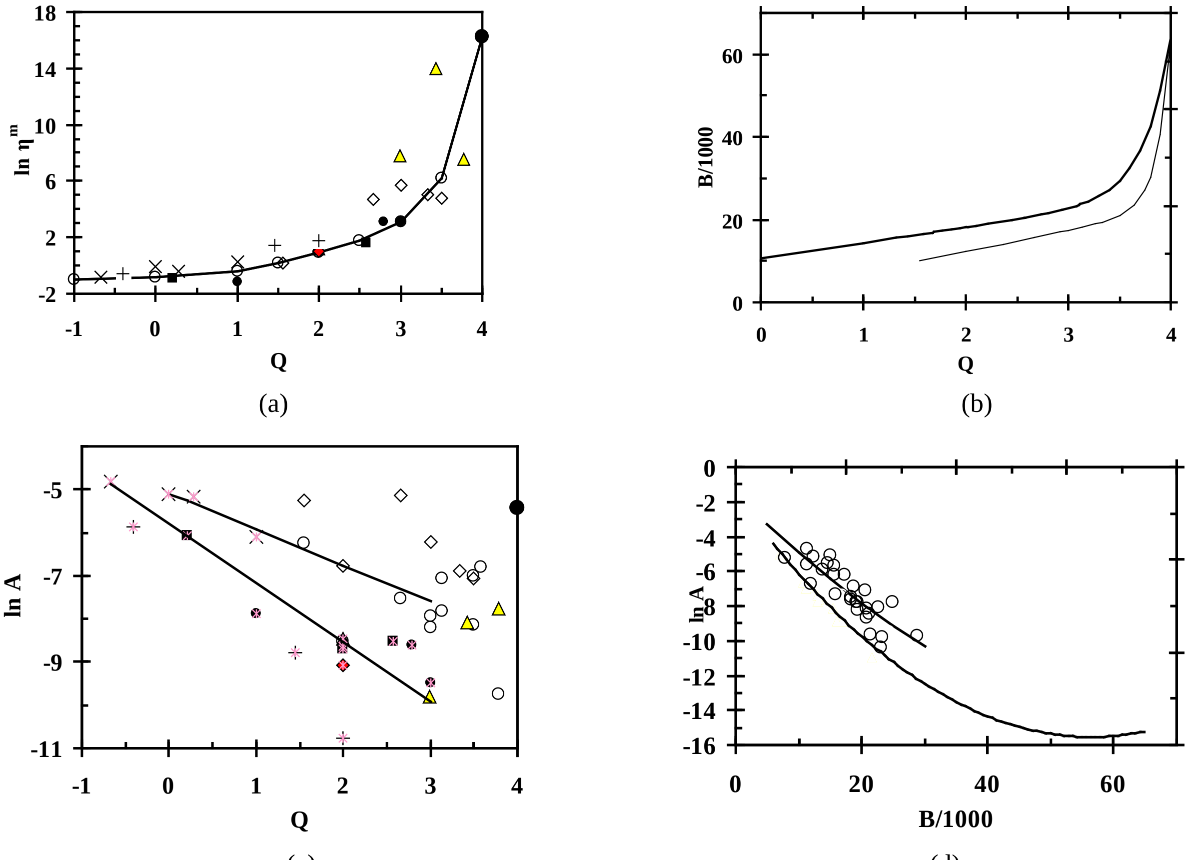
The activity coefficient is a measure of the ability for a species to escape; thus it would be expected to decrease as the M-O bond strength increases (*ie.* increasing z/r^2). Mills [13] showed that the activity coefficient of SiO_2 (f_{SiO2}) increased with decreasing (z/r^2) for any specific SiO_2 content (*ie* Q value) for both MO-SiO_2 and M_2O-SiO_2 systems. It was also shown that the entropy of fusion (ΔS^{fus}) increased with increasing (z/r^2) *ie.* increasing M^+-O^- bond strength [13].

2.3 Viscosity (η)

2.3.1 Effect of Q on viscosity

Viscosity represents the resistance to the movement of one layer of molecules over another layer. The viscosities of slags are largely determined by the degree of polymerisation of the silicate anions (*ie.* Q). However, as will be seen below, the cations, have a smaller, but decisive, effect on the viscosity.

The logarithm of the viscosity at the melting point ($\ln \eta^m$) is plotted against Q in Figure 3a. It can be seen that the viscosity (η) increases as the degree of polymerisation in the silicate anions (*ie.* Q) increases. There is a steady increase in $\ln \eta^m$ between Q=0 to 3 followed by a sharp increase between Q=3 and 4. Although the data in Figure 3a show considerable scatter, the majority of the data points lying above the curve are for larger cations (eg. K denoted by Δ).



(a) (b)

(c) (d)

Figure 3 The dependence of (a) the viscosity of the slag at T_{liq} ($\ln \eta^m$) on Q; ◊=Li_2O;○=Na_2O; Δ =K_2O; ■=MgO; ●=CaO; ▲=SrO; ♦=BaO; x= FeO; += MnO; ●=SiO_2; line=suggested curve, (b) the term (B_A) for viscous flow as a function of Q; upper curve=MO-SiO_2 and lower curve M_2O-SiO_2 systems, (c) the pre-exponential term ($\ln A_A$) as a function of Q; symbols as in (a) and ●= values for the FeO-SiO_2 system; O= Values for MnO-SiO_2 system, and (d) the term ($\ln A_A$) as a function of (B_A/1000); lower curve for MO-SiO_2 system and o and upper curve for M_2O-SiO_2 system.

2.3.2 Effect of temperature on viscosity

Increasing temperature tends to loosen the network structure and thus causes a decrease in viscosity. The temperature dependence of the viscosity of the liquid phase is usually represented by the Arrhenius or the Weymann equations (Equations 3 and 4, respectively) which are denoted by the subscripts A and W, respectively.

$$\ln \eta = \ln A_A + (B_A/T) \qquad (3)$$

$$\ln (\eta/T) = \ln A_W + (B_W/T) \qquad (4)$$

The supercooled liquid (scl) exists between T_g and T_{liq} and it can be seen from Figure 4 that the gradient (d $\log_{10} \eta$ /dT) increases sharply in the region close to T_g ($\eta_{Tg}= 10^{13.4}$ dPas) but gradually attenuates with increasing temperature. It is customary to express the temperature dependence of the scl phase by the Vogel-Fulcher-Tammann (VFT) equation where T_o is a variable; this type of equation is denoted here by the subscript V.

$$\ln \eta = A_V + B_V/(T-T_o) \qquad (5)$$

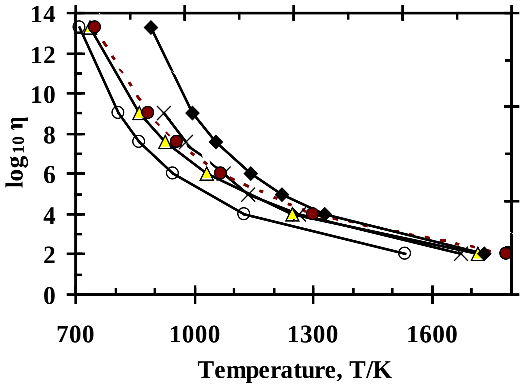


Figure 4 The temperature dependence of the viscosities of slags in the supercooled liquid phase; ♦=$0.1Na_2O$-$0.2CaO$-$0.7SiO_2$; x=$0.2Na_2O$-$0.1CaO$-$0.7SiO_2$; ● =$0.2Na_2O$-$0.8SiO_2$; Δ=$0.25Na_2O$-$0.75SiO_2$; O=$0.333Na_2O$-$0.667SiO_2$ [14,15].

The parameter B_A is plotted as a function of Q in Figure 3b and the pre-exponential term ln A_A as function of Q in Figure 3c. It can be seen from Figure 3b that:

(i) B_A is a non-linear function of the degree of polymerisation Q.

(ii) the curve for M_2O-SiO_2 systems is different to that for MO-SiO_2 systems.

It was also observed that within any one system, the deviation of B_A values from the curve, although small, tend to increase with increasing cation radius *ie.* they appear to be affected by the *hindrance factor* (as seen in Figure 3a).

Also it was noted that B_A values for alumino-silicates tended to be lower than those for silicates, the deviation increasing with increasing absorption of Al_2O_3 into the network.

The parameter B_A (or B_W) are obtained from the slope of ln η (or ln (η/T)) as a function of (1/T) and ln A_A is derived from the intercept where (1/T) =0 which corresponds to infinite temperature. Any uncertainties in the viscosity measurements, or a small temperature range for the measurements, can lead to significant uncertainties in ln A. This can be clearly seen in Figure 3c where the measured values of ln A_A show considerable scatter. To avoid this problem, Urbain [16] and others [6, 17] assumed that ln A was a linear function of B *eg.* Equation 6 [16].

$$- \ln A_w = 0.29B_w + 11.57 \qquad (6)$$

The experimental values of ln A_A and B_A for a large number of silicates and alumino-silicates [8] are plotted in Figures 3d and 5 and it can be seen that:

(1) ln A_A is not a linear function of B_A but does approximate to a linear relation at lower B_A values (corresponding to $Q < 3$).

(2) The data for M_2O-SiO_2 systems lie on a different curve to the data for MO-SiO_2 systems (Figure 3d).

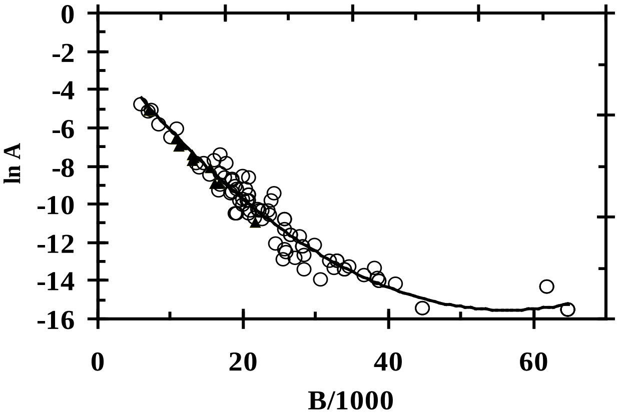


Figure 5 The parameter ln A_A as a function of the parameter B_A for liquid MO-SiO_2 and MO-Al_2O_3-SiO_2 slags .

It was also noted that, despite the scatter of the data in Figure 3c, the ln A_A values for M_2O-SiO_2 slags fell on a higher (less negative) curve than those for MO-SiO_2 systems.

2.3.3 Effect of cations on viscosity

It was noted above that ln η^m values for larger cations tended to lie above the curve indicating that viscosity tended to increase with increasing cation size. A similar observation was made when B_A values (which are related to the activation energies for viscous flow) are plotted against Q. Furthermore, a similar comparison of calculated viscosities for the supercooled phase at a specific temperature and for identical Q values indicated that $\eta_{K_2O} > \eta_{Na_2O} > \eta_{Li_2O}$ [14, 15]. Thus, the findings of the study indicate that both the viscosity and activation energy for viscous flow, increase slightly with increasing cation size. In another study [18] the hierarchy of viscosities for the liquid at a specific temperature were found to be $\eta_{K_2O} > \eta_{Na_2O} > \eta_{Li_2O}$ but for MO-SiO_2 systems reported $\eta_{MgO} > \eta_{BaO} \approx \eta_{SrO} > \eta_{CaO}$ which is not in agreement with the trend observed here. One possible reason is that the results were affected by the *T_{liq} effect ie*. differences in T_{liq}.

The fact that both B_A and ln A_A for M_2O-SiO_2 systems lie on different curves to those for MO-SiO_2 systems (Figures 3b and c) may well be due to the "*bridging of chains*" (Section 1.3.1) by a M^{2+} ion which does not occur with a M^+ ion.

In summary, it appears that the nature of the cations does affect the viscosity via the *"hindrance"* and *"bridging of chains"* effects

2.4 Density (ρ) and Thermal Expansion Coefficient (α, β)

The density of the crystalline phase is higher than that of the glass because of the tighter packing. It has been shown [19] that the densities (ρ) of some slag systems can be satisfactorily described in terms of partial molar volumes ,V, (Equations 7 and 8) where M=molecular weight and subscripts 1, 2, 3 represent different slag components eg. CaO *etc.*

$$V = \Sigma\ X_1V_1 + X_2V_2 + X_2V_2 + \ldots \qquad (7)$$

$$V\ \rho = M \qquad (8)$$

However, in liquid silicate systems it was found that the formation of a network structure resulted in an apparent increase in density (or decrease in molar volume) with increasing SiO_2 content (or Q) [19]; thus the molar volume of SiO_2 is not a constant value but can be represented as a function of X_{SiO2}. In alumino-silicates, the addition of Al_2O_3 to the silicates results in an apparent reduction in the density (*ie*. increase in molar volume) which can be represented by a polynomial equation. Fluegel et al. [20] noted that M_2O additions tended to increase the densities of glasses at temperatures below T_g but reduced the density above T_g (*ie.* in supercooled phase). It would appear that increased expansion at higher temperatures with M_2O additions (Figure 7a) offsets the increases in density derived from the additions.

2.5 Thermal expansion and temperature dependence of density

Thermal expansion results from the asymmetry of thermal vibrations produced when a slag is heated. These asymmetric vibrations are affected by (i) the chemical bonding in the slag and (ii) the thermal history of the specimen (*ie*. the cooling rate in formation). The thermal expansion coefficient is usually expressed as either the volume expansion coefficient (β) or as the linear expansion coefficient (α) where V and L are the volume and length of the sample and the subscript ref refers to the reference temperature (usually 293K) and $T^* = 0.5\ (T+T_{ref})$.

$$\beta_{T^*} = (V_T - V_{ref}) / V_{ref}\ (T - T_{ref}) \qquad (9)$$

$$\alpha_{T^*} = (L_T - L_{ref}) / L_{ref}\ (T - T_{ref}) \qquad (10)$$

When a glassy slag is heated the thermal expansion coefficient (α) increases dramatically above the glass transition temperature (T_g) by a factor of about three. Crystalline samples have a similar expansion coefficient to that of the glass below T_g but do not show this dramatic increase in α above T_g. However, crystalline slags do show an increase in volume when they melt whereas glasses do not.

2.5.1 Factors affecting thermal expansion

Liquids

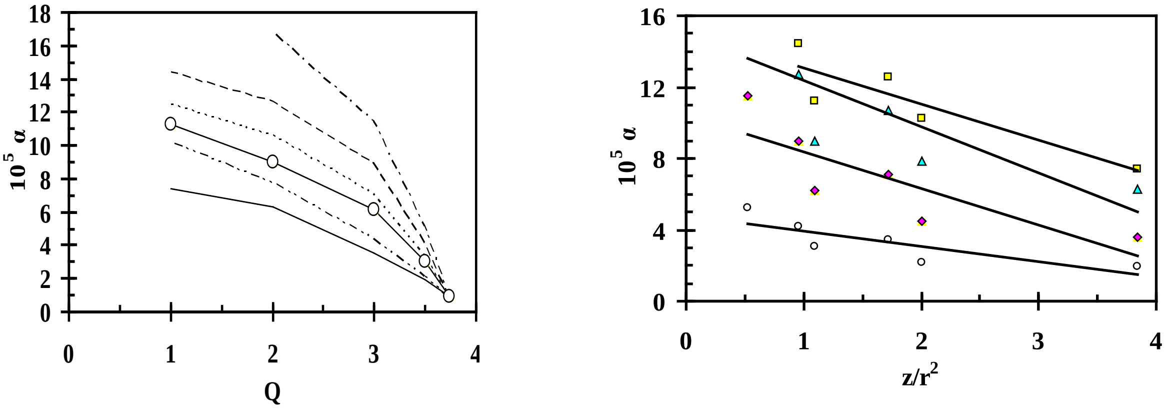
Thermal expansion data for liquid slags due to Bockris et al. [21, 22] were analysed and it was found that (i) α increased as polymerisation decreased (α ↑ as Q ↓) and (ii) α increased as the M^+-O^- bond strength decreased (α ↑ as M-O bond strength ↓ or α ↑ as (z/r^2) ↓) as shown in Figure 6.

A plot of α versus the corrected Optical basicity indicates lower values of α for alumino-silicates than for silicates [13] which may be due to the reduction in the concentrations of network-breaking cations resulting from charge balancing of the Al^{3+} ions.

Solids and supercooled liquids

Fluegel [23] has reported that the same trend in the supercooled phase as that observed in liquids (*ie.* $\alpha \uparrow$ as $(z/r^2) \downarrow$) and, furthermore, for glasses below T_g. Fluegel [23] also reported that the combination of Na and Ca resulted in a tightening of the silicate network and a reduction in α. It was also reported that increases in levels of Al_2O_3, ZrO_2 and TiO_2 tend to reduce the thermal expansion.

Thus in both solids and liquids, thermal expansion increases with both decreasing polymerisation ($Q \downarrow$) and with decreasing M-O bond strength.



(a) (b)

Figure 6 Thermal expansion coefficient (α) values for liquid MO- and M_2O-SiO_2 slags (after Bockris et al. [21,22]) as a function of (a) the parameter Q, from the bottom; solid line=MgO; CaO; BaO(o); Li_2O; Na_2O and K_2O, and (b) (z/r^2) *ie*. a measure of the M-O bond strength; o=Q=3.5; ♦=Q=3; ▲=Q=2; ■=Q=1 lines are "best fit" trend lines of data.

2.6 Electrical Conductivity (κ) and Resistivity (R)

The electrical conductivity (κ) is the ability to transport electrons (provided by the cations) under the influence of an applied electrical field. The electrical resistivity (R) is the reciprocal of the conductivity ($R=1/\kappa$).

2.6.1 Factors affecting the Electrical Resistivity (R)

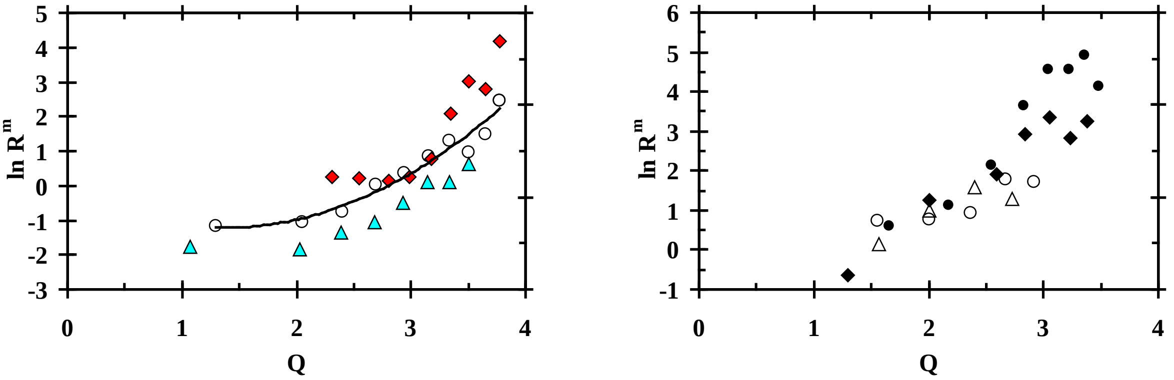
There are several factors affecting the electrical resistivity:

Effect of silicate network on resistivity

The covalent silicate network resists the movement of the cations thus the conductivity decreases (and resistivity increases) as the network becomes more polymerised *ie.* as Q increases (($R\uparrow$ ($\kappa\downarrow$)as $Q \uparrow$)). It can be seen from Figure 7 that the resistivity (*ie.* $\ln R^m$) clearly increases with increasing Q and that there is a particularly sharp rise between Q=3 and 4, similar to that seen for the viscosity (Figure 3a). The following equation could be used to calculate $\ln R^m$ for slags from the Na_2O-SiO_2 system with Q values between 1 and 3.75.

$$\ln R^m = -0.0917 - 1.64Q + 0.597\,Q^2 \qquad (11)$$

Some workers have used the slag viscosity to represent the resistance of the silicate network [24]. The validity of this approach is demonstrated in Figure 8 where measured $\log_{10} R$ values [25] for $0.199Na_2O+0.801SiO_2$ were found to be linear functions of the calculated $\log_{10} \eta$ values [14] plotted for the supercooled liquid region.



(a) (b)

Figure 7 The logarithm of electrical resistivity of molten slags at T_{liq} (ln R^m) vs the parameter Q, for (a) molten M_2O-SiO_2 slags; Δ=Li_2O; o=Na_2O; ♦= K_2O, and (b) for molten MO-SiO_2 slags, Δ =MgO; o=CaO; ♦= SrO and ●= BaO.

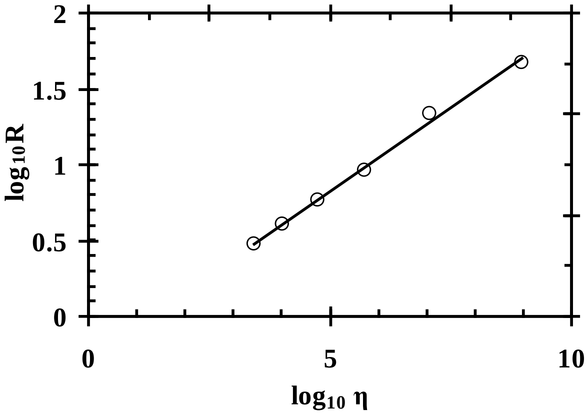


Figure 8 The measured resistivity $\log_{10}R$ [25] vs the calculated viscosity ($\log_{10}\eta$ (dPas)) [14] for the $0.199Na_2O$+ $0.801SiO_2$ system in the supercooled region.

Effect of Cations on resistivity

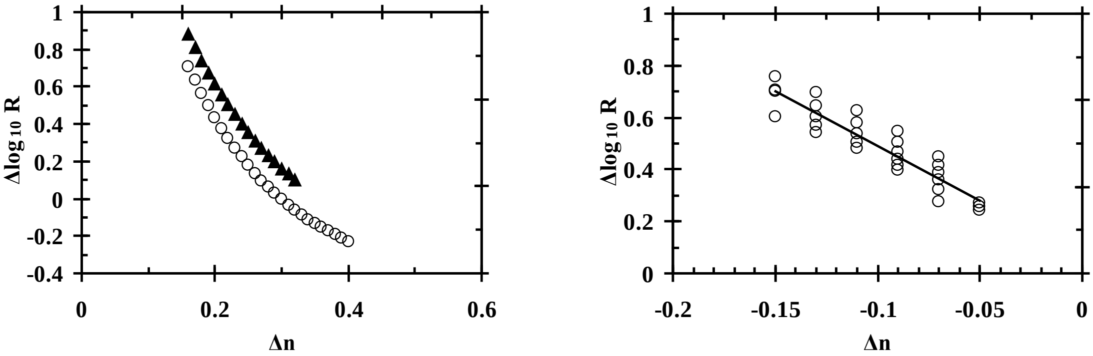
Intuitively, it would be expected that electrical resistivity would increase with increasing cation size since (i) a larger cation would find more difficulty to pass through the silicate network and (ii) larger cations have been seen to increase the viscosity (and hence the resistance to cation movement). It can be seen from Figures 7a and 9a that ln R^m values are in hierarchy $R_{K_2O} > R_{Na_2O} > R_{Li_2O}$ and from Figure 7b that, despite the scatter, ln R^m data tend to be in the order R_{BaO}> R_{SrO}> R_{CaO}> $R_{MgO.}$ Thus it appears that R increases as the size of the cation increases. Other workers have explored the effects of cations. Suginohara et al. [26] reported resistivities when different oxides were added to a PbO-SiO_2 slag; the following hierarchies were observed $R_{K_2O} > R_{Na_2O} > R_{Li_2O}$ and R_{MgO}> R_{CaO}> R_{BaO}. The resistivities at a specific temperature for slags from 0.35 MO (or M_2O) +0.3SiO_2 +0.35 TiO_2 were found to be in the hierarchy R_{BaO}> R_{SrO} > R_{CaO} > R_{MgO} > $R_{K_2O} > R_{Na_2O} > R_{Li_2O}$ [27]. Thus the majority of the evidence supports the view that within any group larger cations increase the resistivities. It has also been observed that the resistivities of MO-silicates are higher than than those of M_2O-silicates [24]. It has been assumed here that this is due to the increase in the number of cations (n) available in the M_2O-silicates to move through the silicate network (see Section 1.3.6).

Fluegel [7] has reported reference data for the resistivities of liquid slags from the Na_2O-SiO_2, K_2O-SiO_2 and Na_2O-CaO-SiO_2 systems at 1273, 1473 and 1673 K. These data have been used here to determine the effects of (i) cation size and (ii) the number of cations (n) on $\log_{10}R$ since the replacement of $2Na^+$ ions by one Ca^{2+} ion results in a decrease in

n. Analysis of the data allows one to deduce (i) the change in $\log_{10}$ R (denoted $\Delta_{cat}\log_{10}$ R) due to cation size between equivalent Na_2O-SiO_2 and K_2O-SiO_2 compositions and (ii) the effect of changes in the number of cations (Δn) on $\Delta_n\log_{10}$ R. The differences in $\log_{10}$ R were calculated for equivalent slag compositions (*eg.*$0.2M_2O$. $0.8SiO_2$) as shown in Equation 12

$$\Delta_{cat}\log_{10} R = \Delta\log_{10} R_{K_2O-SiO_2} - \Delta\log_{10} R_{Na_2O-SiO_2} \qquad (12)$$

The results for $\Delta_{cat}\log_{10}$ R are plotted against Δn in Figure 9a. The compositional range covered X_{M2O} =0.16 to 0.32 and it was found that there $\Delta\log_{10}$ R was reasonably constant (= 0.174) and showed little variation with either composition (X_{M2O}) or temperature in the range studied.



(a) (b)

Figure 9 (a) $\Delta_{cat}\log_{10}$ R as a function of M_2O mole fraction for Na_2O-SiO_2 (O) and K_2O-SiO_2 (▲) at 1473K; (b) the difference ($\Delta_n\log_{10}R$) in values between Na_2O-CaO-SiO_2 and Na_2O-SiO_2 systems at 1473K as a function of difference in numbers of cations available.

The effect of changes in the number of available cations (Δn) on $\log_{10}$ R was studied using the data for Na_2O-SiO_2 and Na_2O-CaO-SiO_2 systems. The differences in $\log_{10}$ R for equivalent compositions (*ie.* identical X_{SiO2}=identical Q values) were calculated according to Equation 13 and the change in the number of available cations (Δn) by Equation14.

$$\Delta_n \log_{10} R = \Delta\log_{10} R_{Na_2O-CaO-SiO_2} - \Delta\log_{10} R_{Na_2O-SiO_2} \qquad (13)$$

$$\Delta n = (2X_{Na_2O} + X_{CaO})_{Na_2O-CaO-SiO_2} - (2X_{Na_2O})_{Na_2O-SiO_2} \qquad (14)$$

The plot of $\Delta_n\log_{10}$ R vs Δn is shown in Figure 9 b; similar plots were obtained for 1273 and 1673K. It can be clearly seen that a decrease in number of cations, Δn (resulting from the replacement of X_{Na_2O} by X_{CaO}) causes an increase in $\Delta_n\log_{10}$ R, showing that the number of available cations does affect the electrical conductivity. Inspection of Figure 9b indicates that points tend to lie in vertical groups; these points within a group represent a constant X_{CaO}. Within these groups the lowest point corresponded to the largest (X_{Na_2O}/X_{CaO}) and the highest R value to the lowest value of this ratio within the group. However, at any specific value of Δn, the replacement of Na^+ by Ca^{2+} is accompanied by an increase in Q. Thus the vertical spread, (eg. Δn=-0.07) is due to the increase in resistivity resulting from this increase in Q. Consequently, the $\Delta\log_{10}$ R data were arranged into groups with identical Q values and then plotted against Δn. The results (shown in Figure 10) indicate that $\Delta_n\log_{10}R_{1473}$ values for identical Q values, increases as Δn becomes more negative. Thus the resistivity increases as the number of available cations decrease.

It should be noted that cations are needed to charge balance Al^{3+} ions incorporated into the silicate chain. In multi-component slags the electrical resistivity will be affected by the nature of the charge-balancing cation; *eg.* if a Li^+ cation carries out the charge-balancing duties, there will be a lower concentration of smaller cations available. This will result in a lower conductivity, or a higher resistivity, than if a larger cation was to carry out the charge-balancing duties.

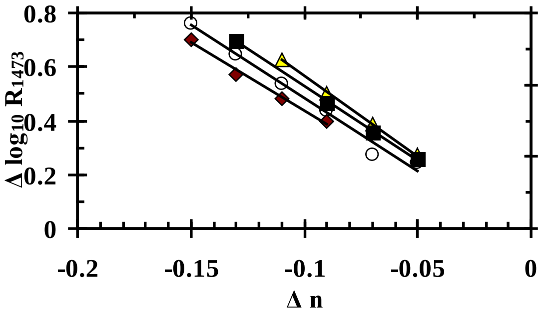


Figure 10 Change in resistivity ($\Delta_n \log_{10} R_{1473}$) of Na_2O-CaO-SiO_2 and Na_2O-SiO_2 slags as a function of the change in the number of cations (Δn) for groups with identical Q values ♦ Q=2.97; O Q=3.14; ■ Q=3.22; Δ Q=3.30.

No evidence was found to support the view that the M-O bond strength affected the electrical resistivity. Thus the resistivity is affected by Q, n and the cation size so it is proposed that $\log_{10}R$ could be represented by Equation 15, where k_1, k_2 and k_3 are constants.

$$\log_{10}R = k_1 Q + k_2/n + k_3 (r^3) \tag{15}$$

2.6.3 Temperature dependence of electrical resistivity

Increasing temperature loosens the silicate structure and hence causes the conductivity to increase and the resistivity to decrease. It can be seen from Figure 11 that the resistivity increases sharply with increasing temperature at lower temperatures above T_g but the gradient (dR/dT) attenuates at higher temperatures. Since the silicate network hinders the movements of the cations, the viscosity has been used by some workers to represent the resistance of the silicate network [24]. It follows that the temperature dependence of the resistivity for the liquid and supercooled phases can be represented by Arrhenius and Vogel-Fulcher-Tamman equations, respectively. The linear relation between $\log_{10}R$ and $\log_{10} \eta$ shown in Figure 8 shows the validity of using the VFT relation to represent the temperature dependence of electrical resistivity in the supercooled phase.

Thus, in summary, the electrical resistivity increases (R ↑) with (i) increasing polymerisation (Q ↑), (ii) decreasing number of cations (n ↓) and (iii) increasing cation size (r ↑).

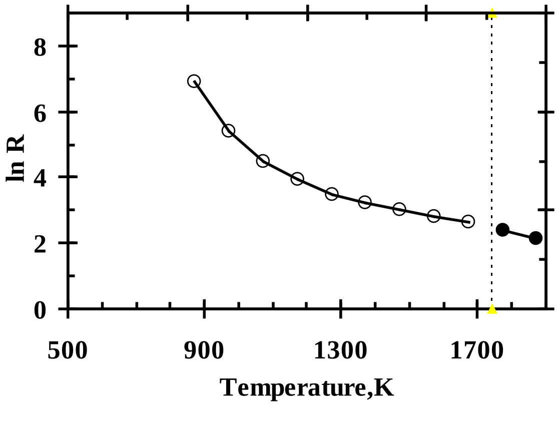


Figure 11 The logarithm of electrical resistivity (ln R) as a function of Temperature, O= scl ●=liquid; dotted line=T_{liq}.

2.7 Thermal conductivity (k)

2.7.1 Measurement problems

There are two severe problems affecting the measurements of thermal conductivity. The first is the magnitude of any contributions from *convection* in the liquid and consequently, transient methods are used to minimise convection, *eg.* by using laser pulse (LP) or transient hot wire (THW) methods. The second problem is *radiation conduction*. This was first observed when it was found that conductivity (k) values for solid glass samples tended to increase as the thickness of the sample increased until a certain critical point was attained, whereupon, k remained constant; the sample is said to be *"optically thick"* at the critical point. Radiation conduction involves a mechanism of radiation and re-emission through the various layers of the sample. Radiation conductivity (k_R) increases rapidly with increasing temperature. Slags, like glasses are semi-transparent media to infra-red radiation and so measurements of the effective thermal conductivity ($k_{eff}= k_c+k_R$) at temperatures above 800K tend to contain significant contributions from k_R. These contributions can be reduced by (i) absorption of IR (by incorporating transition metal oxides, FeO, CrO etc. into the slag) or (ii) by scattering (via crystallites, grain boundaries, pores).

In this study we have only adopted data obtained by THW methods [28-34] since the surface area of the wire is ca 10% of that for LP sample and hence the k_R contributions are much smaller in THW studies than in LP experiments.

2.7.2 Factors affecting the thermal conductivity

When slags are heated the molecules become agitated and vibrate and heat is conducted by phonons *ie.* lattice waves.

Liquids

Mills [13] showed that thermal conductivity of slag melts increased with decreasing NBO/T (*ie.* increasing Q). Subsequently, Susa [29] showed that k for the liquid phase increased as the SiO_2% increased *ie.* as Q increased. Kang and Morita [34] showed that the temperature dependence of liquid slag could be represented with an Arrhenius equation. These facts suggest that there may be a direct correlation between thermal conductivity and viscosity. This behaviour is in contrast to that for electrical conductivity which has an inverse relation with viscosity.

Susa and co-workers [28-31] have shown that the thermal conductivities of liquid slags are low (0.1 to 0.2 $Wm^{-1}K^{-1}$) and the experimental uncertainties are of similar magnitude (ca ± 0.1 $Wm^{-1}K^{-1}$). This makes it difficult to determine the effects of different cations on the thermal conductivity of liquid slags. Ozawa et al. [30] compared the thermal conductivities of liquids of similar compositions from the following systems (in mole fractions); $0.37CaO+0.63SiO_2$ and $0.1M_2O+0.3CaO+0.6SiO_2$. Values of k^m were found to be in the hierarchy: $k^m_{CaO} > k^m_{Na_2O} \approx k^m_{Li_2O} > k^m_{K_2O}$. These workers also showed that the replacement of M_2O by CaO lead to an increase in thermal conductivity.

Susa et al [28] have shown that replacement of Na_2O by NaF results in a decrease in thermal conductivity.

The measurements reported by Kang and Morita [34] indicate that the replacement of SiO_2 by Al_2O_3 had little effect on the thermal conductivity of the liquid.

Solids and supercooled liquids

The measurements of thermal conductivity reported by Susa and co-workers [28-33] for both the glass and the supercooled liquid show clearly that:

(i) thermal conductivities increased as the SiO_2 % (*ie*. Q) increased.

(ii) at any specific temperature, $k_{Li_2O} > k_{Na_2O} \approx k_{K_2O}$ and k_{CaO} appeared to be significantly higher than k_{Na_2O} .

(iii) replacement of M_2O by CaO always resulted in an increase in thermal conductivity of slags from the system 0.1M2O+0.2CaO+0.7SiO_2.

(iv) replacement of M_2O by 2MF resulted in a decrease in thermal conductivity [28].

(v) the thermal conductivity of a slag where $X_{Al_2O_3} \approx 2 X_{SiO_2}$ was higher than other alumino-silicates with the same Q value [34]. The slag probably contained calcium aluminates.

2.7.3 Temperature dependence of thermal conductivity

The thermal conductivity (k) is shown as a function of temperature for the three glassy slags from the Na_2O-SiO_2 system in Figure 12 [32]. It can be seen that all three curves show a dramatic decrease in thermal conductivity at some critical temperature above 900K. Mills [36] suggested that this critical point was T_g. If this is true, the curve can be split into 3 regimes, namely, *glass* (298K-T_g); *supercooled liquid* (T_g-T_{liq}) where there is a sharp drop in k and *liquid* ($T>T_{liq}$). The possible relation between thermal conductivity and viscosity, mentioned above, suggests that (i) the sharp decrease in k is associated with changes when passing through T_g [36] and (ii) that the temperature dependence of k for a scl can be represented by a VFT relation. Consequently, it was decided to investigate whether a relation exists between thermal conductivity and viscosity for slags in the supercooled phase.

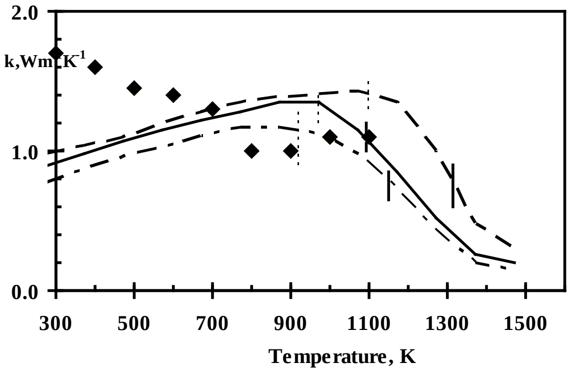


Figure 12 Thermal conductivity as a function of temperature for $Na_2O{\cdot}2SiO_2$=dash-dot line; $Na_2O{\cdot}3SiO_2$= solid line and $Na_2O{\cdot}4SiO_2$=dashed line [32]; ♦=crystalline $CaO{\cdot}SiO_2$ [35]; vertical lines; solid=T_{liq} and dotted =T_{peak}.

Susa and co-workers [28-33] have measured thermal conductivities for a number of slags using the THW method. Unfortunately, there are no viscosity data available for these slag compositions. Consequently, viscosities were estimated for the supercooled phase using the software developed by Fluegel [14, 15] for glasses. Unfortunately, it was not possible to calculate viscosities for many of the slag compositions used in thermal conductivity measurements [29, 31, 34] because their compositions were outside the range of the model. The results, where the viscosity could be calculated, are given in Figure 13 a and b and show that:

(i) the k-T relation does not follow the form of the VFT relation since this would result in a linear correlation similar to that for $\log_{10}$ R and $\log_{10}$ η (Figure 8); instead the relation has the form of a "*dog's leg*" where k remain fairly constant to a viscosity of 10^6 dPas and then drops markedly.

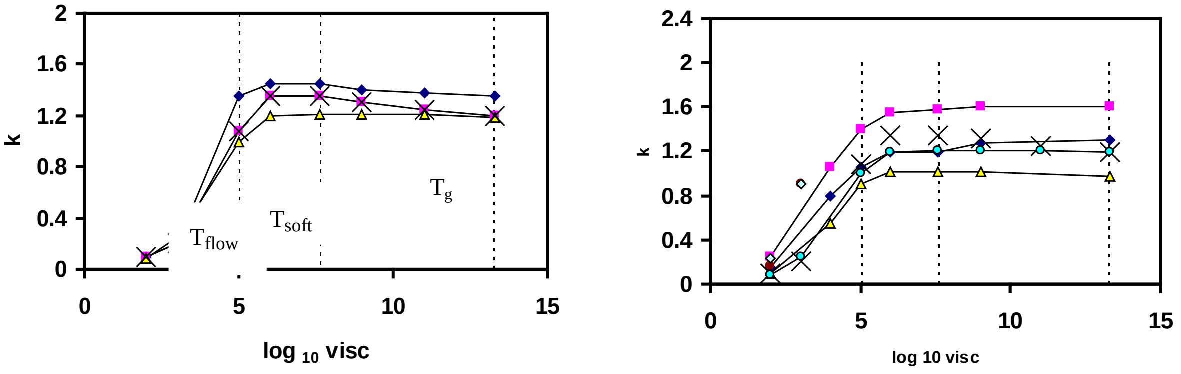
(ii) the sharp drop in k occurred between the Littleton softening point (T_{soft}, where $\eta = 10^{7.6}$ dPas and the sample deforms under its own weight) and the flow point (T_{flow} where $\eta = 10^5$ dPas,) as can be seen in Figure 12.

(iii) The replacement of Na_2O by CaO resulted in a marked increase in k for a given viscosity value.

The results shown in Figure 13 indicate that the thermal conductivity in the supercooled state does not follow the viscosity. In fact, the results appear to indicate the magnitude of the thermal conductivity is linked to the rigidity of the silicate network and when this rigidity is lost (between T_{soft} and T_{flow}) there is a marked decrease in the thermal conductivity value. Thus the dramatic decrease in k with increasing temperature is not associated with transition from a glass to a supercooled liquid but is associated with the loss of rigidity of the silicate lattice.

The above results suggest that (i) the magnitude of the thermal conductivity correlates directly with the rigidity of the network and (ii) the rigidity of the network is lost when the viscosity drops below 10^6 dPas which lies between the *softening point* and the *flow point*. The results also suggest that the replacement of Na_2O by CaO increases the network rigidity and hence increases the thermal conductivity. Fluegel [23] has reported that the combination of Na_2O and CaO tightened the network and thereby reduced the thermal expansion of solid glasses.

It might be anticipated that the rigidity of the lattice would increase with (i) increasing polymerisation of the slag and (ii) increasing M-O bond strength (*ie*. high z/r^2 value). The increase in the value of thermal conductivity with increasing SiO_2 content is consistent with this theory, as are the high k values for slags containing CaO and Li_2O in the glass and supercooled liquid phases. Similarly, the increasing thermal conductivity obtained with increasing Al_2O_3 content can also be explained by increased rigidity of the lattice. The rigidity concept can also account for the decrease of thermal conductivity obtained with F additions; the glass viscosity software [14, 15] was used to determine the effect of a 1% addition of fluorine on the softening point and it was found T_{soft} decreased by 25K $(\%F)^{-1}$ indicating loss in the rigidity of the network



(a)

(b)

Figure 13 Thermal conductivity as a function of log viscosity in the supercooled liquid state for (a) slags from the Na_2O-SiO_2 system due to Nagata [32]; ♦= $Na_2O{\cdot}4SiO_2$; ■ = $Na_2O{\cdot}3SiO_2$; Δ= $Na_2O{\cdot}2SiO_2$ and (b) slags from the Na_2O+CaO+ SiO_2 compared with the values reported for $Na_2O{\cdot}2SiO_2$ and $Na_2O{\cdot}3SiO_2$ [28, 32, 33].

For the liquid state it would appear that thermal conductivity increases with increasing SiO_2 and polymerisation (increasing Q) but it is not possible to discern any cation effects at this stage.

2.8 Surface Tension (γ)

Surface tension is a surface property and not a bulk property. The layer of molecules at the free surface tends to have high concentrations of constituents with low surface tension (*"surfactants") eg.* B_2O_3, K_2O in slags. Surface tensions of systems like $CaO-SiO_2$ can be estimated from partial molar values ($\gamma=\Sigma X_1\gamma_1+ X_2\gamma_2 +\ldots$) where 1 and 2 denote CaO, SiO_2 etc. [19] but the presence of surfactants tends to lower the overall surface tension significantly.

It is noted that (i) surface tensions of Group II oxides (γ_{MO}) are greater than those for Group I oxides (γ_{M2O}) *ie.* $\gamma_{MO} > \gamma_{M2O}$ and (ii) for Group I oxides γ_{M2O} decreases as M-O bond strength decreases (*ie.* decreasing z/r^2 value) $\gamma_{K2O}< \gamma_{Na2O}< \gamma_{Li2O}$. Both of these facts suggest a relation between γ for the oxide and M-O bond strength or z/r^2 (Figure 14).

It should also be noted that the surface tension of SiO_2 is relatively low (*cf.* γ values for CaO, MgO) and so, for many slags, the surface tension tends to decrease with increasing SiO_2 content (*ie.* increasing polymerisation). The concentration of SiO_2 in the surface layer will be dependent upon the activity of SiO_2 in the melt and the activity coefficient of silica (f_{SiO2}); in M^nO-SiO_2 melts is promoted by low values of the M-O bond strength (or low values of (z/r^2) for the oxide).

When the concentration of surfactants at the free surface exceeds a certain critical value the temperature dependence ($d\gamma/dT$) tends to change from a negative value to a positive value (the best known example of this behaviour is in metal-sulphur systems *eg.* Fe-S systems and its effect on welding [37]). Silica is a mild surfactant and in molten silicates this critical point is reached when SiO_2 mass % exceeded 50% [38]. It might be expected that for M^nO-SiO_2 melts, systems with high f_{SiO2} values (*eg* $K_2O>Na_2O>Li_2O>$ BaO) would assist positive ($d\gamma/dT$) values.

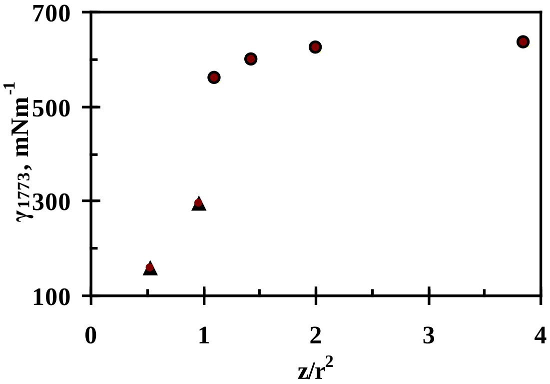


Figure 14 Surface tension of MO (●) and M_2O (▲) oxides at 1773 K as a function of bond strength (*ie.* z/r^2).

3 Discussion and Comments

3.1 Cation effects on properties

The different effects of cations on thermophysical properties of slags are summarised in Table 2. It can be seen that:

(i) the strength of the M-O bond affects the magnitude of T_{liq}, the chemical activity coefficient and the entropy of fusion and probably influences surface tension and the thermal conductivity through its effect on the rigidity of the silicate lattice.

(ii) the bridging of two chains by M^{2+} affects the viscosity and possibly affects the electrical resistivity and the thermal conductivity values

(iii) the cation size affects the viscosity and the electrical resistivity

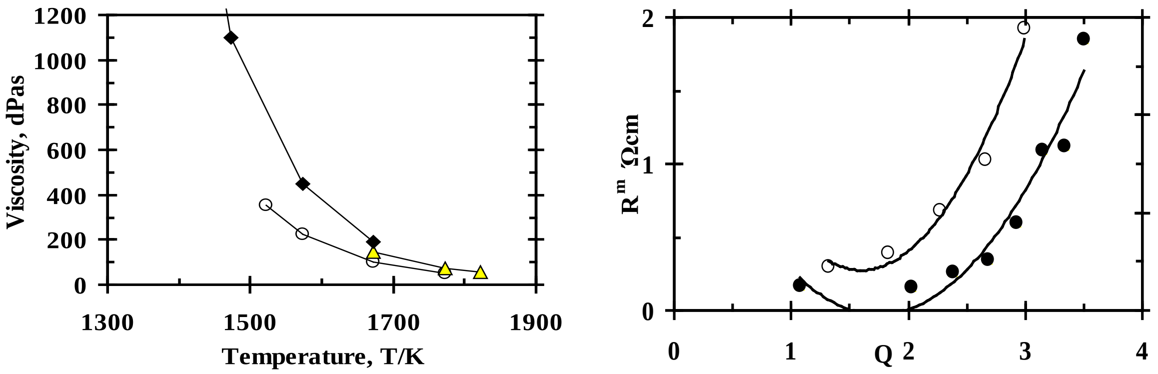
(iv) the number of cations has a significant effect on the electrical conductivity and possibly the diffusion coefficient.

Table 2 Summary of the factors affecting various properties of slags; ↑ indicates an increase in property obtained, for instance, by a decrease (↓) in M-O bond strength; f_{SiO2}= activity coefficient of SiO_2

Property	Factors	Bridging	M-O bond strength	M-O covalence	Cation size	Mixed cation effect	Number of cations
T_{liq} ↑			↑				
f_{SiO2} ↑	Q↑ (z/r^2)↓		↓				
ΔS^{fus} ↑	Q↓ (z/r^2)↑		↑				
α, β ↑	Q↓ (z/r^2)↓		↓	Possibly			
η ↑	Q↑ (r^3)↑	↑			(r^3)↑		
$R(=\kappa^{-1})$ ↑	Q↑ n↓ (r^3)↑	Probably			(r^3)↑	↑	↑
k↑	Rigidity↑ Q↑ (z/r^2)↑	Probably	↑	Possibly		Possibly	
γ↑	X_{SiO2}↓ Q↓		Probably				

3.2 Database of recommended thermophysical property data for slags

During the work carried out in this study it became apparent that in some cases there were large differences in the property values reported for the slags of very similar compositions. Two examples are given in Figure 15, the viscosity values at 1673K of $0.2Na_2O$-$0.8SiO_2$ reported by Sumita et al. [40] and Eipeltauer [39] are ca 44 and 90% higher than the values given by Bockris et al. [22] and the discrepancy in the results [21, 41] for the electrical conductivity of Li_2O-SiO_2 slags is of a similar magnitude. In recent years, a considerable number of models have been reported to calculate thermophysical properties, and property data are needed to check their predictions. Workers tend to select the data which gives the best fit with their predictions. A database of recommended thermophysical data is needed to provide modellers with an independent check on the accuracy of their predictions. The Thermodynamic fraternity successfully provided a database of thermodynamic and phase equilibrium data which has provided the foundation of reliable models to predict unknown systems. There is an urgent need for the establishment of international committees to provide recommended thermophysical data for the various slag systems.



(a) (b)

Figure 15 Examples of property variations reported for (a) Viscosity as a function of temperature; ○=Bockris [22]; ♦ = Eipeltauer [39]; Δ= Sumita [40] of $0.2Na_2O$-$0.8SiO_2$ and (b) R^m vs Q for Li_2O-SiO_2 slags o=Bockris [21]; ●=Tickle [25].

4 Conclusions

1. The degree of polymerisation of the silicate network is the principal factor affecting the magnitude of the thermo-physical property. As the polymerization parameter (Q) increases there are resultant decreases in the thermal expansion, and electrical conductivity and increases in viscosity, thermal conductivity and electrical resistivity.

2. The effects of individual cations on the property values tend to be smaller than those due to the polymerisation of the silicate network but, nevertheless, they are significant. Cations affect different physical properties in different ways:

Liquidus temperatures decrease as M-O bond strength (usually represented by (z/r^2)) decreases *ie*. $T_{liq} \uparrow$ as $(z/r^2)\downarrow$;

Thermal expansion values increase with decreasing M-O bond strength so $\alpha\uparrow$ as $(z/r^2)\downarrow$;

Viscosity values are affected by two factors (i) larger cations tend to hinder the flow of one layer of molecules over another so viscosity increases as cation radii increase ($\eta \uparrow$ as $r^3\uparrow$) and (ii) Na^+ bonds with a non-bonding O (NBO) ion whereas a Ca^{2+} must bond with 2 NBOs, resulting in the formation of a bridge formed which leads to a higher viscosity.

Electrical conductivity is also affected by two factors (i) κ increases as the size of the cation decreases ($\kappa\uparrow$or $R\downarrow$ as $r^3 \downarrow$) and (ii) it increases as the number of available cations, n, increase (eg.Na_2O provides 2 ions but CaO produces only one).

Thermal conductivity values for the solid and supercooled states appear to be determined by the rigidity of the silicate lattice; thus oxides with high (z/r^2) values tend to have high thermal conductivities. It proved difficult to identify any cation effects for liquid slags because of the high levels of experimental uncertainty and the low values of the thermal conductivity.

3. The temperature dependence of the electrical resistivity in the supercooled region can be satisfactorily expressed as a Vogel-Fulcher-Tamman equation.

4. There is an urgent need for a database of recommended property data for slags.

Acknowledgements

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