Calculation of Physical Properties for Use in Models of Continuous Casting Process-Part 1: Mould Slags

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1. Introduction

Recent mathematical models1–3) have shown that they are capable of providing (i) accurate predictions of both the heat flux and the powder consumption (a measure of the lubrication supplied to the shell) and (ii) valuable insights into the mechanisms underlying problems and defects (e.g. slag entrapment and oscillation mark formation). These models are being further developed to identify the causes of defects. However, models require accurate values for the physical properties of both the steel and mould slag (as input data). Properties of both mould slag and steel vary considerably with composition and a large number of steels and mould powders are in use. Consequently, a model of the continuous casting process requires a large amount of property data for the steel and mould powder used in the casting. The most satisfactory solution is to develop routines to calculate the required properties from their chemical composition, since the latter is available on a routine basis. Reliable models have been developed to calculate these property values as a function of temperature from their chemical composition since this is available on a routine basis. Models have been developed to calculate the following properties: heat capacities, enthalpies, thermal expansion coefficient, density, viscosity, thermal conductivity and surface tension. Solid mould slags can exist as glassy or crystalline phases or as mixtures of the two (i.e. slag films) and the properties for the various phases can vary considerably; methods have been developed to calculate property values for these various states. The software used to calculate the properties is available via the link (i) http://www.mxif.manchester.ac.uk/resources/software (ii) https://sites.google.com/site/shyamkaragadde/software/thermophysical-properties.

KEY WORDS: mould slags; continuous casting; thermophysical properties; steels.

1.1. Effect of Structure on Slag Properties

The properties of slags are principally determined by the structure of the slag. In silicate slags the basic building carbonates decompose to form CO2(g) (ii) Carbon particles in the powder start to oxidise (iii) the oxide components sinter and (iv) then melt when the carbon is consumed, and molten globules mix to form a molten slag pool. Slag from the molten pool then infiltrates into the channel between the steel shell and the mould to form a slag film (Fig. 1); this consists of (i) a liquid layer (ca. 0.1 mm thick) and (ii) a solid layer (ca. 1–2 mm thick). The heat flux between shell and mould is determined, principally, by the thickness of this solid layer (and the amount of crystalline phase present) and the lubrication supplied to the shell is determined by the thickness of the liquid layer. Lubrication involves the following properties: viscosity (η), density (ρ) surface tension (γ) and break (or solidification) temperature (Tbr). The heat flux involves the following properties of the mould slag: thermal conductivity (k), Tbr, the fraction of crystalline phase formed in the slag film (fcr) and the optical properties of the mould slag.

The objective of this study was to develop routines to provide reliable values of the thermo-physical properties of mould slags from their chemical compositions, for input into the model of the continuous casting process. The other aim was to make these routines available as Excel software; open access is provided at (i) http://www.mxif.manchester.ac.uk/resources/software (ii) https://sites.google.com/site/shyamkaragadde/software/thermophysical-properties.
block is the Si–O tetrahedron, in which one Si$^{2+}$ cation is surrounded by 4 O$^{−}$ ions. Furthermore, in pure silica, each of these O$^{−}$ ions bonds to Si$^{4+}$ ions in other tetrahedra to form a 3-dim. structure (these bonds are known as bridging O's (BOs)). When a cation, such as Na$^{+}$, is introduced into SiO$_2$, the Na$^{+}$ breaks the bridging O bond and forms a non-bridging O (NBO); this results in de-polymerisation of the slag. In highly-depolymerised slags some O ions are not bonded to Si ions, these are referred to as free oxygens (FOs).

In alumino- silicates, Al$^{3+}$ ions are readily introduced into the Si$^{4+}$ chain or ring but a Na$^{+}$ or 0.5 Ca$^{2+}$ is needed for charge-balancing (i.e. to form NaAl$^{1+}$); cations on charge-balancing duties are not available for network-breaking. Thus the introduction of Al$^{3+}$ ions result in an increase in the polymerisation of the slag, however, the Al–O bond is weaker than the Si–O bond.

Some properties, such as viscosity, electrical resistivity, diffusion coefficient and thermal conductivity are very dependent upon the degree of polymerisation. Several parameters have been used to represent the degree of polymerisation. In this paper the parameter, Q, is used; it can be calculated from Eqs. (1) and (2) where MO

$$\text{NBO} / T = \frac{2 \left( \sum_{i} X_{M0} + \sum_{i} X_{M20} - \sum_{i} X_{M02} \right)}{\sum_{i} X_{M02} - 2 \sum_{i} X_{M202}}$$

$$Q = 4 - \frac{\text{NBO}}{T}$$

The O$^{−}$ ions bonded to cations tend to be arranged into an octahedral array (i.e. they have 6-fold coordination) but this varies with cation size. In general, the effect of different cations on the physical properties is much smaller than the effect of polymerisation. Nevertheless, the nature of the cations affects both the structure and the physical properties. The parameter usually used to represent the effect of cations is the field strength (=z/r$^2$ where z and r are the charge and radius of the cation). Increasing field strength has been reported to bring about (i) a wider spread of polymerised silicate anions (i.e. a wider spread of Q$^+$ species) (ii) a decrease in coordination number which affects the concentrations of BOs and NBOs (iii) increasing disorder in the melt or glass and (iv) a lower probability that they will carry out charge-balancing duties (which are usually carried out in the hierarchy K$^+$>Na$^+$>Li$^+$=Ba$^{2+}$ etc.). Cations affect properties (i) directly or (ii) indirectly through their effect on the structure; two examples of direct effects are (a) the electrical conductivities ($\kappa$) and diffusion coefficients (D) are affected by the number of available cations and for X$_{Na2O}$=X$_{CaO}$ there are twice as many Na$^{+}$ ions as Ca$^{2+}$ cations (so K$_{Na2O}$ slag>K$_{CaO}$ slag and D$_{Na2O}$ slag>D$_{CaO}$ slag) and (b) the mixed alkali effect occurs where some properties for slags are significantly affected by cations with differing size (e.g. K$^+$ and Li$^+$).

Increasing temperature has a similar effect to that of increasing the number of cations, i.e. it reduces the degree of polymerisation; thus increasing temperature reduces viscosity and increases electrical conductivity and diffusion rates.

1.2. Crystalline, Glassy and Liquid Phases

In the solid state, slags can exist as crystalline or glassy phases or as a mixture of the two phases (e.g. slag film). In crystalline solids, the ions occupy regular positions and the amount of disorder (or configurational entropy) is low. In contrast, in glasses the ions are more disordered and the configurational entropy is much higher than that in crystals.

The formation of glasses is promoted by (i) slags with high Q (degree of polymerisation) values (i.e. high SiO$_2$ contents) and (ii) fast cooling rates. When a frozen glass is heated, it transforms at the glass transition temperature (T$_{g}$) into a supercooled liquid (scl). This transition is accompanied by step-increases in both C$_p$ and thermal expansion coefficient ($\alpha$) and results in a concomitant increase in configurational entropy.

When a liquid slag is cooled, if crystals are precipitated, there is a sharp increase in viscosity at a certain temperature, often denoted as the break temperature (T$_{bs}$). In contrast, if a scl is formed the viscosity increases smoothly with decreasing temperature.

2. Model Details

2.1. Composition, Modelling Parameters

The mould slag compositions covered by the model include conventional F- containing powders and F- free powders but do not include, at this time, the mould slags (based on calcium aluminates) now being used to cast...
high- Al- Mn steels. Furthermore, B₂O₃ additions have been reported to both reduce and increase slag viscosities of mould slags by various investigators; for this reason the effect of B₂O₃ on viscosity has been excluded.

As received, casting powders contain both free carbon and carbonates; these constituents are lost on ignition (LOI) in the process of forming a casting slag. The fraction of powder forming slag (f⁎) can be calculated from the chemical composition using either Eqs. (3) or (4)

\[ f^* = \left( 100 - \% \text{LOI} \right) / 100 \]  

(3)

\[ f^* = (100 - \% \text{C}_{\text{free}} - (44 / 12) (\% \text{C}_\text{total} + \% \text{C}_{\text{free}}) \]  

(4)

The composition of the cast slag can then be calculated by (i) multiplying by (1/f⁎) and normalising the composition. The software (covering these models) has the option to take into account typical pick-up values for Al₂O₃, FeO and MnO during casting. If this option is used the slag composition is re-normalised.

**Mole fractions** (X) are then calculated from these normalised compositions using Eq. (5) (where i refers to the constituents e.g. CaO, SiO₂ etc.); the %F present is converted into XCaF₂ and the Ca²⁺ associated with the F⁻ ions is deducted from XCaO.

\[ X_i = \left( X_i / M_i \right) / \Sigma \left( X_i / M_i \right) \]  

(5)

The **mean molecular weight** (M) is calculated using Eq. (6)

\[ M = \Sigma (X_i M_i) \]  

(6)

The **parameter** (NBO/T) is used as a measure of the depolymerisation of the slag. It is calculated from Eq. (1) where \( \Sigma X_{\text{SiO}} = X_{\text{CaO}} + X_{\text{MgO}} + X_{\text{MnO}} \) etc. and \( \Sigma X_{\text{CaO}} = X_{\text{Na₂O}} + X_{\text{K}_2\text{O}} \) etc. The parameter, Q is a measure of the polymerisation of the slag and is calculated from (NBO/T) using Eq. (2). It should be noted that both X₁CaF₂ and X₁SO₂ are ignored in Eq. (5) (on the basis of structural evidence) and the calculated Q value is that of the remaining slag (Q^\text{rem}).

**The fraction of crystalline phase in the slag film** (fₚ) was calculated using the relation proposed by Li et al.\(^3^\) where (NBO/T)\(^*\) indicates that the parameter differs from that calculated with Eq. (1), in that (i) CaF₂ is included in network breakers and (ii) when %MgO and %MnO are >7% and >4%, respectively, they are included in the denominator of Eq. (1). The calculation of both T br and T liq involve an uncertainty of ±25 K.

\[ f_{\text{sys}} = -2.84 + 1.41 (\text{NBO} / \text{T})* \]  

(7)

\[ \%_{\text{sys}} = 100. f_{\text{sys}} \]  

(8)

### 2.2. Temperatures (Tₜ, Tcrit, Tliq and Tbr)

These temperatures are calculated from chemical composition by the software and the temperature scale in the program is adjusted automatically.

**The glass transition temperature** (Tg) is the temperature where, on heating, a frozen glass transforms into a super-cooled liquid (scl). This transition is accompanied by step-increases in Cp and thermal expansion coefficient (TEC) (i.e. 3α / Tg = α > Tg). The viscosity of a glassy slag is taken to have a value of 10^17.4 (d Pas) at Tg (i.e. log₁₀ η (d Pas) = 13.4).

Numerical analysis of a database of Tg values (840–910 K) obtained from Cp and TEC data\(^6\) and chemical composition data for 23 mould slags was carried out in this study. Inspection of Tg values for mould slags indicates that values of mould slags tend to have similar values (Tg = 870±30 K). The best fit results are shown in Eq. (9) and are used in the software. The uncertainty in the calculation is ca. ±20 K.

\[ T_g(K) = 906 - 330.5X_{\text{SiO}_2} + 190X_{\text{CaO}} + 440X_{\text{Al}_{2}O_{3}} - 449X_{\text{Na}_{2}O} - 11X_{\text{MgO}} + 154X_{\text{CaF}_2} - 309X_{\text{MnO}} - 1391X_{\text{FeO}} \]  

(9)

**The critical (or deformation) temperature** (T crit) is the temperature above which, the thermal conductivity, decreases rapidly with increasing temperature (this can be seen in Fig. 6). Thermal conductivity- viscosity plots reveal that T crit occurs when log₁₀ η / T (d Pas) = 6 i.e. between the softening and flow temperatures.\(^7\) Values of the thermal conductivity as a function of temperature for a number of mould slags indicate that T crit occurs at 1 040±10 K.\(^8,^9\)

**The liquidus temperature** (T liq) is the temperature where the slag becomes fully molten. A numerical analysis of T liq values (from DSC experiments) and composition data gave Eq. (10); the calculated values are subject to uncertainties of ±30 K.

\[ T_{\text{liq}}(K) = 1464 - 11.4X_{\text{SiO}_2} - 11X_{\text{CaO}} + 4.2X_{\text{Al}_2O_3} + 5.7X_{\text{MgO}} - 10.1X_{\text{Na}_2O} - 15.8X_{\text{K}_2O} + 10X_{\text{Li}_2O} .. \]  

(10)

\[ + 1.9X_{\text{FeO}} + 11.6X_{\text{MnO}} \]

More recently, numerical analysis was carried out on a database of T liq and chemical composition data for 23 mould slags\(^8,^9\) and the Eq. (11) was obtained and is preferred. Values are subject to uncertainties of ±25 K.

\[ T_{\text{liq}}(K) = 1473 - 1.518X_{\text{SiO}_2} + 2.59X_{\text{CaO}} + 1.56X_{\text{Al}_2O_3} - 17.1X_{\text{MgO}} - 9.06X_{\text{Na}_2O} - 6.0X_{\text{K}_2O} + 18X_{\text{Li}_2O} + 4.8X_{\text{FeO}} - 9.87X_{\text{MnO}} \]  

(11)

**The solidification temperature** (T br) is the temperature where solids are first precipitated on cooling. It is frequently represented by the break temperature (T br), which is the temperature below which the viscosity shows a sharp increase in viscosity during cooling. The break temperature decreases with increasing cooling rate and often T br is cited for a cooling rate of 10 Kmin⁻¹. The thickness of the solid slag layer (Fig. 1) is partially determined by the break temperature. The following equation was obtained from numerical analysis of T br and chemical composition data;\(^10\) these values are subject to uncertainties of ±30 K.

\[ T_{\text{br}}(K) = 1393 - 3.3X_{\text{SiO}_2} + 8.65X_{\text{CaO}} - 8.45X_{\text{Al}_2O_3} - 17.1X_{\text{MgO}} - 3.2X_{\text{Na}_2O} - 2.2X_{\text{K}_2O} - 6.6X_{\text{Li}_2O} - 6.47X_{\text{FeO}} - 18.4X_{\text{MnO}} \]  

(12)

In general, super-cooling will ensure that T br < T liq. However, the calculation of both T br and T liq involve an uncertainty of ±25–30 K, so cases where T liq < T br do occur occasionally; in these cases a warning is issued on the printed Collectool Worksheet.

### 2.3. Heat Capacity (Cₚ) Enthalpy (H – H₂98)

The Cₚ- T relationships are different for different phases. Consequently, the mould slags are first sorted into individual phases i.e. (i) crystalline (b) glass (iii) slag film and (iv) liquid. The Cₚ and enthalpy of mould slags are little affected by the slag structure and it has been shown\(^11,^13\) that they can be calculated using routines based on partial molar quantities.

\[ P = \sum_{i=1}^{X}(X,P_i) \]  

(13)
and \( i=1,2,3,\ldots N \) denotes the different components (e.g. CaO, SiO\(_2\) etc.). The values of \( C_p \) and \((H_{\text{fus}} - H_{298})\) are calculated in units of \( \text{kJ mol}^{-1} \) and \( \text{kJ kg}^{-1} \), respectively; values were converted from \( \text{mol}^{-1} \) to \( \text{kg}^{-1} \) by multiplying by \( (1 \, 000/M) \) where \( M \), the average molecular weight of the slag.

The temperature dependence of \( C_p \) for crystalline solids is usually expressed in the form:

\[
C_p = a * + b * T - c * /T^2. \quad (14)
\]

where \( a * \), \( b * \) and \( c * \) are constants (given in Table 1). In the model the parameters \( a * \), \( b * \) and \( c * \) are treated as partial molar quantities.\(^{10} \) e.g.

\[
dT = \sum_{i=1}^{N} (X_i dT_i) \quad (15)
\]

The parameters \( b * \) and \( c * \) are calculated in a similar manner to \( a * \).

The enthalpy \((H_{Tg} - H_{298})\) is given by:

\[
(H_{Tg} - H_{298}) = \int_{298}^{Tg} C_p dT = a * (T - 298) + 0.5b * (T^2 - 298^2) + (c * /T) - (c * /298) \quad (16)
\]

The enthalpy of fusion, \( \Delta H_{\text{fus}} \), is calculated by assuming the entropy of fusion \((\Delta S_{\text{fus}})\) can also be calculated from partial molar terms.

\[
\Delta S_{\text{fus}} = \sum_{i=1}^{N} (X_i \Delta S_{\text{fus}}) \quad (17)
\]

\[
\Delta H_{\text{fus}} = T_{298} \Delta S_{\text{fus}} \quad (18)
\]

The \( C_p \) for the liquid phase is also calculated from partial molar terms\(^{11} \) using Eq. (19) and the enthalpy for the liquid is determined from Eq. (20).

\[
C_p = \sum_{i=1}^{N} (X_i C_{p,i}) \quad (19)
\]

\[
(H_{Tg} - H_{298})_{\text{sol}} = (H_{Tg} - H_{298}) + \Delta H_{\text{fus}} + C_p \text{ liq} (T - T_{298}) \quad (20)
\]

The \( C_p \) for the glass phase is close to that of the crystalline phase for temperatures below \( T_g \). At \( T_g \) the frozen glass transforms to a super-cooled liquid (\( \text{scl} \)); this is accompanied by a step- increase in \( C_p \). Measured values of \( C_p \) for the \( \text{scl} \) (\( C_p \text{ sic} \)) were between 1 \( 400 \) and 1 \( 500 \) \( \text{JK}^{-1} \text{mol}^{-1} \).\(^{12} \) These values are in close agreement with the value calculated for the liquid.

Consequently it was assumed that \( C_p \text{ sic}=C_p \text{ liq} \) for the range between \( T_g \) and \( T_{298} \). Values of the enthalpy for the \( \text{scl} \) in the temperature range between \( T_g \) and \( T_{298} \) are given in Eq. (21).

\[
(H_{Tg} - H_{298})_{\text{scl}} = (H_{Tg} - H_{298}) + C_p \text{ sic} (T - T_g) \quad (21)
\]

It should be noted that:

(i) Crystallisation occurs around 50–100 K above \( T_g \) (this is an exothermic reaction and results in an apparent decrease in \( C_p \) in DSC measurements); thus the state of the sample remains largely undefined in this temperature range.

(ii) When \((H_{\text{liq}} - H_{298})\) is calculated for both crystalline and \( \text{scl} \) it was found that \((H_{\text{liq}} - H_{298})\) for mould slags\(^6,12\) which suggests that \( \Delta H_{\text{fus}} \neq 0 \) for the \( \text{scl} \); high temperature \( C_p \) measurements are needed to resolve this anomaly. The slag film consists of a mixture of glass and crystalline phases; the \( C_p \) and enthalpy for a slag film is calculated using the rule of mixtures (Eqs. (22) and (23), respectively).

\[
C_p \text{ slag film} = f_{\text{cryst}} C_p \text{ cryst} + (1 - f_{\text{cryst}}) C_p \beta \quad (22)
\]

\[
(H_{Tg} - H_{298})_{\text{scl}} = f_{\text{cryst}} (H_{Tg} - H_{298})_{\text{cryst}} + (1 - f_{\text{cryst}}) (H_{Tg} - H_{298})_{\beta}. \quad (23)
\]

There are only a few measurements of the \( C_p \) and \((H_{1\text{\%}} - H_{298})\) available for mould slags\(^6,12\) and these are restricted to temperatures below 1 \( 000 \) K. There are no reported measurements for the liquid. Thus the model is based on a generic data for oxides and fluorides. Although, the predicted \( C_p \) and \((H_{1\text{\%}} - H_{298})\) values are within \( \pm 2\% \) of the experimental values for \( T<1 \) \( 000 \) K, the uncertainty is probably \( \pm 5\% \) for \( T>1 \) \( 000 \) K. It should also be noted that when a glass is heated to a temperature of \( ca. (T_g + 80 \) K) the sample will partially crystallise and the exothermic enthalpy released causes a sudden apparent decrease in \( C_p \) values measured by DSC; this is not a true effect and the values calculated by the model will not show this effect.

2.4. Density (\( \rho \)) Thermal Expansion Coefficient (\( \alpha \))

Thermal expansion coefficients reported for 10 glassy samples over the temperature \((298–T_g)\) range between 9 and \( 11 \times 10^{-6} \text{ K}^{-1} \) and for one sintered mould flux \((298–1 \) \( 000 \) K).\(^6 \) These measurements indicated that \( \alpha \) decreased slightly with increasing \( Q \) (\( 10^6 \alpha =15.2–2.14 \) Q) but the scatter was such that \( (\alpha =10 \times 10^{-6} \text{ K}^{-1}) \) has not been preferred in the calculations. There are few data available for partially-crystallised samples of mould slag; one sample\(^5 \) exhibited a value of \( \alpha (298–1 \) \( 000 \) K)=\( 10 \times 10^{-6} \text{ K}^{-1} \); this value was adopted.

The thermal expansion coefficient data for binary silicates in the liquid indicate that it is dependent upon both \( Q \) and \( (z/r)^2 \).\(^{13} \) However, there are few reported \( \rho \)– \( T \) data for liquid mould slags and individual \( \rho \) values are subject to uncertainty. Consequently, thermal expansion values for the liquid phase were obtained with a generic model for oxide slags\(^{14} \) containing CaF\(_2\).

The densities of silicate and alumino-silicate slags exhibit only a small dependence on the slag structure. Reasonable estimates can be obtained using partial molar volumes (\( V \)) for the various slag constituents but special procedures are
needed for SiO₂ and Al₂O₃.¹¹)

There are few reported data for the density of mould slags. Values have been reported for the glassy phase³⁻¹⁶ for the liquid state¹⁷,¹⁸) and for some slag films.¹²)

The density of the liquid mould slag is calculated from partial molar volumes (V̅M/ρ where M=molecular weight) as shown in Eqs. (24)–(26) (using the data given in Table 2) but special treatment is given to SiO₂ (V̅SiO₂=19.55 +7.966X SiO₂) and Al₂O₃ (V̅Al₂O₃ = 28.31 +32XAl₂O₃ +31.45 (XAl₂O₃)²) to account for the effect of structure on the molar volume and hence the density (ρ).¹¹) These routes were calculated from studies of density values for a wide range of slag compositions.¹¹)

\[ V_T = V_{1773} + 0.01(T - 1773 \text{ K}) \]  \[ V_T = M / \rho T \]  \[ V_T = \Sigma X_i V_i \] 

Stebbins et al.¹⁹) have also reported values of \( V_{1873} \) and dV/dT based on regressions of V-T and (dV/dT) data for most of the components shown in Table 2. These data were used to calculate both \( V_{1873} \) and (dV/dT). Values for the missing components in Table 2 were derived here from \( V_{1773} \) and V-T data.

The recommended values of \( V_T \) were calculated using the \( V_{1773} \) value and Eq. (27) and are preferred to values calculated by Eq. (25). The values calculated using the Stebbins value for \( V_{1873} \) are given on the Density Worksheet. Although \( V_T \) values in Table 2 vary, the density values (Table 2) and (V̅SiO₂=23.76 +3.5X SiO₂) and (V̅Al₂O₃=40.4). However, when a glassy sample crystallises it is accompanied by shrinkage (since ρcrys > ρscl). This results in porosity in the sample; the porosity levels were not determined for the density measurements on slag films but would be expected to lower the density values.

There are very few data reported for mould slags. The glassy phase has a lower density than the crystalline phase but there are no experimental data for mould slags to validate this statement. Thus, it has been assumed that ρscl=ρscl, for temperatures between \( T_g \) and \( T_{liq} \); the density of the super-cooled liquid was calculated by assuming that (i) there was no density change associated with the (scl → liquid) transition (ii) \( \rho_{scl} \) is a linear function over this temperature range (i.e. \( \rho_T = \rho_T^{scl} + (T - T_g)\rho_{T_g} \)).

Values of \( \rho_T \) for solids (both the glassy and sintered samples) were calculated using a value of \( \alpha = 10^{-5} \text{ K}^{-1} \). Normally, the calculations produce a density decrease at \( T_{liq} \) but the uncertainty in the calculations of \( \rho_T \) for both solid and liquid phases can lead (with certain compositions) to an apparent increase in density at \( T_{liq} \); this is not a true effect and is caused by the combined uncertainties. In such circumstances a warning is given on the Collected Worksheet.

There are few reported density data for mould slags. Nevertheless, the estimated values for the density for temperatures below 1 000 K, the uncertainties are probably 2–3% and are within ±5% for T > 1 000 K. Data are needed for the density change associated with glass→crystalline phase change.

### Table 2

<table>
<thead>
<tr>
<th>Component</th>
<th>SiO₂</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>Li₂O</th>
<th>FeO</th>
<th>MnO</th>
<th>CaF₂</th>
<th>ZrO₂</th>
<th>TiO₂</th>
<th>B₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_{1773} )</td>
<td>20.7</td>
<td>16.1</td>
<td>33.1</td>
<td>51.8</td>
<td>16</td>
<td>15.8</td>
<td>16.5</td>
<td>17</td>
<td>28.5</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( V_{298} )</td>
<td>14.4</td>
<td>40.4</td>
<td>12.5</td>
<td>20.2</td>
<td>33.5</td>
<td>11</td>
<td>16.5</td>
<td>17</td>
<td>28.5</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( V_{1873} )</td>
<td>26.75</td>
<td>16.9</td>
<td>37.7</td>
<td>11.95</td>
<td>29.5</td>
<td>48.5</td>
<td>17.3*</td>
<td>13.7</td>
<td>13.3*</td>
<td>31*</td>
<td>24.25</td>
<td>27*</td>
<td></td>
</tr>
<tr>
<td>l₀dV/dT</td>
<td>−0.42</td>
<td>3.97</td>
<td>1.02</td>
<td>2.22</td>
<td>7.4</td>
<td>2</td>
<td>1.5*</td>
<td>4.15</td>
<td>4*</td>
<td>5.1*</td>
<td>0.8</td>
<td>4*</td>
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</tr>
</tbody>
</table>

![Fig. 2](image-url)

(a) Viscosity (ln η₁₉₀₀,K) and (b) the parameter, B₉₀, as functions of Q; note the upper curve in (b) is for MO-silicates and the lower curve is for MnO-silicates.³⁻⁵)
The introduction of Al³⁺ into the Si⁴⁺ structure for slags with Q > 2.8 results in a small linear increase in viscosity with increasing Q for alumina-silicates, in contrast with the dramatic increase in viscosity with increasing Q for silicates shown in Fig. 2(a).

Viscosity measurements on mould slags have been reported by several workers. Experimental uncertainties can be up to 25%; McCauley cites six sets of viscosity measurements on the same slag and the reported viscosities were found to vary by ±25%. Another source of uncertainty is that few workers cite chemical analysis on the post-mould slag.

The new model to calculate the viscosities of mould slags is based on an earlier model proposed for slags in general but which has required certain modifications in applying it to mould slags. In the original model, ln(η₁ ₅₇₃ K) is based on an earlier model proposed for slags in general (i.e. mean structure for slags etc.). The activation energy term, Bₐ, is dependent upon two factors (Q and XCaF₂), the various slags were then sorted into individual groups according to their XCaF₂ values (e.g. 0–0.05; 0.05–0.1; etc.) and allocated a mean XCaF₂ value (e.g. 0.025; 0.075, respectively). The departure of experimental values (Bₐ exp) from the curve (i.e. from Eq. (28), calculated using the remaining slag composition, Bₐ rem Eq. (28)) is denoted ∆Bₐ = (Bₐ rem Eq. (28) – Bₐ exp) (31)

The same approach can not be adopted to treat the ln η ₁ ₅₇₃ K data because of the large differences in ln η values for 1 900 K and 1 573 K. Consequently, it is difficult to calculate a value of ln η ₁ ₅₇₃, CaF₂=0 for CaF₂-free slags, since both Q and XCaF₂ affect the viscosity simultaneously.

The experimental data were first sorted into the same groups of similar XCaF₂ values and these values were then plotted as function of Q (Fig. 4(a)) and equations were derived for ln η ₁ ₅₇₃ K as a function of Q. A linear best fit of the data (ln η ₁ ₅₇₃ K=3.073 + 1.93Q) was then derived since the relationship is close to linear in the range Q=1.5 to 3. Then the database was divided into groups of similar Q values and plotted against the mole fraction of CaF₂ (Fig. 4(b)). The mean gradient of these plots (Δln η ₁ ₅₇₃/dXCaF₂) was then derived from these plots. Values of ln η ₁ ₅₇₃, CaF₂=0 were then calculated using Eq. (33); the values of ln η ₁ ₅₇₃, CaF₂=0 were then plotted against Q (Fig. 5) and the best fit curve for ln η ₁ ₅₇₃, CaF₂=0 is given in Eq. (34). It can be seen that the mean scatter in ln η ₁ ₅₇₃ K values is about 0.3 which corresponds to an uncertainty of ca. ±25% in ln η. Attempts will be made in the future to reduce this uncertainty from a best fit regression of ln η ₁ ₅₇₃ data as functions of Q and XCaF₂. The calculated viscosity values are compared with values calculated by the Riboud and Iida models in the Viscosity worksheet and mean values for the three models were also calculated.

Fig. 3. (a) The parameter, Bₐ, as a function of Q for slags containing varying XCaF₂: for following XCaF₂ ranges: line = 0; ○ = 0–0.05; ⋄ = 0.05–0.1; Δ = 0.1–0.15; ⋅ = 0.15–0.2; □ = 0.2–0.25; ■ = >0.25 and (b) ∆Bₐ as a function of XCaF₂.
are available for minerals and glasses, measurements on slags are rare for metallurgical slags and the authors were unable to obtain any experimental data for the slc state of mould slags. However, it is possible to calculate values for these slags in the slc range since log 10 \( \eta (d\text{Pas}) \) has values of 13.4 and 6, respectively, at \( T_g \) and \( T_{crit} \) (\( 1040 \pm 10 \text{ K} \)). These data can be coupled with calculated values for the liquid range since log 10 \( \eta (d\text{Pas}) \) has values of 13.4 and 6, respectively, at \( T_g \) and \( T_{crit} \) (\( 1040 \pm 10 \text{ K} \)). Attempts were made to obtain a best fit for these data using a polynomial relation (log 10 \( \eta (d\text{Pas}) = a + bT + cT^2 + dT^3 \)) where \( a, b, c \) and \( d \) are constants). Unfortunately, the resulting value for log 10 \( \eta \) at \( T_g \) departed significantly from log 10 \( \eta (d\text{Pas}) = 13.4 \) in some cases. Consequently, values of log 10 \( \eta (d\text{Pas}) \) were obtained from linear relationships between \( T_g \) and \( T_{crit} \) and between \( T_{crit} \) and \( T_{lg} \); these values should not be regarded as accurate values for the slc but do provide the reader with approximate values which are unavailable in the literature.

The performance of the new model was tested by calculating the viscosity at 1 573 K and comparing it with the experimental values for the Riboud26) and Iida27) models. It was found that performances of the new model, the Riboud and Iida models were similar (\( \Delta_{mean} = 35\%\); 35\% and 43\%, respectively). It was found that the mean \( T_{crit} \) value for the three studies was closer to the experimental values (\( \Delta_{mean} = 27\% \)). It should be noted the experimental uncertainties associated with both the viscosity measurements and changes in chemical composition during the measurement sequence are ca. \( \pm 25\% \) for most of the reported data.

### 2.6. Thermal Conductivity (k) and Thermal Diffusivity (a)

The thermal conductivity of the slag film is important in controlling the heat transfer from the shell. Thermal conductivities of liquid slags are difficult to measure since it is difficult to eliminate contributions from convection. This is usually achieved by using transient methods where the experiment is completed before convection is initiated. The two principal, transient techniques are the laser pulse (LP) and the Transient Hot wire (THW) methods.

However, glassy and liquid slags are also semi-transparent to infra-red radiation and heat transfer can occur simultaneously by both lattice conductivity (\( k_{lat} \)) and radiation conductivity (\( k_R \)). Most investigators try to determine the values of \( k_{lat} \) and \( k_R \) individually and then combine them to give a total value. However, recent measurements of \( k_{lat} \) on mould slags using the LP and THW methods reveal that:

- Values of \( k_{LP} \)32) values recorded on cooling after melting.

**Fig. 4.** Values of ln \( \eta_{T_{crit}} \) as functions of (a) \( Q \); \( X_{CaF_2} = (0.025 \pm 0.025) = 0 \); black line (0.075 \( \pm \) 0.025) = , and red line, (0.125 \( \pm \) 0.025) = and green line (0.175 \( \pm \) 0.025) = , (0.225 \( \pm \) 0.025) = and (b) mole fraction \( CaF_2 \); \( O = (Q = 1.5) \); = (Q = 2); = (Q = 2.5); = (Q = 3).

**Fig. 5.** Values of ln \( \eta_{T_{lg}} \) for various mould slags as a function of the parameter \( Q \); = Lanyi; = McCauley20) = Persson22) = Elahipanah.23)

**Fig. 6.** Thermal conductivity of mould slags as a function of temperature; Glassy phase: faint line = \( k_{THW} \) and = \( k_{LP} \) values for solid and liquid calculated from 10 7\( a = 4.5 \) and 4 m\(^2\)s \(^{-1}\). Respectively; partially- crystalline slags = \( X_c \) + and dashed, bold line and bold line: \( \Delta_{mean} \) = partially-melted powders \( ^{(2)} \) values recorded on cooling after melting.
agreement up to 1 000 K (Fig. 6) but deviate markedly at higher temperatures.

(ii) The $k_{\text{THW}}$ values for mould slags drop markedly for temperatures $>1$ 040 K, in contrast to $k_{\text{LP}}$ values which continue to rise (Fig. 6); this contradictory behaviour has been attributed variously, to electrical leakage in the THW measurements or to $k_{\text{LP}}$ contributions to $k_{\text{THW}}$ in the LP measurements.

The source of the discrepancy between $k_{\text{LP}}$ and $k_{\text{THW}}$ is unresolved at the present time. Here it has been assumed that $k_{\text{LP}}$ measurements contain contributions from $k_{\text{c}}$ and the $k_{\text{THW}}$ measurements have been adopted.

The thermal conductivities of slags are also affected by (i) the degree of crystallinity developed in the slag (i.e. $f_{\text{crys}}$) since $k_{\text{crys}} \approx 2 k_{\text{glass}}$ due to the higher packing density in the crystalline phase than in the glass and (ii) porosity which tends to reduce the thermal conductivity. Note crystallisation is accompanied by shrinkage and results in the formation of fine pores in slag films.

Plots of $k_{\text{THW}}$ for glassy, $\text{MgO} - \text{CaO} - \text{SiO}_2$ slags versus the calculated viscosities indicated that the sharp drop in $k_{\text{THW}}$ occurs until the temperature exceeds the critical (or deformation of fine pores in slag films.

Measurements of $k_{\text{THW}}$ for 15 mould slags indicated that the sample can no longer support its own weight) and the collapse in $k_{\text{THW}}$ occurs for the softening temperature (where $k_{\text{THW}}$ is calculated from Eq. (7). Note $k_{298}$ values between 295 K and 1 040 K can be calculated using Eq. (35). Note that if $k_{298} > 1.65$ Wm$^{-1}$K$^{-1}$ the temperature coefficient (dk/dT) will be negative and if $k_{298} < 1.65$ Wm$^{-1}$K$^{-1}$, (dk/dT) will be positive

$$k_{298} = 1.07 + 0.7 f_{\text{cry}}$$  \hspace{1cm} (38)

When the glass is heated above ca. 1 000 K, crystallisation of the sample occurs; note crystallisation occurs roughly in the same temperature range as $T_{\text{crys}}$ the model takes no account of any subsequent change in $f_{\text{crys}}$. Values of $k_{\text{c}}$ for partially-crystalline samples in the temperature range (1 040 K - $T_{\text{crys}}$) are calculated using Eq. (37). The few measurements of the thermal conductivity of liquid mould slags using the LP method which yields values for $k_{\text{c}}$ which are about 10 x higher than $k_{\text{THW}}$ values (Fig. 6). The $k_{\text{THW}}$ values have been tentatively, adopted. Eq. (39) was obtained from a relation reported for slags covering a wide compositional range.

$$k_{\text{THW}} = 0.139 + 3.65 \times 10^{-5} \exp (Q / 0.3421)$$  \hspace{1cm} (39)

Values of $k_{298}$ have been reported for slag films taken from the mould.

(iii) Approximate values for $k_{298}$ of the slag film can be calculated by using Eq. (40) where $f_{\text{crys}}$ is calculated from Eq. (7). Note $k_{298} = 1.77$ Wm$^{-1}$K$^{-1}$ is calculated with Eq. (38) for $f_{\text{crys}} = 1$ and refers to a sample containing pores.

$$k_{298} = 1.77 f_{\text{cry}} + 0.7 (1 - f_{\text{cry}})$$  \hspace{1cm} (40)

There are two outstanding problems to be resolved concerning thermal conductivity measurements, namely (i) the differences between $k_{\text{THW}}$ and $k_{\text{LP}}$ for temperatures above 1 040 K and (ii) the degree of porosity in slag film and partially-crystalline samples which has not yet been determined and which makes it difficult to determine the $k$ value for a fully-dense slag. The calculated thermal conductivity values of the glass and partially-crystalline phases are probably prone to uncertainties of ca. ±5% and ±10% respectively, for temperatures between 298 and 1 040 K. However for temperatures $> 1$ 040 K, it is difficult to attribute uncertainties until the differences between $k_{\text{THW}}$ and $k_{\text{LP}}$ are fully explained.

2.7. Surface Tension (γ) and Interfacial Tension (γgalement)

Surface tension is a surface property and not a bulk property. The magnitude of the surface tension is determined by the composition of the surface. Components with low surface tension (denoted surfactants) tend to occupy the surface layer and hence largely determine the surface tension. Components such as CaO, MgO and Al$_2$O$_3$ have high surface tensions (Table 3) compared with the surface tension of SiO$_2$ and the surfactants (B$_2$O$_3$, K$_2$O, Na$_2$O and CaF$_2$).

The temperature dependence of surface tension (dγ/dT) is usually negative for most components but as the concentration of surfactants increases (dγ/dT) becomes less negative.
Table 3. Values for slag components of surface tension (γ, mN m⁻¹), temperature coefficient (dγ/dT, mN m⁻¹ K⁻¹) and Gibbs energy of formation for liquid oxides per O atom (−ΔG, kJ mol⁻¹) used to calculate interaction parameter, Φ.

<table>
<thead>
<tr>
<th>Component</th>
<th>SiO₂</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>Li₂O</th>
<th>FeO</th>
<th>MnO</th>
<th>CaF₂</th>
<th>ZrO₂</th>
<th>TiO₂</th>
<th>B₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ (mN m⁻¹)</td>
<td>260</td>
<td>625</td>
<td>655</td>
<td>635</td>
<td>297</td>
<td>160</td>
<td>[300]</td>
<td>645</td>
<td>530</td>
<td>290</td>
<td>400</td>
<td>350</td>
<td>110</td>
</tr>
<tr>
<td>dγ/dT (mN m⁻¹ K⁻¹)</td>
<td>0.031</td>
<td>−0.094</td>
<td>−0.177</td>
<td>−0.13</td>
<td>−0.11</td>
<td>−0.11</td>
<td>−0.11</td>
<td>−0.11</td>
<td>−0.1</td>
<td>−0.1</td>
<td>−0.07</td>
<td>−0.15</td>
<td>−0.15</td>
</tr>
<tr>
<td>−ΔG (kJ mol⁻¹)</td>
<td>292.2</td>
<td>408.2</td>
<td>354.6</td>
<td>368.4</td>
<td>195.2</td>
<td>140</td>
<td>357</td>
<td>158</td>
<td>240.5</td>
<td>466</td>
<td>365</td>
<td>304</td>
<td></td>
</tr>
</tbody>
</table>

and eventually changes to a positive value.

Few surface tension measurements have been reported for mould slags. The model is based on a previous model in which the following assumptions were made:

(i) The various slag components were divided into, surfactants and bulk components.

(ii) The surface tension of bulk components (Fig. 7(a)) at 1773 K were calculated using partial molar values for the various components (γ = X₁γ₁ + X₂γ₂ + X₃γ₃) bulk.

(iii) It was found that X₁γ₁ contributions for surfactants resulted in a sharp drop in surface tension until a certain point was achieved (in the range, X₁ = 0.1 to 0.12) and the relation (up to this point) is expressed as, (X₁γ₁) = a' + b'X₁ + c'X₁². Above this point, γ increased gradually (Fig. 7(b)) with increasing X₁ (in range, 0.12 to 1.0) and is expressed as, (X₁γ₁) = d' + e'X₁.

When this model was applied to mould slags (which contain a reasonably high concentration of surfactants) it was found that it tended to produce low values for the surface tension. Consequently, the model was modified and the following assumptions were made:

(i) That the minimum in the surfactant curve in Fig. 7(b) corresponded to the point where the slag surface was saturated with surfactants (Xsurf = 0.12).

(ii) That the surface is occupied preferentially by B₂O₃ > K₂O > Na₂O > CaF₂ until the surface becomes saturated with surfactant at ΣXsurf = 0.12; (Xsurfγsurf) is calculated using the values for surfactants given in Table 3.

(iii) Any excess surfactant (left after ΣXsurf = 0.12) is treated as a bulk component (γ = X₁γ₁ + X₂γ₂ + X₃γ₃).

(iv) The temperature dependence (dγ/dT) was calculated from Eq. (41).

The surface tension is then calculated from Eqs. (42) and (43)

\[ \gamma_T = \gamma_\text{m} + \gamma_\text{a} - 2\varphi(\gamma_\text{m}\gamma_\text{a})^{0.5} \] .......................... (44)

\[ \varphi = 0.89 - 1.5 \times 10^{-3} \Delta G_\text{D} \] .......................... (45)

\[ \Delta G_\text{D} = \Delta G_{\text{mol}} - \Sigma X_i \Delta G_i \] .......................... (46)

There is a limited amount of data to test the predictions and the reported data show significant variation. Nevertheless, the calculated values are in good agreement with the measured values. 1,18,35–40 The uncertainty associated with the estimations is probably ca. ±10%.

The interfacial tension (γmol) can be calculated from Eq. (44) where γmol = metal surface tension, γa can be derived from Eqs. (42) and (43) and the interaction coefficient, φ, can be calculated using Eqs. (45) and (46), where AGD is the free energy of formation of the individual, liquid oxides and the values being given in Table 3. Thus, φ is treated as a measure of the oxide components in the slag to supply soluble oxygen in the metal and thereby, decrease the interfacial tension, γmol. The value of γmol is largely determined by γm since γm is (4 to 5) γa and the value of γm, in turn, is largely determined by the S content of the steel. The calculated values of γmol obtained with this procedure were reported to lie within ±100 mN m⁻¹ of the experimental values. Values of γmol are calculated in steel property estimation software, worksheet “surface tension”.

\[ \gamma_\text{mol} = \gamma_\text{m} + \gamma_\text{a} - 2\varphi(\gamma_\text{m}\gamma_\text{a})^{0.5} \] .......................... (44)

\[ \varphi = 0.89 - 1.5 \times 10^{-3} \Delta G_\text{D} \] .......................... (45)

\[ \Delta G_\text{D} = \Delta G_{\text{mol}} - \Sigma X_i \Delta G_i \] .......................... (46)

2.8. Emissivity (εTN)

Total normal emissivity measurements have been reported for mould slags; values were recorded for the solid (at T > 1030 K) εTN = 0.92 ± 0.05 and liquid, εTN = 0.91 ± 0.03.

3. Results and Discussion

Routines have been developed in this study to calculate the following properties of mould slags from their chemical composition for subsequent use as input data in mathematical models of the continuous casting process: Tₙₐₑ₅, Tₚ; Tₛₑₙ, Tₛₐₑ; Tₑₑₑ; Cₛ (H₁−H₂₉); density and α, viscosity, thermal conductivity, surface and interfacial tension and emissivity.

Although mould slags have relatively low melting points and are benign in their behaviour, there are few measure-
ments available for some properties (e.g. C_p, enthalpy, density and surface tension). By contrast, there are a large number of reported data for viscosity and for thermal conductivity/diffusivity. However, there is high level of experimental uncertainty with viscosity measurements (±10–25%) and there is an unresolved dispute regarding the thermal conductivity values at temperatures at > 1 040 K derived using the THW and LP methods. It is important that this dispute be settled quickly. One further problem is that many workers fail to report post-measurement analysis of their samples and F and Na losses can be significant during a measurement campaign and affect the property values. This study aims to provide reliable property data for the mould slags for use in mathematical models of continuous casting. Consequently, it is intended to update the existing software as new data become available. The following improvements in the software are planned:

(i) The present software does not include B_2O_3 additions since various workers report B_2O_3 causes both increases and decreases in slag viscosity.

(ii) To include calcium-aluminate-based slags used for slag for use in mathematical models of continuous casting.

(iii) To improve the viscosity model for the super-cooled liquid phase.

4. Conclusions

(1) Routines have been developed to calculate the thermo-physical properties of mould slags from their chemical composition for their subsequent use in mathematical models of heat and fluid flow in the continuous casting mould.

(2) The accuracies of estimated values are affected by the limitations in the experimental data.

(3) The cause of the huge discrepancies in thermal conductivities for T = 1 050 K must be resolved.

Acknowledgements

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Symbols Abbreviations

\( a \) = Thermal diffusivity (m^2 s^{-1})

\( C_p \) = Heat capacity (JK^{-1} mol^{-1} or JK^{-1} kg^{-1})

\( f_{cryst} \) = Fraction crystalline phase

\( f_p \) = Fraction of powder forming slag

(\( H_T - H_{298} \)) = Enthalpy relative to 298 K (J mol^{-1} or J kg^{-1})

\( k \) = Thermal conductivity (W m^{-1} K^{-1})

\( S \) = Entropy (JK^{-1} kg^{-1})

\( T \) = Temperature (K)

\( X \) = Mole fraction

\( \alpha \) = Thermal expansion coefficient (K^{-1})

\( \gamma \) = Surface tension (mN m^{-1})

\( \chi_{int} \) = Interfacial tension (mN m^{-1})

\( \eta \) = Viscosity (dPas)

\( \rho \) = Density (kg m^{-3})

\( B_O \) = Bridging Oxygens

\( F_O \) = Free Oxygens

\( L_P \) = Laser pulse method

\( NBO \) = Non-bridging Oxygens

\( NBO/T \) = Measure of de-polymerisation

\( S = \) transient hot wire method

\( Q = \) measure of polymerisation

\( scf = \) super-cooled liquid

Subscripts and Superscripts

\( m = \) Value for liquid at T_{liq}.

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