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

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Physical properties of both steels and mould slags are needed as input data for the mathematical modelling of the continuous casting process. Routines for calculating the properties of mould slags and for estimating steel properties have been developed and are described in Parts 1 and 2, respectively. Many mould powders, with differing compositions, are used in casting practice and their properties vary significantly. 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. 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. The relationships developed to estimate the physical properties of mould slags from their chemical composition are described here in Part 1 and those used for steels are described in Part 2. The two models are linked to calculate the metal/slag interfacial tension.

Mould powders play an important role in the continuous casting process. They are added to the top of the mould and as they heat up the following events occur, sequentially (i) 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 (Tₜᵢₚ). The heat flux involves the following properties of the mould slag: thermal conductivity (k), Tₜᵢₚ, the fraction of crystalline phase formed in the slag film (fcₗₑₙ) 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.

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
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$^{2+}$ chain or ring but a Na$^{+}$ or 0.5 Ca$^{2+}$ is needed for charge-balancing (i.e. to form NaAl$^{5+}$); 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=CaO, MnO etc. and M$_2$O=Na$_2$O etc. Summation index N$_{MO}$ etc. represents the number of different oxides. Other properties, such as density, are affected by the structure but to a much smaller extent than that in the above properties.

\[
NBO/T = \frac{2 \left( \sum_{i} X_{MO} + \sum_{i} X_{M2O} - \sum_{i} X_{M2O3} \right)}{\sum_{i} X_{M2O3}} \quad \text{(1)}
\]

\[
Q = 4 - NBO/T \quad \text{(2)}
\]

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.$^9$ 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$^{n}$ 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 $\kappa_{Na2O}$ slag>$\kappa_{CaO}$ 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 ($T_b$). 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, high-Mn steels. Furthermore, B$_2$O$_3$ additions have been reported to both reduce and increase slag viscosities of mould slags by various investigators; for this reason the effect of B$_2$O$_3$ on viscosity has been excluded.

As received, casting powders contain both free carbon and carbonate; 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)

$$f^* = \left(100 - \% \text{LOI}\right)/100 \quad \text{(3)}$$

$$f^* = \left(100 - \% C_{\text{free}}\right)/\left(44/12\right)\left(\% C_{\text{total}} - \% C_{\text{free}}\right) \quad \text{(4)}$$

The composition of the casting 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 Al$_2$O$_3$, 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, SiO$_2$ etc.); the $X$ present is converted into $X_{\text{CaF}_2}$ and the Ca$^+$ associated with the $F^-$ ions is deducted from $X_{\text{CaO}}$.

$$X_i = \left(X_i / M_i\right)/\Sigma \left(X_i / M_i\right) \quad \text{(5)}$$

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

$$M = \Sigma \left[X_i M_i\right] \quad \text{(6)}$$

The parameter ($NBO/T$) is used as a measure of the de-polymerisation of the slag. It is calculated from Eq. (1) where $\Sigma X_{\text{MGO}} = X_{\text{CaO}} + X_{\text{MgO}} + X_{\text{FeO}}$ etc. and $\Sigma X_{\text{XN}20} = X_{\text{XN}20} + X_{\text{XK}20}$ 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 $X_{\text{CaF}_2}$ and $X_{\text{TiO}_2}$ 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** ($f_{\text{cryst}}$) was calculated using the relation proposed by Li et al.\(^3\)

$$f_{\text{cryst}} = -2.84 + 1.41 \left(NBO / T\right)^* \quad \text{(7)}$$

$$\% f_{\text{cryst}} = 100. f_{\text{cryst}} \quad \text{(8)}$$

### 2.2. Temperatures ($T_{\text{br}}, T_{\text{crit}}, T_{\text{liq}}$ and $T_{\text{so}}$)

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

The **glass transition temperature** ($T_g$) is the temperature where, on heating, a frozen glass transforms into a super-cooled liquid (scl). This transition is accompanied by step-increases in $C_p$ and thermal expansion coefficient (TEC) (i.e. $3\alpha < T_g < \alpha > T_g$). The viscosity of a glassy slag is taken to have a value of $10^{11-14}$ (d Pas) at $T_g$ (i.e. $\log_{10} \eta$ (d Pas) = 13.4).

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

$$T_g(K) = 906 - 330.5X_{\text{SiO}_2} + 190X_{\text{CaO}} + 440X_{\text{Al}_203} - 44.9X_{\text{CaF}_2} - 11X_{\text{MgO}} + 154X_{\text{FeO}} - 309X_{\text{MnO}} - 1391X_{\text{FeO}}$$

... (9)

**The critical (or deformation) temperature** ($T_{\text{crit}}$) 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 $T_{\text{crit}}$ occurs when $\log_{10} \eta_{\text{crit}}$ (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 $T_{\text{crit}}$ occurs at 1 040 $\pm 10$ K.\(^8,9\)

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

$$T_{\text{liq}}(K) = 1464 + 11.4X_{\text{SiO}_2} - 11X_{\text{CaO}} + 4.2X_{\text{Al}_203} + 5.7X_{\text{MgO}} - 10.1X_{\text{Na}_20} - 15.8X_{\text{K}_20} + 10X_{\text{Li}_20} \quad \text{(10)}$$

+1.9%F + 8.3%FeO + 11.6%MnO

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

$$T_{\text{liq}}(K) = 1473 - 1.518X_{\text{SiO}_2} + 2.59X_{\text{CaO}} + 1.56X_{\text{Al}_203} - 17.1X_{\text{MgO}} - 9.06X_{\text{Na}_20} - 6.0X_{\text{K}_20} + 18X_{\text{Li}_20} + 4.8% F - 9.87% FeO - 2.12%MnO$$

... (11)

**The solidification temperature** ($T_{\text{so}}$) is the temperature where solids are first precipitated on cooling. It is frequently represented by the **break temperature** ($T_{\text{br}}$) 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 $T_{\text{br}}$ is cited for a cooling rate of 10 K min$^{-1}$. 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 $T_{\text{br}}$ and chemical composition data\(^6\); these values are subject to uncertainties of $\pm 30$ K.

$$T_{\text{br}}(K) = 1393 - 3.3X_{\text{SiO}_2} + 8.65X_{\text{CaO}} - 8.45X_{\text{Al}_203} - 17.1X_{\text{MgO}} - 3.2X_{\text{Na}_20} - 2.2X_{\text{K}_20} - 6.6X_{\text{Li}_20} - 6.47% F - 18.4% FeO - 3.2%MnO$$

... (12)

In general, super-cooling will ensure that $T_{\text{br}} < T_{\text{liq}}$. However, the calculation of both $T_{\text{br}}$ and $T_{\text{liq}}$ involve an uncertainty of $\pm 25-30$ K, so cases where $T_{\text{br}} < T_{\text{liq}}$ do occur occasionally; in these cases a warning is issued on the Collected Worksheet.

### 2.3. Heat Capacity ($C_p$) Enthalpy ($H_1$–$H_{298}$)

The $C_p$–$T$ 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 $C_p$ and enthalpy of mould slags are little affected by the slag structure and it has been shown\(^11,14\) that they can be calculated using routines based on partial molar quantities

$$P = \sum_{i=1}^{N} \left(X_i P_i\right) \quad \text{(13)}$$

where $P$ is a property, or coefficient, $X$ is the mole fraction
and \( i = 1, 2, 3, \ldots N \) denotes the different components (e.g., CaO, SiO$_2$ etc.). The values of \( C_p \) and \((H_T - H_{298})\) are calculated in units of JK$^{-1}$mol$^{-1}$ and kJ$^{-1}$kg$^{-1}$, respectively; values were converted from mol$^{-1}$ to 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:

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

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.,

\[
a^* = \sum_{i=1}^{N} (X_i a_i^*). \tag{15}
\]

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

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

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

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

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

\[
\Delta H_{fus}^i = T_{liq} \Delta S_{fus}^i \tag{18}
\]

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),

\[
C_p = \sum_{i=1}^{N} (X_i C_{pi}) \tag{19}
\]

\[
(H_T - H_{298})_{liq} = (H_{liq} - H_{298}) + \Delta H_{fus} + C_{p, liq} (T - T_{liq}) \tag{20}
\]

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 \((scf)\); this is accompanied by a step- increase in \( C_p \). Measured values of \( C_p \) for the \( scf \) \((C_p, scf)\) were between 1 400 and 1 500 JK$^{-1}$kg$^{-1}$\(^{12}\). These values are in close agreement with the values calculated for the liquid.

Consequently it was assumed that \( C_{p, scf} = C_{p, liq} \) for the range between \( T_g \) and \( T_{liq} \). Values of the enthalpy for the \( scf \) in the temperature range between \( T_g \) and \( T_{liq} \) are given in Eq. (21).

\[
(H_T - H_{298})_{scf} = (H_{scf} - H_{298}) + C_{p, scf} (T - T_g) \tag{21}
\]

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 \((H_{liq} - H_{298})\) is calculated for both crystalline and \( scf \) it was found that \((H_{liq} - H_{298})_{cryst} > (H_{liq} - H_{298})_{scf} \) which suggests that \( \Delta H_{fus} \neq 0 \) for the \( scf \); 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),

\[
C_p \text{ slag film} = f_{cryst} C_p \text{ cryt} + (1 - f_{cryst}) C_p \text{ gl} \tag{22}
\]

\[
(H_T - H_{298})_{\text{slag film}} = f_{cryst} (H_T - H_{298})_{\text{cryst}} + (1 - f_{cryst}) (H_T - H_{298})_g. \tag{23}
\]

There are only a few measurements of the \( C_p \) and \((H_T - H_{298})\) available for mould slags\(^{8,12}\) 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 \((H_T - H_{298})\) 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 \( ca. (T_g + 80) \) 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 \( 11 \times 10^{-6} \) K$^{-1}$ and for one sintered mould flux \((298–1\,000) \) K$^{-1}$\(^6\). These measurements indicated that \( \alpha \) decreased slightly with increasing \( Q \) \((10^6 \, \alpha = 15.2–2.14 \) Q but the scatter was such that \((R^2 = 0.41)\) that a constant value of \( \alpha = 10 \times 10^{-6} \) K$^{-1}$ has been preferred in the calculations. There are few data available for partially-crystallised samples of mould slag; one sample\(^9\) exhibited a value of \( \alpha = 10^{-6} \) 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 \( \beta \). However, there are few reported \( \beta \) 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\(^{11}\) 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 SiO$_2$ and Al$_2$O$_3$.\textsuperscript{11)}

There are few reported data for the density of mould slags. Values have been reported for the glassy phase\textsuperscript{14–16)} the liquid state\textsuperscript{17,18)} and for some slag films.\textsuperscript{12)}

The density of the liquid mould slag is calculated from partial molar volumes (V = M/\(\rho\) where M = molecular weight) as shown in Eqs. (24)–(26) (using the data given in Table 2) but special treatment is given to SiO$_2$ (V\textsubscript{SiO$_2$}=19.55 +7.966X\textsubscript{SiO$_2$}) and Al$_2$O$_3$ (V\textsubscript{Al$_2$O$_3$}= 28.31 +32X\textsubscript{Al$_2$O$_3$} +31.45 (X\textsubscript{Al$_2$O$_3$}))\textsuperscript{30)} to account for the effect of structure on the molar volume and hence the density (\(\rho\)).\textsuperscript{11)} These routines were calculated from studies of density values for a wide range of slag compositions.\textsuperscript{11)}

\[ V_{1773} = \sum_{i=1}^{N} (X_iV_i) \] \hspace{1cm} (24)

\[ V_T = V_{1773} + 0.01(T - 1773 \text{ K}) \] \hspace{1cm} (25)

\[ V_T = M / \rho_T \] \hspace{1cm} (26)

Stebbins et al.\textsuperscript{19)} have also reported values of V\textsubscript{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\textsubscript{1873} and (dV/dT). Values for the missing components in Table 2 were derived here from \(\rho_T\) and V-T data.

The recommended values of V\textsubscript{T} were calculated using the V\textsubscript{1773} value and Eq. (27) and are preferred to values calculated by Eq. (27). The values calculated using the Stebbins values lie within 1% of those calculated by Eq. (27).

\[ V_T = \sum X_iV_{1773} + \sum X_i(dV / dT)(T - 1773 \text{ K}) \] \hspace{1cm} (27)

A similar approach to that used for the liquid is taken for solid phase with different values for the molar volume (Table 2) and (V\textsubscript{SiO$_2$}=23.76 +3.5X\textsubscript{SiO$_2$}) and (V\textsubscript{Al$_2$O$_3$}=40.4). However, when a glassy sample crystallises it is accompanied by shrinkage (since \(\rho_{\text{cryst}} > \rho_{\text{glass}}\)). This results in porosity in the sample; the porosity levels were not determined for the density measurements on slag films\textsuperscript{12)} 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 \(\rho_{\text{glass}} = \rho_{\text{cryst}}\) for temperatures between T\textsubscript{g} and T\textsubscript{liq}; the density of the super-cooled liquid was calculated by assuming that (i) there was no density change associated with the (scI \rightarrow liquid) transition (ii) \(\rho_{\text{cryst}}\) is a linear function over this temperature range (i.e. \(\rho_T = \rho_{\text{g}} + (T-T_g)(\rho_{\text{liq}} - \rho_{\text{g}})/(T_{\text{liq}} - T_g)\)).

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\textsubscript{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\textsubscript{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 \(\pm 5\%\) for T > 1 000 K. Data are needed for the density change associated with glass\rightarrow crystalline phase change.

### 2.5. Viscosity (\(\eta\))

The principal factor affecting the viscosities of slags is the degree of polymerisation present in the slag; this can be clearly seen in Fig. 2 where both ln \(\eta\)\textsubscript{900 K} and the parameter, B\textsubscript{S1} exhibit considerable sensitivity to the parameter, Q (which is a measure of the polymerisation). The scatter of individual points in Fig. 2(a) is due to the effect of different

| SiO$_2$ | CaO | Al$_2$O$_3$ | MgO | Na$_2$O | K$_2$O | Li$_2$O | FeO | MnO | CaF$_2$ | ZrO$_2$ | TiO$_2$ | B$_2$O$_3$ |
|--------|-----|-------------|-----|---------|-------|--------|-----|-----|--------|--------|--------|--------|
| V\textsubscript{1773} \textsuperscript{[11]} | a | 20.7 | 6.3 | 16.1 | 33 | 51.8 | 16 | 15.6 | 31.3 | 24 | 10 |
| V\textsuperscript{298} \textsuperscript{[1]} | c | 14.4 | 40.4 | 12.5 | 20.2 | 33.5 | 11 | 16.5 | 17 | 28.5 | – | – |
| V\textsuperscript{1873} \textsuperscript{[21]} | 26.75 | 16.9 | 37.7 | 11.95 | 29.5 | 48.5 | 17.3* | 13.7 | 13.3* | 31* | 24.25 | 27* |
| 10$^3$dV/dT\textsuperscript{[21]} | −0.42 | 3.97 | 1.02 | 2.22 | 7.4 | 2 | 1.5* | 4.15 | 4* | 5.1* | 0.8 | 4* |

Fig. 2. (a) Viscosity (ln \(\eta\)\textsubscript{900 K}) and (b) the parameter, B\textsubscript{S1} as functions of Q; note the upper curve in (b) is for MO-silicates and the lower curve is for M$_2$O-silicates.\textsuperscript{27)
cations (with viscosity increasing with increasing cation size or decreasing field strength $z/r^2$).

The introduction of $Al^{3+}$ into the Si$^{4+}$ 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-measurement sample and fluorine and sodium losses can be significant during the experiment.

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, $\ln(\eta_{T=900\,K})$ and the activation energy term, $B_\eta$, are represented as functions of $Q$ as double exponential relations (Fig. 2). The small deviations from the curve due to cation effects can be accommodated in terms of the field strength for the cations (i.e. mean $z/r^2$). The activation energy term, $B_\eta$, can also be represented as a function of $Q$ by two different double exponential equations for MO-silicates and $M_2O$-silicates (Fig. 2(b) and Eqs. (28) and (29)). In mould slags, the charge balancing duties are carried out by $K^+$ and $Na^+$ ions, and this coupled with the fact that $X_{MO} > > X_{M2O}$ implies that the upper curve in Fig. 2(b) and Eq. (28) is more appropriate for casting slags.

The viscosities at temperatures other than the reference temperature can be calculated from the Eq. (30).

$\ln\eta = \ln(\eta_{T=900\,K}) + (B_\eta/Q - T) - (B_\eta/1900)$ \hspace{1cm} (30)

The above model must be modified to apply it to mould slags since:

(i) the reference temperature, 1 573 K, is far removed from 1 900 K; this would have little effect on $B_\eta$ but would have a dramatic effect on the $\ln\eta$ term since viscosity is sensitive to temperature changes.

(ii) both $B_\eta$ and $\ln\eta_{T=900\,K}$ are affected by both $Q$ and the CaF$_2$ content, simultaneously.

Consequently, it is necessary to separate the effects of CaF$_2$ and $Q$. In the case of $B_\eta$ (little affected by temperature) a value for a CaF$_2$-free slag can be obtained from Eq. (28); this is denoted as a solid curve in Fig. 3(a). It can be seen that $B_\eta$ (i) increases with increasing $Q$ and (ii) departs from the curve with deviations increasing with increasing CaF$_2$. Since $B_\eta$ is dependent upon two factors ($Q$ and $X_{CaF2}$), the various slags were then sorted into individual groups according to their $X_{CaF2}$ values (e.g. 0.0–0.25; 0.25–0.5; etc.) and allocated a mean $X_{CaF2}$ value (e.g. 0.025; 0.075, respectively). The departure of experimental values ($\eta_{exp}$) from the curve (i.e. from Eq. (28), calculated using the remaining slag composition, $B_\eta_{rem}$ Eq. (28)) is denoted $\Delta\eta_{rem}$ (defined in Eq. (31)) and was then plotted as a function of $X_{CaF2}$ for specific groups of similar $Q$ (e.g. 1.5±0.25; 2.2±0.25 etc.).

$\Delta\eta_{rem} = B_\eta_{rem} - \eta_{exp}$ \hspace{1cm} (31)

$B_q = (B_{\eta_{rem}} - \Delta\eta_{rem}) = B_{\eta_{rem}} - 32.7X_{CaF2}$ \hspace{1cm} (32)

The same approach can not be adopted to treat the $\ln\eta_{1573\,K}$ data because of the large differences in $\ln\eta$ values for 1 900 K and 1 573 K. Consequently, it is difficult to calculate a value of $\ln\eta_{1573\,K}$ for CaF$_2$-free slags, since both $Q$ and $X_{CaF2}$ affect the viscosity simultaneously.

The experimental data were first sorted into the same groups of similar $X_{CaF2}$ values and these values were then plotted as function of $Q$ (Fig. 4(a)) and equations were derived for $\ln\eta_{1573\,K}$ as a function of $Q$. A linear best fit of the data ($\ln\eta_{1573\,K} = 3.073 + 1.93Q$) 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 CaF$_2$ (Fig. 4(b)). The mean gradient of these plots ($d\ln\eta/dX_{CaF2}$) was then derived from these plots. Values of $\ln\eta_{1573\,K}$, $CaF2=0$ were then calculated using Eq. (33); the values of $\ln\eta_{1573\,K}$, $CaF2=0$ were then plotted against $Q$ (Fig. 5) and the best fit curve for $\ln\eta_{1573\,K}$, $CaF2=0$ is given in Eq. (34). It can be seen that the mean scatter in $\ln\eta_{1573\,K}$ values is about 0.3 which corresponds to an uncertainty of ca. ±25% in $\eta$. Attempts will be made in the future to reduce this uncertainty from a best fit regression of $\ln\eta_{1573\,K}$ data as functions of $Q$ and $X_{CaF2}$. 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.

$\ln\eta_{1573\,K, CaF2=0} = \ln\eta_{1573\,K, CaF2=0} - 9X_{CaF2}$ \hspace{1cm} (33)

$\ln\eta_{1573\,K,ref} = 0.1227exp(1.1454\times Q)$ \hspace{1cm} (34)

Although viscosity measurements for supercooled liquids are carried out by $K$ (28) and (29)). The activation energy term, $B_\eta$, i.e. dated in terms of the field strength for the cations (with viscosity increasing with increasing cation size or decreasing field strength $z/r^2$). The same approach can not be adopted to treat the $\ln\eta_{1573\,K}$ data because of the large differences in $\ln\eta$ values for 1 900 K and 1 573 K. Consequently, it is difficult to calculate a value of $\ln\eta_{1573\,K}$ for CaF$_2$-free slags, since both $Q$ and $X_{CaF2}$ affect the viscosity simultaneously.

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Although viscosity measurements for supercooled liquids

![Fig. 3.](image-url)

(a) The parameter, $B_\eta$, as a function of $Q$ for slags containing varying $X_{CaF2}$: for following $X_{CaF2}$ ranges: line=0; $a=0–0.05; 0=0.05–0.1; \Delta=0.1–0.15; \bullet=0.15–0.2; \times=0.2–0.25; \ast=>0.25$ and (b) $\Delta\eta_{rem}$ as a function of $X_{CaF2}$. 

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Fig. 4. The parameter, ln $\eta_{1573}$ as functions of (a) $Q$; $X_{CaF_2}$=(0.025±0.025)=O, +(0.075±0.025)=● and red line, (0.125±0.025)=▲ and green line(0.175±0.025)=♦; (0.225 ±0.025)= ■; > 0.25 = ● and (b) mole fraction $CaF_2$: O=(Q=1.5); ■=(Q=2); ▲=(Q=2.5); ♦=(Q=3).

Fig. 5. Values of ln $\eta_{1573,Caf2=0}$ for various mould slags as a function of the parameter $Q$: ○=Lanyi;●=x=McCauley;21) ✶=Persson;22) ♦=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.30) partially- crystalline slags $= X_+$ and dashed, bold line and bold line: $\Delta\omega$= partially-melted powders25) values recorded on cooling after melting.

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 scl state of mould slags. However, it is possible to calculate values for these slags in the scl range since $\log_{10} \eta$ (d Pas) has values of 13.4 and 6, respectively, at $T_g$ and $T_{crit}$ (1040 ±10 K). These data can be coupled with calculated values for the liquid range at $T_{liq}$, 1 573 and 1 673 K. Attempts were made to obtain a best fit for these data using a polynomial relation ($log_{10} \eta$(d 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 Pas)=13.4 in some cases. Consequently, values of $log_{10} \eta$ (d Pas) were obtained from linear relationships between $T_g$ and $T_{crit}$ and between $T_{crit}$ and $T_{liq}$; these values should not be regarded as accurate values for the scl 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 some cases. Consequently, values of $log_{10} \eta$ (d Pas) were obtained from linear relationships between $T_g$ and $T_{crit}$ and between $T_{crit}$ and $T_{liq}$; these values should not be regarded as accurate values for the scl but do provide the reader with approximate values which are unavailable in the literature.

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: (i) Values of $k_{LP}$ and $k_{THW}$ are in good agreement with $\Delta\omega$, respectively). It was found that the mean $\eta_{1573}$ value for the three studies was closer to the experimental values ($\Delta\omega$=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. 2% for most of the reported data.

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

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agreement up to 1 000 K (Fig. 6) but deviate markedly at higher temperatures.

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

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

The thermal conductivities of slags are also affected by (i) the degree of crystallinity developed in the slag (i.e., $f_{crys}$) since $k_{crys} = 2 k_{glass}$ 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 $k_{THW}$ for glassy, $M_2O$–$CaO$–$SiO_2$ slags versus the calculated viscosities indicated that the sharp drop in $k_{THW}$ occurred at the temperature where $\eta = 10^6$ d Pas;\[^{7,13}\] thus $T_{cen}$ occurs midway between the softening temperature (where the sample can no longer support its own weight) and the flow temperature.\[^{7,13}\] The collapse in $k_{THW}$ occurs for the scl phase (i.e., in glassy samples). This strongly suggests that the magnitude of the thermal conductivity is linked to the rigidity of the silicate lattice.\[^{7,13}\] Measured $k_{THW}$ values ranged from 1.05–1.09 W m$^{-1}$ K$^{-1}$ at 298 K for glass samples;\[^{8,9}\] so a value of $k_{298} = 1.07 \pm 0.02$ W m$^{-1}$ K$^{-1}$ was adopted for all glassy mould fluxes.

The following values were also reported for the glassy phase, $T_{cen} = 1 000 \pm 10$ K and $k_{cen} = 1.65 \pm 0.05$ W m$^{-1}$ K$^{-1}$.\[^{7}\] Measurements of $k_{THW}$ for 15 mould slags indicated that $k_{1 040 K} = 1.65 \pm 0.05$ W m$^{-1}$ K$^{-1}$,\[^{8,9}\] so a value of $k_{298} = 1.07 \pm 0.02$ W m$^{-1}$ K$^{-1}$ was calculated using Eq. (37).

There are two outstanding problems to be resolved concerning thermal conductivity measurements, namely (i) the differences between $k_{THW}$ and $k_{LP}$ 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 $ca. \pm 5\%$ and $\pm 10\%$, 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 $k_{THW}$ and $k_{LP}$ are fully explained.

2.7. Surface Tension ($\gamma$) and Interfacial Tension ($\gamma_{slag}$)

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 ($d\gamma/dT$) is usually negative for most components but as the concentration of surfactants increases ($d\gamma/dT$) becomes less negative since ($k_{crys}$ > $k_{glass}$). Values of $k_{298}$ for partially-crystalline slags are calculated from Eq. (38)\[^{8,9}\] using the $f_{crys}$ derived with Eq. (7). It should be noted that Eq. (38) may produce a slightly low $k_{298}$ value for a 100% crystalline slag (i.e., $k = 2 W m^{-1} K^{-1}$) since crystallisation is accompanied by porosity, which lowers the conductivity of the sample. A fully-crystalline sample would not be expected to show the collapse in $k_1$ above $T_{cen}$ indicated by glasses (Fig. 6); thermal diffusivity values for a fully crystalline sample appear to remain reasonably constant with increasing temperature above 1 040 K. Thus, $k_r$ has been assumed to remain constant for crystalline samples until the sample melts. However, slag films with a reasonable amount of glassy phase would be expected to show some collapse in $k_1$ above $T_{cen}$.

$$k_{298} = 1.07 + 0.7 \gamma_{crys}.$$

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 $T_{cen}$; the model takes no account of any subsequent change in $\gamma_{crys}$. Values of $k_1$ for partially-crystalline samples in the temperature range (1 040 K - $T_{cen}$) are calculated using Eq. (37).

There are few measurements of the thermal conductivity of liquid mould slags using the $k_{THW}$ method,\[^{3,22,24}\] but several workers\[^{3,28-31}\] have reported values for the thermal diffusivity of liquid mould slags ($\alpha_{LP} = 4 \times 10^{-4} m^2 s^{-1}$) using the LP method which yields values for $\kappa_{298}$ which are about 10 x higher than $k_{THW}$ values (Fig. 6). The $k_{THW}$ values have been tentatively adopted. Eq. (39) was obtained from a relation reported for slags covering a wide compositional range.\[^{7}\]

$$k_{298} = 0.139 + 3.65 \times 10^5 \exp (Q/0.3421)$$

Values of $k_{298}$ have been reported for slag films taken from the mould.\[^{9,12}\] Approximate values for $k_{298}$ of the slag film can be calculated by using Eq. (40) where $\kappa_{crys}$ is calculated with Eq. (7). Note $k_{298} = 1.77 W m^{-1} K^{-1}$ is calculated with Eq. (38) for $\gamma_{crys} = 1$ and refers to a sample containing pores.

$$k_{298} \text{ (slag film)} = 1.77 \gamma_{crys} + 1.07 (1 - \gamma_{crys}) W m^{-1} K^{-1}.$$
Table 3. Values for slag components of surface tension (γ, mN m⁻¹), temperature coefficient (dγ/dT, mN m⁻² K⁻¹) and Gibbs energy of formation for liquid oxides per O atom (−ΔGi) used to calculate interaction parameter, φ.

| Component | SiO₂ | CaO | Al₂O₃ | MgO | Na₂O | K₂O | Li₂O | FeO | MnO | CaF₂ | ZrO₂ | TiO₂ | B₂O₃ |
|-----------|------|-----|-------|-----|------|-----|-----|-----|-----|------|------|------|------|
| γ (K)     |      |     |       |     |      |     |     |     |     |      |      |      |      |
| dγ/dT     |      |     |       |     |      |     |     |     |     |      |      |      |      |
| ΔGi kJ mol⁻¹ |      |     |       |     |      |     |     |     |     |      |      |      |      |

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

\[ \gamma_T = \gamma_1 + (d\gamma / dT)(T - 1773) \] ........................ (43)

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 \(±10\%\).

The interfacial tension \(\gamma_{\text{int}}\) can be calculated from Eq. (44) where \(\gamma_m=\text{steel surface tension, } \gamma_0\) can be derived from Eqs. (42) and (43) and the interaction coefficient, \(\phi\), can be calculated using Eqs. (45) and (46), where \(\Delta G\) is the free energy of formation of the individual, liquid oxides \(^{12,23}\) with the values being given in Table 3. \(^{41}\) Thus, \(\phi\) 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, \(\gamma_{\text{int}}\). The value of \(\gamma_{\text{int}}\) is largely determined by \(\gamma_m\) since \(\gamma_m=\gamma_f\) (4 to 5) \(\gamma_0\) and the value of \(\gamma_m\) in turn, is largely determined by the S content of the steel. The calculated values of \(\gamma_{\text{int}}\) obtained with this procedure were reported to lie within \(±100\text{ mN m}^{-1}\) of the experimental values. \(^{42}\) Values of \(\gamma_{\text{int}}\) are calculated in steel property estimation software, worksheet “surface tension”:

\[ \gamma_{\text{int}} = \gamma_m + \sum \phi \gamma_i \] ........................ (44)

\[ \phi = 0.89 - 1.5 \times 10^{-3} \Delta G_i \] ........................ (45)

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

2.8. Emissivity (εTN)

Total normal emissivity measurements have been reported for mould slags; \(^{6}\) values were recorded for the solid (at \(T>1030\) K) \(ε_{\text{TN}}=0.92±0.05\) and liquid, \(ε_{\text{TN}}=0.91±0.03\).

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: \(T_{\text{lin}}, T_{\text{g}}, T_{\text{cr}}, C_{\text{p}}, P_{\text{H}_2}\); density and \(\alpha\), 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 ($\pm 10$–$25\%$) and there is an unresolved dispute regarding the thermal conductivity values at temperatures at $>1040 \text{ K}$ 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 slag 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$_2$O$_3$ additions since various workers report B$_2$O$_3$ causes both increases and decreases in slag viscosity.
(ii) To include calcium-aluminate- based slags used for casting high Al steels.
(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 $T=1050 \text{ K}$ must be resolved.

Acknowledgements

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Symbols Abbreviations

\[
\begin{align*}
\alpha & = \text{Mole fraction} \\
\beta & = \text{Fraction of crystalline phase} \\
\gamma & = \text{Surface tension (mNm}^{-1}\text{)} \\
\eta & = \text{Viscosity (dPas)} \\
\rho & = \text{Density (kgm}^{-3}\text{)} \\
\gamma_{\text{int}} & = \text{Interfacial tension (mNm}^{-1}\text{)} \\
\gamma_{\text{BO}} & = \text{Bridging Oxygens} \\
\gamma_{\text{FO}} & = \text{Free Oxygens} \\
\gamma_{\text{NBO}} & = \text{Non-bridging Oxygens} \\
\gamma_{\text{NBO/T}} & = \text{Measure of de-polymerisation} \\
\gamma_{\text{THW}} & = \text{transient hot wire method} \\
\gamma_{\text{Q}} & = \text{measure of polymerisation} \\
s_{\text{cl}} & = \text{super-cooled liquid}
\end{align*}
\]

\[m = \text{Value for liquid at } T_{\text{lat}}.\]

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