Numerical Study into Gravity Separation of Phosphorus from BOS Slag during Solidification

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Phosphorus is known to partition to a dicalcium silicate – tricalcium phosphate solid solution (C_2S-C_3P) during the solidification of basic oxygen steelmaking (BOS) slag. Typically, C_2S-C_3P solidifies first and has a lower density than the remaining liquid slag, suggesting that gravity separation may be possible. This study simulated the cooling behaviour of BOS slag, and predicted the potential for spherical C_2S-C_3P particles to float. A lumped parameter heat transfer model based on ordinary differential equations was developed to predict the temporal variations of slag temperature in a 5 mm diameter Pt crucible. Hydrodynamic calculations were also carried out to study the floating behaviour of the spherical particles. The results showed reasonable agreement between predictions and experimental measurements for the slag's cooling rate. In the separation experiments, coarse C_2S-C_3P crystals were observed in the upper section of the crucible, while a glassy slag was observed in the lower section. This is consistent with the hydrodynamic calculations that showed the single particles floating up to the interface. Preliminary approximations were also performed for industrial slag pots which showed the higher possibility of separation for a shallow and insulated slag pot. Further studies are required to confirm the nucleation and growth behaviour in the experiments.

KEY WORDS: heat transfer; radiation; cooling rate; viscosity; solidification; latent heat; floating; separation.

1. Introduction

Slag produced from the basic oxygen steelmaking (BOS) process is one of the major by-products in integrated steelmaking plants. The main components in the BOS slag include CaO , SiO_2 , MgO , FeO and P_2O_5 .¹⁻⁴⁾ Recycling of the slag is advantageous because of its iron and lime content, however, it can only be recycled within the steelmaking plant if the phosphorus content is low enough. A separation process to lower the level of phosphorus in the recycle slag stream would allow higher rates of recycling within the steel plant, whereas the production of a P-rich stream could potentially be utilised externally as a fertilizer or for soil improvement.⁵⁾

Phosphorus is known to associate with the dicalcium silicate (C_2S) phase forming a solid solution of dicalcium silicate – tricalcium phosphate (C_2S-C_3P) whereas iron containing and other minerals are known to partition in the low phosphorus phases,⁶⁾ allowing the separation of phos-

phorus and iron to occur simultaneously. Conventional slag treatment to recover iron involves grinding and magnetic separation of cooled slag.^{4,7-9)} This process cannot recover the phosphorus and is limited by the high energy cost of grinding. Removing phosphorus by leaching has been extensively investigated in the literature,¹⁰⁻¹⁴⁾ and to be effective if the slag was cooled with a very low cooling rate (~ 5 K/min or less) and crushed into small size (order of ~ 50 μm). These conditions may restrict the use of acid leaching on an industrial scale. Ideally, separation should be undertaken whilst the slag is in the molten state and grinding would not be needed.

The C_2S-C_3P phase has a lower density than the remaining liquid slag phases, suggesting that gravity separation may be possible during cooling and solidification if enough time is spent in the temperature range where a liquid-solid “mushy zone” exists. Slow cooling rates are known to favour the separation as the solid particles have more time to float up in the molten stage.^{3,4)} Therefore, knowing the cooling rate is essential for any subsequent numerical modelling for the separation.

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The cooling process takes place from the time the slag is tapped into a slag pot from the BOS vessel until it is cooled down in the slag pit. As it is experimentally challenging to study this at industrial scale, most experimental studies on steel slag cooling have been carried out at laboratory scale.^{3,4,8,15–23} The main aim of these studies was to examine the phase transformation, structure and composition of the slag during the cooling process. The cooling rate is usually a variable or tuning parameter to investigate its effect (slow or fast) on the phase transformation, structure and composition of the slag.

The findings from these studies are summarised in the following:

- Cooling methods including: air cooling; water quenching or water granulation, which have a significant impact on the resulting mineralogical properties;^{3,19–21,23} air quenching, *i.e.* steel slag poured onto a slot is cooled rapidly by compressed air which is blown through an air nozzle placed at the bottom of a slot;^{24,25} slag film on a rotating copper wheel at laboratory scale.²¹

- The *in-situ* cooling rate of BOS slags is ~1.0–5.0 K/min; the figure of 1.0 K/min is frequently quoted as the industrial linear cooling rate, giving a cooling time of about 24 hours.^{9,16,18}

- For better separation of dicalcium silicate, the cooling rate should not exceed 2.0 K/min.^{3,26}

- The slag completely solidifies (solidus temperature) in the range 1 403 to 1 572 K.

From a numerical point of view, determining the temperature dependent physical properties of the slag containing different components during the solidification is a critical first step. Very few modelling studies have been carried out to estimate the slag's cooling rate/time. The 1D model by Matino *et al.*⁹ predicted the internal and external temperature of BOS slag using multiple conductive layers, and showed that the external slag layer can be cooled down from its initial temperature to room temperature within one day. The model proposed by Kriskova *et al.*²¹ calculated the cooling rate of a thin slag layer on a cold copper surface based on heat conduction and radiation. The computational fluid dynamics (CFD), simulation reported by Sun *et al.*²⁷ provided the cooling rate and temperature gradient within a slag droplet in finite ambient air, however validation could not be implemented. The model by Pandelaers *et al.*²⁸ was a 1D model predicting the slag temperature variation in the vertical direction for a rectangular slag pit, in which the lower layers gain heat by conduction from the additional hot layers poured on top. Cooling in such a slag pit is a fast cooling process which may not support gravity separation.

In this study, the slag cooling rate is calculated, and validated with laboratory scale experimental data. The potential for separation of the solid phase C_2S-C_3P during solidification is then calculated, based on the calculated cooling rate. Cooling and separation behaviours for the industrial scale slag pots are also investigated using the simplified modelling approaches.

This paper reports on a preliminary numerical analysis of the cooling behaviour of BOS slag and the potential for C_2S-C_3P particles to float. Its two aims are:

- to develop and experimentally validate a heat transfer model to calculate the slag cooling rate during solidifica-

tion; and

- to predict the potential floating distance for the solid C_2S-C_3P phase in the slag during solidification based on the predicted cooling rate.

2. Experimental and Numerical Modelling

2.1. Experimental

Experiments were carried out at laboratory scale with small Pt crucibles (thickness of 0.1 mm, diameter of 4.8 mm, and height of 4.3 mm – Fig. 1). A synthetic slag with composition shown in Table 1 was placed in a crucible, heated up to 1 873 K in an air atmosphere at a flow rate of 1 L/min, and then taken out from the furnace and cooled in air on an alumina plate until it reached room temperature. A type R thermocouple was inserted into the slag to monitor the slag temperature during cooling. A curved gas-slag interface was observed, likely a result of interfacial tension and wetting effects in the small crucible. This curvature was assumed to remain unchanged during the cooling process.

The temperature profile for the cooling rate experiments is shown in Fig. 2(a). The first reading of the thermocouple was 1 783 K (not 1 873 K) due to the delay between removal of the crucible from the furnace and fitting of the thermocouple. Temperature was then recorded approximately every 15 seconds during cooling to establish the cooling rate.

The temperature profile of the separation study is shown in Fig. 2(b). Slag was heated up to 1 873 K at a heating rate of 10 K/min, held at 1 873 K for 60 minutes to homogenise the slag. It was then cooled at the same rate of 10 K/min to a separation temperature of 1 723 K, held at this temperature for 60 minutes, then removed from the furnace and cooled to room temperature in air, as shown in Fig. 2(b). The cold sample was sectioned, polished and prepared for SEM and Energy Dispersive X-ray Spectroscopy (EDS) analysis.

2.2. Lumped Parameter Model

2.2.1. Heat Transfer Model

Assuming uniform temperature of the slag inside the crucible, a lumped parameter model to estimate the temporal change of the slag temperature (T) accounting for heat loss contributions from the conductive, convective and radiative heat transfer components, can be written as follows:

Fig. 1. Schematic diagram of the Pt crucible containing synthetic slag during air cooling.

Table 1. Input parameters.

No	Descriptions	Value	Unit	Source/reference/note		
Slag thermal physical properties						
	Density ^(*)	$f(T_{\text{slag}})$	kg/m ³	Mills <i>et al.</i> ⁴²⁾		
	emissivity	0.8	–	Pandelaers <i>et al.</i> , ²⁸⁾ Kriskova <i>et al.</i> ²¹⁾		
	thermal cond.	2.0	W/mK	Rojacz <i>et al.</i> ⁴⁴⁾		
	heat capacity ^(**)	1 000	J/kgK	Matino <i>et al.</i> ⁹⁾		
	viscosity	$f(T_{\text{slag}})$	Pa s	FactSage 7.2 & empirical models		
	latent heat	235 000	J/kg	Kashiwaya <i>et al.</i> ⁴⁵⁾		
	molecular weight	74.6	g/mol	Based on composition		
	liquidus temp.	1 989	K	MTDATA		
	solidus temp.	1 436	K	MTDATA		
C ₂ S–C ₃ P particle properties						
	density		2 750	kg/m ³		
	diameter		100	μm		
Slag composition						
Component	CaO	SiO ₂	Fe ₂ O ₃	P ₂ O ₅	MgO	Al ₂ O ₃
% wt.	39.1	14.8	30.8	5.8	4.7	4.95
Model conditions						
	Initial temp.	1 783	K			For cooling model
	Initial temp.	1 873	K			For floating model
	Room temp.	300	K			
	Pt thermal cond.	71.6	W/mK			Omega source for Platinum
	Pt emissivity	0.05	–			Omega source for Platinum
	Pt thickness	0.1	mm			
	Alumina plate thickness	5.0	mm			
	Alumina thermal cond.	18	W/mK			Accuratus source

^(*) The calculated density lies between ~3 000 and 3 200 kg/m³ which is comparable with the published data, *i.e.* $\rho = 2\,650\text{ kg/m}^3$ was used by Pandelaers *et al.*,²⁸⁾ $3\,140\text{ kg/m}^3$ by Ono *et al.*,³⁾ $3\,300\text{ kg/m}^3$ by Matino *et al.*,⁹⁾ $3\,530\text{ kg/m}^3$ by Engstrom,¹⁾ and $3\,200\text{ kg/m}^3$ by AISE steel foundation 11th edition.

^(**) The heat capacity of the slag has been reported over a range of values in literature such as $1\,400\text{ J/kg.K}$ by Rojacz *et al.*,⁴⁴⁾ $\sim 800\text{--}1\,400\text{ J/kg.K}$ by Mills *et al.*⁴²⁾ $\sim 65\text{--}80\text{ J/mol.K}$ by Sun *et al.*²⁷⁾

Fig. 2. a) Cooling rate experiment temperature profile; b) separation experiment temperature profile. (Online version in color.)

$$\begin{aligned}
 -m \left(C_p + L_f \frac{\partial \phi_v}{\partial T} \right) \frac{dT}{dt} = & \frac{A_w k_w}{\delta_w} (T - T_w) \\
 & + \frac{A_b}{r_b} (T - T_a) \quad \dots (1) \\
 & + A_{top} h_{top} (T - T_a) \\
 & + c_{eff} \sigma A_{top} \varepsilon_{top} (T^4 - T_a^4)
 \end{aligned}$$

The heat gain term shown in the left-hand side of Eq. (1) includes the sensible heat and the latent heat of solidification, L_f . The product of the change of the solid volume fraction with temperature, $\frac{\partial \phi_v}{\partial T}$, and the change of temperature with time, $\frac{dT}{dt}$, was used to represent the solidification rate $\frac{\partial \phi_v}{\partial t}$, which is given as:

$$\frac{\partial \phi_v}{\partial t} = \frac{\partial \phi_v}{\partial T} \cdot \frac{dT}{dt} \quad \dots (2)$$

On the right hand side of Eq. (1), the 1st and 2nd terms are the heat conduction through the side and bottom wall respectively (assuming the internal wall is at the same temperature as the slag); the 3rd and the 4th term are the heat loss due to natural convection and radiation at the top surface, respectively. The subscript 'w' stands for side wall, 'b' stands for bottom, 'a' stands for air, and 'top' stands for the top interface of the slag (surface area of a hemispherical shaped surface which fits quite well the real top surface was assumed as A_{top}). m (kg) is the slag mass; A (m^2) is the surface area; δ (m) is the wall thickness; k (W/mK) is thermal conductivity; r_b is the total thermal resistance to heat conduction across the crucible bottom and the alumina plate ($r_b = \delta_w/k_w + \delta_{Al}/k_{Al}$); h (W/m²K) is the heat transfer coefficient; c_{eff} is the view factor that accounts for the fraction of radiative heat transfer intercepted at the concave curvature at the top which was estimated to be 0.5 assuming a hemispherical shaped slag-air interface; $\sigma = 5.67 \times 10^{-8}$ W/m²K⁴ is the Stefan–Boltzmann constant; and ε is the emissivity of the slag.

The heat conduction across the wall – the first term in Eq. (1) – can be balanced with the heat loss due to external convection and radiation, which is given as:

$$\frac{k_w}{\delta_w} (T - T_w) = h_w (T_w - T_a) + \sigma \varepsilon_w (T_w^4 - T_a^4). \quad \dots (3)$$

The side wall temperature of the crucible, T_w , can be obtained from Eq. (3) which is given as

$$T_w = T - \frac{\delta_w h_w}{k_w} (T_w - T_a) - \frac{\sigma \varepsilon_w \delta_w}{k_w} (T_w^4 - T_a^4). \quad \dots (4)$$

The top curved surface was considered as a heating surface of a horizontal bath facing upwards in air;²⁹⁾ the free convection heat transfer coefficient of the top surface is given as, h_{top}

$$Nu_{top} = 0.2 Ra_g^{1/3} \quad \dots (5)$$

$$h_{top} = \frac{Nu_{top} k_g}{d_{cr}} \quad \dots (6)$$

Note that the cooling rate calculated using Eqs. (5) and (6)

was compared with the cooling rate calculated for flat surface ($Nu_{top} = 0.54 Ra_g^{1/4}$); the mean absolute percentage error was found negligible, *i.e.* less 1%.

The heat transfer coefficient at the side wall, h_w , in Eqs. (3) and (4) was calculated using the correlation for vertical cylinder natural convection, which is given as:

$$Nu_w = 0.68 + \frac{0.67 Ra_g^{1/4}}{[1 + (0.49 / Pr_g)^{9/16}]^{4/9}} \quad \dots (7)$$

$$h_w = \frac{Nu_w k_g}{d_{cr}} \quad \dots (8)$$

In the above Eqs. (5) to (8), Ra_g is Rayleigh number of the gas phase, $Ra_g = Gr_g \cdot Pr_g$, where $Gr_g = g \beta (T - T_a) d_{cr}^3 / \nu_g^2$ and $Pr_g = C_{p,g} \nu_g / k_g$ are the Grashof and Prandtl numbers for air, respectively; d_{cr} is the diameter of the crucible ($d_{cr} = 4.8$ mm); $C_{p,g}$, ν_g and k_g are the heat capacity, kinematic viscosity, and thermal conductivity of the gas phase respectively. The temperature dependency of these values were evaluated at the gas-film temperature using the one third rule ($T_g = T + (T_a - T)/3$) which can be seen detail in^{30,31)}

The underlying assumption of uniform temperature used in Eq. (1) was based on the value of system Biot number expressed as a ratio of conductive to convective heat transfer resistance. A Biot number less than 0.1 means that the conductive heat inside the body is much larger than the convective heat at the outer surface, which implies that temperature gradients within the body are insignificant, therefore a uniform temperature assumption is applicable. The Biot number is given as:

$$Bi = \frac{\bar{h} d_{cr}}{k_{sl}} \quad \dots (9)$$

where k_{sl} is the thermal conductivity of the slag; $\bar{h}$ is the overall heat transfer coefficient at the outer surface incorporating the effect of both convection and radiation component (the top surface in this case), which can be written as:

$$\bar{h} = h_{top} + c_{eff} \sigma \varepsilon_{top} (\bar{T}^2 + T_a^2) (\bar{T} + T_a) \quad \dots (10)$$

where $\bar{T}$ is the average of initial slag, T_0 , and air temperatures, T_a , *i.e.* ($\bar{T} = T_0 + T_a$).

Equations (1) and (4) were solved simultaneously for the slag temperature (T) and the outer wall temperature (T_w), respectively using the Runge-Kutta method implemented in Matlab (ver. R2018b). The temperature dependent thermo-physical properties of slag are shown in Table 1 from published reference sources while the phase volume fraction data were obtained from MTDATA property package, which is a commercial thermodynamic software package developed at the National Physical Laboratory in the United Kingdom (MTDATA is able calculate complex multi-component phase equilibria in gas-liquid-solid systems; it uses a Gibbs Energy minimization routine to establish the thermodynamic equilibrium of a defined system.³²⁾

2.2.2. Floating Model

As previously discussed, the C_2S – C_3P phase has lower density than the remaining liquid slag phases suggesting the possibility of the gravity separation, *i.e.* the C_2S – C_3P particles may float up during the cooling process. The floating speed of the particle is a function of the particle's size, and

the apparent viscous resistance of the slag that considers the solid volume fraction increasing during cooling.

The crystal grain size in the solidifying slag system is quite small, reported to be less than 110–200 μm for BOS slag by Rao *et al.*³³⁾ and Ono *et al.*³⁾ respectively, and $\sim 100 \mu\text{m}$ found in the present study for the solid solution $\text{C}_2\text{S}-\text{C}_3\text{P}$ in the BOS slag system (see Fig. 9). Although the grains of the solid solution have complex crystal structure,³⁾ for modelling purposes in this preliminary study they were assumed to be spherical particles with constant size. In future work the increased drag due to the complex shape and orientation of the crystals will be incorporated to refine the simulation. In practice the particles may also collide and agglomerate or grow in size as solidification proceeds, however, these phenomena are very complex and are not considered in this preliminary study. Due to the small grain size and the high system viscosity, a laminar flow field obeying Stokes equation was assumed to exist around the particles. Three different approaches were utilised to compute the rise (floating) velocity of a single particle in the slag system which are briefly discussed below. Note that the time taken for the particle to reach terminal velocity was not considered in this study.

In the first approach, viscosity of the melt μ_m was calculated using thermodynamic computation package FactSage (ver.7.2) excluding any solid phase formed during the solidification process. Viscosity thus estimated provided a lower limit of viscous resistance and therefore allowed the highest possible floating velocity, considered to be the upper limit for velocity in this study. Detail analysis for the drag force and velocity of floating particles in metallurgical systems can be seen in.^{34–36)} In the present work, Stokes' law was assumed for the drag coefficient, and terminal velocity of a spherical solid particle sinking or floating in the melt was calculated by balancing the drag force to the net buoyancy force which is given as:

$$v_{p,m} = \frac{g d_p^2 (\rho_{app} - \rho_p)}{18 \mu_m} \quad (11)$$

However, motion of the particle will be hindered by the presence of a growing number of surrounding particles as the solidification process continues, which rapidly increases the apparent viscosity of the system. Several expressions are suggested in literature for calculating the hindered settling velocity, however, the Einstein-Roscoe equation,³⁷⁾ and the Steinour equation³⁸⁾ are the most common approaches referred to in ironmaking and steelmaking applications^{3,39–41)} which are also used in this study.

The second approach in this study utilised the Einstein-Roscoe equation³⁸⁾ to estimate the floating velocity of the solid particles as follows:

$$v_{ER} = v_{p,m} \frac{\mu_m}{\mu_{ER}} \quad (12)$$

where $v_{p,m}$ was obtained from Eq. (11), and the Einstein-Roscoe apparent viscosity μ_{ER} was written as:

$$\mu_{ER} = \frac{\mu_m}{(1 - 1.35 \phi_v)^{2.5}} \quad (13)$$

where the factors 1.35 and 2.5 were suggested by Roscoe (1952). Note that Eq. (13) is valid for a wide range solid

volume fraction ϕ_v from zero to 0.74.

The third approach applied Steinour's empirical correlation to determine the apparent viscosity of the system. The floating velocity of the $\text{C}_2\text{S}-\text{C}_3\text{P}$ using the third approach can be expressed as:

$$v_S = v_{p,m} \frac{\mu_m}{\mu_S} \quad (14)$$

where the apparent viscosity μ_S is obtained from the Steinour equation that can be written as:

$$\mu_S = \frac{\mu_m}{(1 - \phi_v)^2 10^{-1.82 \phi_v}} \quad (15)$$

The correction factor, f , accounts for the solid volume fraction ($f = (1 - \phi_v)^2 10^{-1.82 \phi_v}$) and was empirically obtained by Steinour³⁸⁾ in the solid fraction range from 0 to 0.5.

Note that the apparent viscosity obtained from Eqs. (13) and (15) becomes the melt's viscosity at $\phi_v = 0$, but increases sharply with increasing ϕ_v , for example at $\phi_v = 0.5$, $\mu_{ER} = \sim 16 \mu_m$ and $\mu_S = \sim 32 \mu_m$.

To determine the rising distance of a single floating crystal particle, the velocity expressions in Eqs. (11), (12) and (14) were separately integrated using the temperature dependent viscosity parameter wherein the slag's temperature was obtained by solving the heat balance expressions given in Eqs. (1) and (4).

3. Results and Discussion

3.1. Slag Compositions and Physical Properties

For the initial compositions shown in Table 1, MTDATA was used to simulate the phase volume fraction within the temperature range, 1 273–2 073 K. Figure 3 shows the predicted volume fractions of $\text{C}_2\text{S}-\text{C}_3\text{P}$, total solids and liquid. The liquidus temperature of 1 989 K and solidus temperature of 1 436 K are also shown in Fig. 3. From this figure it can be seen that between 1 989 K and 1 723 K, the $\text{C}_2\text{S}-\text{C}_3\text{P}$ phase was the only solid phase predicted to exist.

The model of Mills *et al.*⁴²⁾ was used to estimate the temperature dependent liquid and solid density; the calcu-

Fig. 3. Liquid/solid volume fraction as function of temperature obtained from MTDATA.³²⁾ (Online version in color.)

lated density lies between $\sim 3\,000$ and $3\,200\text{ kg/m}^3$ which is comparable with the published data. Values of the density, heat capacity, thermal conductivity and latent heat of solidification are shown in Table 1.

The apparent viscosity of the steel-making slag increases sharply as the solid fraction increases during the solidification process.³⁾ Both liquidus and solidus temperature are dependent on the slag composition. **Figure 4** shows the predicted temperature dependent viscosity which was validated against experimental data available in the literature for steel-making slags.^{3,43)} The predicted viscosity was comparable with the two experimental data sets at higher temperature nonetheless some deviations were observed at lower temperature range from $1\,773$ – $1\,823\text{ K}$. This has been attributed to the different compositions of the slags used in these studies. Only a few of the slag samples used in Ono *et al.*³⁾ had basicity (*i.e.* ratio of CaO/SiO_2) in the range from 2.7 to 2.9 while rest had a much higher basicity range between 3.3 and 4.0 . The basicity of the slag referred in Mills and Sridhar⁴³⁾ is ~ 3.8 which is again much higher than the slag basicity of 2.6 used in this study. A higher slag fluidity or lower slag viscosity is therefore expected in the present study which may explain the deviation between the predicted viscosity and reported values shown in Fig. 4. It is worth noting that the effect of temperature dependent solid volume fraction is already considered in the predicted viscosity profile shown in Fig. 4. This viscosity is referred to as the “apparent viscosity” to distinguish it from the “melt viscosity” discussed in the next section for which the slag was assumed to be in the molten stage during cooling process.

3.2. Phosphate Flotation in a Crucible

3.2.1. Slag Cooling Rate

For simplifying the model calculations, a uniform temperature was assumed within the crucible. To justify this assumption, Biot number was calculated using Eq. (9). The average temperature $\bar{T} = (1\,783 + 293)/2 = 1\,038\text{ K}$ was used to calculate the overall heat transfer coefficient $\bar{h}$ in Eq. (10). The results showed that $\bar{h} = 50.2\text{ W/m}^2\text{K}$, and $\text{Bi} \sim 0.1$, which justifies the use of uniform temperature assumption.

Fig. 4. Apparent viscosity comparison. (Online version in color.)

Figure 5 presents the predicted and experimentally measured temperature profiles during cooling of the crucible. It can be seen that the decrease in slag temperature with time follows a non-linear trend. In the early stages (from initial temperature of $1\,783\text{ K}$ to solidus temperature at $1\,436\text{ K}$), a high cooling rate of $\sim 35\text{ K/s}$ was found which included the latent heat released during the phase-change. The higher cooling rate can be explained by the high temperature gradient between the hot crucible and surrounding air where radiation heat transfer dominates due to its non-linear dependency on the temperature (Eq. (1)). The cooling rate progressively decreases to less than 1.0 K/s towards the end of cooling and approaches an equilibrium state where radiation heat loss gradually weakens and natural convection starts playing a significant role. Reasonable agreement of model predicted temperature with the experimental measurements was obtained with an average standard deviation of $\sim 35\text{ K}$.

The heat flux shown in the right hand side of Eq. (1) is presented in **Fig. 6**. Heat loss due to radiation at the top surface [the 4th term in the right-hand side of Eq. (1)]

Fig. 5. Temperature of the slag during cooling experiments: modelling vs experiments. (Online version in color.)

Fig. 6. Temporal variation of different heat fluxes from the slag. (Online version in color.)

dominates at the beginning as the temperature difference between the slag and the surrounding air is large. The heat loss via conduction through the metallic (platinum) wall of the crucible [the 1st term in the right hand side of Eq. (1)] is also significant because of the high thermal conductivity and lower wall thickness. The heat flux through the bottom wall [the 2nd term in the right hand side of Eq. (1)] is however less significant because of the thick alumina plate placed at the bottom.

3.2.2. Floating Distance

This section investigates the potential for C_2S – C_3P crystal particles to float up to the interface for intended separation according to the predicted cooling rate. For the same cooling rate presented in Fig. 5, the calculated terminal velocity and the floating distance of the solid spheres (C_3S – C_3P) are shown in Fig. 7 for the three different viscosity modelling approaches discussed in section 2.2, *i.e.* (i) the melt viscosity, (ii) the Einstein-Roscoe apparent viscosity, and (iii) the Steinour apparent viscosity. The cooling was stopped at 1 633 K at which point the solid volume fraction reaches ~ 0.5 approaching the limit discussed for Eq. (15). Below this temperature the floating distance does not increase significantly for the Einstein-Roscoe or the Steinour apparent viscosity approach because the velocity reduces sharply with the increasing viscosity. As shown in Fig. 7, the highest velocity obtained by the melt viscosity approach expressed by Eq. (11) results in the highest floating distance of less than 200 μm , which is not considered significant. The Einstein-Roscoe – Eq. (13) and the Steinour approaches – Eq. (15) calculate lower distances due to the use of apparent viscosity. Note that, a sudden reduction shown in the floating velocity (Fig. 7(a)) is the result of a sudden change in liquid/solid volume fraction at the separation temperature at $\sim 1\,723$ K which can be seen in Fig. 3. This has no significant effect on the cumulative distance shown in Fig. 7(b). In summary, as the same cooling rate

presented in Fig. 5 (~ 35 K/s), the extent to which the solid spheres float up to the interface is limited.

Figure 8 shows the particle floating velocity and distance for a much lower cooling rate of 1 K/min based on the Steinour apparent viscosity approach, which is the most conservative option that accounts for slag apparent viscosity. During the first 10 minutes of cooling wherein temperature decreases from 1 873 to 1 863 K, the solid particles are able to float up to the interface with a minimum floating distance of ~ 3.8 mm. These results agree reasonably well with the suggested maximum cooling rate of 2 K/min for separation by Ono *et al.*³⁾ and Chaudhary and Pal.²⁶⁾

Experiments conducted in this study employed different cooling, *i.e.* holding at 1 873 K for 1 h, cooling from 1 873 to 1 723 K for 15 minutes, holding at 1 723 K for 1 h (see temperature profile in Fig. 2(b)). The total holding and cooling time of 135 minutes from 1 873 to 1 723 K resulted in an average cooling rate of ~ 1 K/min, which is the same cooling rate used for the above results shown in Fig. 8. For this cooling rate, all three models confirm the possibility of the particle floating from the bottom to the top of the crucible, with the minimum floating distance of ~ 3.8 mm predicted by Eq. (14). The SEM and energy dispersive x-ray spectroscopy (EDS) analysis of crucibles from the experiments shows the presence of coarse dendritic crystal structures in the upper section of the crucible, and finer crystals in the lower section (Fig. 9). The average EDS analysis for the dendrites was 59.2 wt.% CaO, 21 wt.% SiO_2 and 18.4 wt.% P_2O_5 . The presence of coarse dendrites in the upper portion of the crucible in Fig. 9 are likely to be the result of nucleation at the free surface followed by growth into the remaining hot liquid, combined with the floating and growth during slow cooling of any crystals of C_2S – C_3P that nucleated in the bulk. There was no systematic difference in the composition of the dendrites based on position.

Fig. 7. Velocity and floating distance of C_2S – C_3P particles for the three approaches when temperature reduces from 1 783 to 1 633 K at the same cooling rate presented in Fig. 5. Particle diameter of 100 μm . (Online version in color.)

Fig. 8. Velocity and floating distance of C_2S-C_3P particles for the three approaches as temperature reduces from 1873 to 1863 K at the rate of 1 K/min (10 minutes cooling time). Particle diameter of 100 μm . (Online version in color.)

Fig. 9. EDS images showing dendritic crystals of C_2S-C_3P in the higher section of the crucible. (Online version in color.)

3.3. Analysis of Industrial Scale Slag Pots

Cooling behaviour in a typical industrial scale slag pot of 10 m^3 capacity made of cast-iron⁴⁴⁾ was investigated in this study applying the same modelling approach. Three different insulating options were examined to study the effect of cooling on the floating behaviour of the 100 μm C_2S-C_3P particles in the slag pot, as listed below:

- Typical industrial slag pot with no lid, no insulation
- Slag pot with a lid
- Slag pot with lid and insulated side wall (200 mm brick and 100 mm cast-iron wall).

Figure 10(a) compares the cooling rate predicted for

these three configurations for a typical slag pot (slag pot # 1). It can be seen that an almost linear cooling rate (~ 24.3 K/h) can be obtained with the *lid with wall insulation* option (option 1) while cooling rate is steepest in the *no lid no insulation* option at an early linear cooling rate of 136 K/h (option 3). Option 2 with only lid marginally better than option 3. The predicted particle floating distances are shown in Fig. 10(d) which indicate that given the large height of this slag pot, it is highly unlikely for a 100 μm phosphate crystal particle to float to the surface.

Two other configurations were therefore chosen with the same volume but different diameter to height ratio. Shal-

Fig. 10. Cooling rate and normalised floating distance for industrial slag pots. H is the floating distance and H_{sp} is slag pot height. (Online version in color.)

lower slag pots have the advantage of a smaller height for particles to float, however, the surface area for heat loss is also increased. Figures 10(b) and 10(c) show the cooling rates predicted for slag pots (#2) and (#3). Without insulation, both configurations cool more rapidly compared to slag pot (#1) allowing very small floating distances. However, the addition of a lid and wall insulation significantly decreases the cooling rate. Slag pots (#2) and (#3) show a similar cooling rate of $\sim 0.3\text{ K/min}$ (18 K/h) in the early stage (Figs. 10(b) and 10(c)). The resultant floating distances for slag pots #2 and #3 are shown in Figs. 10(e) and 10(f), with normalised floating distance (floating distance H divided by slag pot height H_{sp}), of $\sim 30\%$ and $\sim 52\%$ respectively. This means that particle collection is possible from the top half of slag pot (#3) with lid and insulation.

Although based on simplified modelling calculations, these findings provide useful guidance for future work; a standard slag pot without addition of insulation is unlikely to be useful for gravity separation, however, a modified geometry with addition of insulation appears to be promising. The modified geometry (slag pot #3) will be studied in more detail using computational fluid dynamics in future work.

4. Conclusion

A theoretical analysis of the potential to separate phosphorus containing $\text{C}_2\text{S}-\text{C}_3\text{P}$ from steelmaking slag during solidification by density difference was presented in this study.

A lumped parameter heat transfer model for slag cool-

ing and solidification was developed and validated with experimental cooling rate data obtained from a laboratory scale crucible test.

The rise velocity for a typical $100\text{ }\mu\text{m}$ size spherical $\text{C}_2\text{S}-\text{C}_3\text{P}$ particle was calculated based on the calculated cooling rate, utilising temperature dependent transport properties including the apparent viscosity of melt containing solid particles. This analysis showed that particles were unable to float up to the top of a crucible in laboratory experiments if fast cooling was applied. However, at slower cooling rates below 2 K/min , floating of particles up to the interface was possible. This prediction was consistent with experimental data, where coarse $\text{C}_2\text{S}-\text{C}_3\text{P}$ crystals were observed to exist in the vicinity of the slag-air interface.

The same approach was also used as an initial step in the analysis of gravity separation for three different configurations of industrial scale slag pots. No separation was predicted for standard industrial slag pots, however, a higher possibility of $\text{C}_2\text{S}-\text{C}_3\text{P}$ crystals separation was predicted in a modified shallow slag pot with insulation to slow the cooling rate and prolong the time for separation. Future work will focus on quantifying the internal temperature gradients, buoyancy driven flows and particle dynamics in a comprehensive CFD model framework for the modified slag pot.

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