

# On a Novel Closed-Form Analytical Solution For Unsteady So-lidification: Theory and Application

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## Abstract

Numerical modeling of transient solidification under convective boundary conditions presents a significant challenge because accurately tracking the solid–liquid interface is essential for obtaining a stable solution. Although analytical solutions are generally straightforward to apply, the growing demand for energy storage driven by mismatches between supply and demand in renewable-energy systems requires reliable predictive tools for latent-heat thermal energy storage (LHTES) applications. In this work we compare a classical analytical solution for the transient solidification of pure and eutectic phase-change materials with a recently derived formulation that provides a complete treatment of the Biot number. The comparison is performed in the context of sizing LHTES reservoirs and selecting appropriate phase-change materials. The results demonstrate that the new formulation accurately predicts the velocity of the solid–liquid interface, the thermal gradient, and the cooling rate, offering improved reliability over the classical approach.

**Keywords:** Closed-form analytical solution; convective boundary condition; solidification kinetics; latent-heat thermal energy storage (LHTES); numerical modeling; experimental validation

## 1. Introduction

Solid–liquid phase transformations are fundamental to a wide range of scientific and technological fields. In geophysics they control weather patterns, the water cycle, igneous rock formation, glacier dynamics, and ice sheet evolution; in materials science and engineering they underpin metal casting, semiconductor fabrication, and cement production; and in chemistry and pharmaceuticals they are central to crystallisation processes used for purification. On a macroscopic scale these transformations are manifested as a moving interface that separates the solid and liquid phases. During melting the liquid–solid interface advances into the material until the solid is completely consumed [1,2]. The motion of this interface is governed by a heat balance condition: the latent heat released (or absorbed) per unit volume must be supplied (or re-moved) by the heat fluxes on the solid and liquid sides of the interface. Problems of this type constitute the classical Stefan problem, named after the Slovenian physicist Jožef Stefan, who first formulated this class of moving boundary problems [3].

Classical analytical solutions for the one dimensional Stefan problem can be found in the literature [4].

In many practical solidification and melting processes the temperature at the exposed surface (usually taken as  $x=0$ ) is governed by a convective (Robin) boundary condition rather than by a prescribed temperature. Analytical solutions that incorporate such a convective condition for pure metals and eutectic alloys are comparatively scarce [5–23]. Clyne and Garcia presented an exact solution for a generalized solidification problem under the assumption of a constant interfacial heat transfer coefficient, using the Virtual Adjunct Method, which treats the interfacial resistance as a set of virtual solid or mould layers [24]. Building on this idea, Garcia and co workers derived analytical solutions for binary alloys [25–28]. Davay obtained a solution for directional solidification that includes the motion of the casting at the interface by simultaneously solving the transient heat equations for the mould, the gas gap, the solid, the liquid, and any contaminating layers [29].

The accelerating threat of global warming, driven by anthropogenic greenhouse gas emissions [30], underscores the need for efficient renewable energy technologies. Latent heat thermal energy storage (LHTES) has emerged as a key enabling technology because phase change materials (PCMs) can store and release large amounts of energy during solid–liquid transitions. Compared with sensible heat storage (SHTES), LHTES can store 5–14 times more heat per unit volume [31–35]. The authors applied lumped capacitance (or “lumped”) solution, which assumes that the solidified material (or PCM) behaves as a spatially uniform body so that internal temperature gradients can be neglected, an assumption that is valid when the Biot number  $Bi = hL/k$  is much smaller than 1. Under this hypothesis the energy balance reduces to an ordinary differential equation,  $\rho V c_p \frac{dT}{dt} = hA(T_\infty - T)$ , whose solution is the classic exponential decay  $T(t) = T_\infty + (T_0 - T_\infty) \exp[-hA / (\rho V c_p) t]$ . For transient solidification the latent heat is incorporated by augmenting the effective heat capacity with the term  $L \frac{d\alpha}{dt}$  (where  $\alpha$  is the solid fraction), giving a piecewise solution: (i) sensible heat phases before and after melting, described by the exponential law above, and (ii) an isothermal phase change interval at the melting temperature  $T_m$  in which the interface position evolves according to  $\rho L \frac{dx}{dt} = hA(T_\infty - T_m)$ . The resulting closed form expressions provide quick estimates of the solid liquid in-terface position, interface velocity, thermal gradient, and cooling rate, but they are accurate only for objects with low Bi and negligible internal conduction resistance. Accurate knowledge of PCM solidification and melting kinetics is therefore essential for sizing thermal reservoirs and for predicting system performance [36].

Mendes Júnior has recently proposed a novel analytical framework for transient solidification, yielding four closed form solutions for pure and eutectic materials in one and three dimensional semi infinite geometries. The approach explicitly incorporates convective surface conditions and melt superheat, and introduces a first order correction term that bridges the gap between second order and first order similarity solutions. This yields accurate predictions of thermal gradients, interface velocities, and cooling rates [37]; a detailed derivation is given in [38]. Nevertheless, the original formulation does not reproduce measured interface velocities satisfactorily nor does it provide a means to evaluate the mean heat transfer coefficient. More recently, Trojan derived an exact solution for non reactive unsteady heat conduction in a semi infinite slab subject to a convective boundary condition, thereby extending the analytical toolbox for such problems [39].

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heat conduction in a semi infinite slab subject to a convective boundary condition, thereby extending the analytical toolbox for such problems [39].

In the present work we evaluate the thermal gradient, solid–liquid interface ve-locity, and cooling rate for a selection of metals and for water using (i) a classical ana-lytical solution for solidification [26] and (ii) the recently introduced solution that fully resolves the Biot number [37]. The predictions are benchmarked against experimental measurements [40,41] and against numerical simulations reported in the literature [42,43]. This comparative study highlights the strengths and limitations of each ana-lytical approach and provides guidance for their use in the design of LHTES systems and in the modelling of natural solidification phenomena.

## 2. Mathematical Formulation and Numerical Method

The numerical model used in this work to simulate the solidification of pure met-als and eutectic alloys is the one originally proposed by Swaminathan *et al.* [42] and subsequently modified for problems of inverse macrosegregation in multicomponent systems [43].

The model incorporates the following features:

1. Coupled thermo chemical fields – it can handle the interaction between temper-ature and composition fields together with multiple reactions that occur during solidification of multicomponent alloys (e.g., primary phase transformation, phase precipitation, eutectic and peritectic reactions).
2. Shrinkage induced flow – it accounts for the density difference between the liquid and the primary and secondary solid phases, which gives rise to flow caused by so-lidification induced shrinkage.
3. Temperature rescaling – a temperature rescaling technique is employed to treat the solidification of pure and eutectic materials.

### 2.1 Model Assumptions

The numerical model for the unsteady solidification of pure met-als/compounds and multicomponent alloys is based on the following assump-tions [42,43]:

#### Domain

The computational domain is finite and extends along the Z axis, i.e.  $0 \leq Z \leq Z_b$  (see Fig. 1).

– At  $Z = 0$  a third kind (Robin) boundary condition is prescribed for heat flux, while a second kind (Dirichlet) condition is applied for mass.

– At the opposite boundary,  $Z = Z_b$ , both heat and mass fluxes are zero (insulated/no mass transfer).

#### Material

The phase change material to be solidified is assumed to be either a pure metal (or pure compound) or a multicomponent alloy.

**Solid phase**

The solid phase is stationary; once formed it has zero velocity.

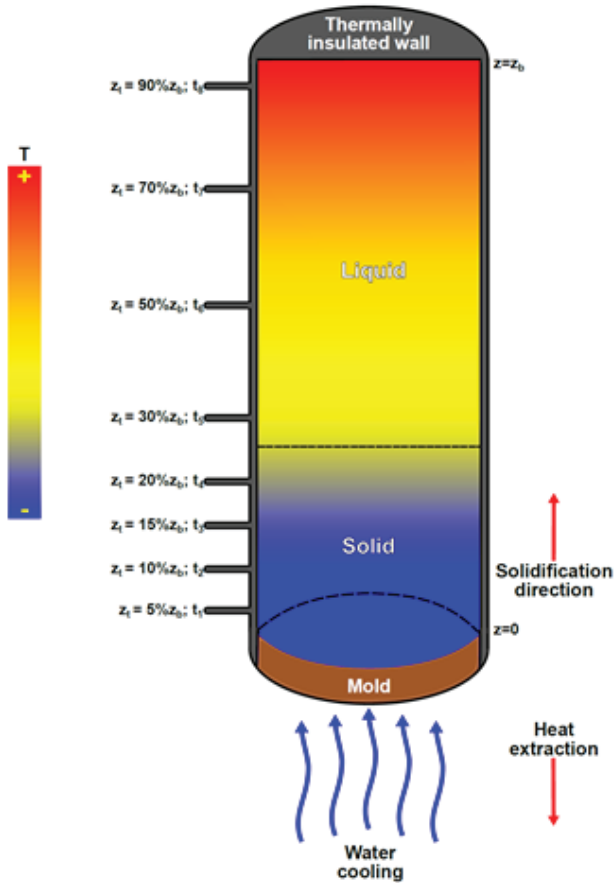


Figure 1. Schematic representation of transient upward solidification cooled from the bottom.

**2.2. Governing Equations**

$$\frac{\partial^2 T_S}{\partial x^2} = \frac{1}{\alpha_S} \frac{\partial T}{\partial t} \quad 0 < x < s(t) \quad (1)$$

$$\frac{\partial^2 T_L}{\partial x^2} = \frac{1}{\alpha_L} \frac{\partial T}{\partial t} \quad s(t) < x < +\infty \quad (2)$$

$$t = 0, \quad 0 < x < +\infty, \quad T = T_P \quad (3)$$

$$t > 0, \quad x = 0, \quad -k \frac{\partial T}{\partial x} \Big|_{x=0} = h(T - T_\infty) \quad (4)$$

$$t > 0, \quad x = s(t), \quad T = T_F \quad (5)$$

$$t > 0, \quad x \rightarrow +\infty, \quad T = T_P \quad (6)$$

$$\rho_S L \frac{ds}{dt} = k_S \frac{\partial T}{\partial x} \Big|_{x=s^-} - k_L \frac{\partial T}{\partial x} \Big|_{x=s^+} \quad (7)$$

The thermal variables that influence solidification kinetics and were selected for this comparison are: position versus time  $S(t)$ , solid-liquid interface velocity  $v = \frac{ds(t)}{dt}$ , thermal gradient of the liquid-phase  $G_L = \frac{\partial T}{\partial x} \Big|_{x=s^+}$ , and cooling rate  $T_x$  for a given set of Biot numbers.

$$A_S = T_F - \frac{(T_\infty - T_F)}{\left\{ 1 - \operatorname{erfc}(\varphi) + \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2}\right) \operatorname{erfc}\left(\varphi + \frac{hs}{2\varphi k_S}\right) \right\}} \left\{ \operatorname{erfc}(\varphi) - \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2}\right) \operatorname{erfc}\left(\varphi + \frac{hs}{2\varphi k_S}\right) \right\} \quad (16)$$

The reference solution for the solid region is the classic one dimensional solution for a semi infinite slab whose boundary condition at  $z = 0$  is of the third kind [39] for non reactive problems. The temperature profile as a function of time and space can be expressed as

$$T(x, t) - T_\infty = A_S + B_S \left\{ \operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha_S t}}\right) - \exp\left(\frac{hx}{k_S} + \frac{h^2 \alpha_S t}{k_S^2}\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha_S t}} + \frac{h\sqrt{\alpha_S t}}{k_S}\right) \right\} \quad (8)$$

where  $A_S$  and  $B_S$  are constants determined from the solid interface at  $s(t) = 0$  and  $s(t) = s$ .

For  $s = 0, t > 0$

$$T_S(s = 0, t) = T_\infty = A_S + B_S \quad (9)$$

This relationship follows from the convective boundary condition that has already been imposed at  $x = 0$  for  $t > 0$  when deriving the base temperature field  $T(x, t)$ . Consequently, the condition  $T(s = 0, t)$  cannot be imposed on the solid-temperature field  $T_S(x, t)$ , because no solid exists until a finite time  $t^* > 0$  has elapsed. In this context,  $B_S$  must be determined from the temperature profile at the moving interface  $x = s$ . Together with the relation  $T_\infty = A_S + B_S$ , this formulation permits the constants  $A_S$  and  $B_S$  to be varied freely.

For  $x = s,$

$$T_S(x = s, t) = T_F = A_S + B_S \left\{ \operatorname{erfc}\left(\frac{s}{2\sqrt{\alpha_S t}}\right) - \exp\left(\frac{hs}{k_S} + \frac{h^2 \alpha_S t}{k_S^2}\right) \operatorname{erfc}\left(\frac{s}{2\sqrt{\alpha_S t}} + \frac{h\sqrt{\alpha_S t}}{k_S}\right) \right\} \quad (10)$$

By introducing the parabolic similarity variable  $\frac{s}{2\sqrt{\alpha_S t}}$  and  $\varphi(s, t) = \frac{s}{2\sqrt{\alpha_S t}}$ , equation (10) becomes

$$T_F = A_S + B_S \left\{ \operatorname{erfc}(\varphi) - \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2}\right) \operatorname{erfc}\left(\varphi + \frac{hs}{2\varphi k_S}\right) \right\} \quad (11)$$

and,

$$T_\infty = A_S + B_S \quad (12)$$

$$T_F = A_S + B_S \left\{ \operatorname{erfc}(\varphi) - \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2}\right) \operatorname{erfc}\left(\varphi + \frac{hs}{2\varphi k_S}\right) \right\} \quad (13)$$

Subtracting Eq. (13) from Eq. (12) leads to

$$T_\infty - T_F = B_S \left\{ 1 - \operatorname{erfc}(\varphi) + \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2}\right) \operatorname{erfc}\left(\varphi + \frac{hs}{2\varphi k_S}\right) \right\} \quad (14)$$

which gives  $B_S$  as

$$B_S = \frac{T_\infty - T_F}{\left\{ 1 - \operatorname{erfc}(\varphi) + \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2}\right) \operatorname{erfc}\left(\varphi + \frac{hs}{2\varphi k_S}\right) \right\}} \quad (15)$$

Similarly, the constant  $A_S$  can be determined as follows: The temperature profile can now be expressed in terms of constant

$A_S$  and  $B_S$ ,

$$\frac{T_S(x, t) - T_F}{T_\infty - T_F} = \frac{\left\{ \operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha_S t}}\right) - \exp\left(\frac{hx}{k_S} + \frac{h^2 \alpha_S t}{k_S^2}\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha_S t}} + \frac{h\sqrt{\alpha_S t}}{k_S}\right) - \operatorname{erfc}(\varphi) + \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2}\right) \operatorname{erfc}\left(\varphi + \frac{hs}{2\varphi k_S}\right) \right\}}{\left\{ 1 - \operatorname{erfc}(\varphi) + \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2}\right) \operatorname{erfc}\left(\varphi + \frac{hs}{2\varphi k_S}\right) \right\}} \quad (17)$$

Aiming to express the temperature profile in a more suitable form, the following auxiliary functions  $\psi(s, \varphi)$  and  $\zeta(s, \varphi)$  can be defined as

$$\psi(s, t) = \left\{ 1 - \operatorname{erfc}(\varphi) + \exp\left(\frac{hs}{k_S} + \frac{h^2 \alpha_S t}{k_S^2}\right) \operatorname{erfc}\left(\varphi + \frac{h\sqrt{\alpha_S t}}{k_S}\right) \right\} \quad (18a)$$

$$\psi(s, \varphi) = \left\{ 1 - \operatorname{erfc}(\varphi) + \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2}\right) \operatorname{erfc}\left(\varphi + \frac{hs}{2\varphi k_S}\right) \right\} \quad (18b)$$

and,

$$\zeta(s, t) = -\operatorname{erfc}(\varphi) + \exp\left(\frac{hs}{k_S} + \frac{h^2 \alpha_S t}{k_S^2}\right) \operatorname{erfc}\left(\varphi + \frac{h\sqrt{\alpha_S t}}{k_S}\right) \quad (19a)$$

$$\zeta(s, \varphi) = -\operatorname{erfc}(\varphi) + \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2}\right) \operatorname{erfc}\left(\varphi + \frac{hs}{2\varphi k_S}\right) \quad (19a)$$

Substituting Eq. (17) and Eq. (18) into Eq. (16) yields

$$\frac{T_S(x, t) - T_F}{T_\infty - T_F} = \frac{\left\{ \operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha_S t}}\right) - \exp\left(\frac{hx}{k_S} + \frac{h^2 \alpha_S t}{k_S^2}\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha_S t}} + \frac{h\sqrt{\alpha_S t}}{k_S}\right) + \zeta(s, t) \right\}}{\psi(s, t)} \quad (20a)$$

$$\frac{T_S(x, s) - T_F}{T_\infty - T_F} = \frac{\left\{ \operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha_S t}}\right) - \exp\left(\frac{hx}{k_S} + \frac{h^2 \alpha_S t}{k_S^2}\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha_S t}} + \frac{h\sqrt{\alpha_S t}}{k_S}\right) + \zeta(s, \varphi) \right\}}{\psi(s, \varphi)} \quad (20b)$$

The thermal gradient  $T_S(x, t)$  in the vicinity of boundary  $x = s^-$  is found by deriving the temperature profile with respect to  $x$ , which has the following form:

$$\frac{\partial T_S(s, t)}{\partial x} \Big|_{x=s^-} = \frac{(T_F - T_\infty)}{\psi(s, t)} \left\{ \frac{h}{k_S} \exp\left(\frac{hs}{k_S} + \frac{h^2 \alpha_S t}{k_S^2}\right) \operatorname{erfc}\left(\varphi + \frac{h\sqrt{\alpha_S t}}{k_S}\right) + \frac{2\varphi}{\sqrt{\pi} s \exp(\varphi^2)} - \frac{2\varphi}{\sqrt{\pi} s \exp\left[\left(\varphi + \frac{h\sqrt{\alpha_S t}}{k_S}\right)^2\right]} \exp\left(\frac{hs}{k_S} + \frac{h^2 \alpha_S t}{k_S^2}\right) \right\} \quad (21a)$$

$$\frac{\partial T_S(s, \varphi)}{\partial x} \Big|_{x=s^-} = \frac{(T_F - T_\infty)}{\psi(s, \varphi)} \left\{ \frac{h}{k_S} \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2}\right) \operatorname{erfc}\left(\varphi + \frac{hs}{2\varphi k_S}\right) + \frac{2\varphi}{\sqrt{\pi} s \exp(\varphi^2)} - \frac{2\varphi}{\sqrt{\pi} s \exp\left[\left(\varphi + \frac{hs}{2\varphi k_S}\right)^2\right]} \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2}\right) \right\} \quad (21b)$$

A common way to write a solution of a partial differential equation to avoid instability concerning the magnitude of the involved dimensional variables in the function evaluation is to express this in terms of dimensionless numbers with physical meaning, such as Ste, Biot and Biot<sup>2</sup>Fo,

$$t = \frac{s^2}{4\alpha_S \varphi^2} \quad (22)$$

$$Fo = \frac{\alpha_S t}{s^2} \quad (23)$$

$$Biot = \frac{hs}{k_S} \quad (24)$$

$$Ste = \frac{C_{PS}(T_F - T_\infty)}{L} \quad (25)$$

$$Biot^2 Fo = \frac{h^2 s^2}{4\varphi^2 k_S^2} = \frac{Biot^2}{4\varphi^2} \quad (26)$$

$$\psi(Biot, \varphi) = \left\{ 1 - \operatorname{erfc}(\varphi) + \exp\left(Biot + \frac{Biot^2}{4\varphi^2}\right) \operatorname{erfc}\left(\varphi + \frac{Biot}{2\varphi}\right) \right\} \quad (27)$$

The derivative of  $s$  with respect to  $t$  gives

$$\varphi = \frac{s}{2\sqrt{\alpha_S t}} - \frac{h\sqrt{\alpha_S t}}{k_S} \quad (28a)$$

$$s = 2\varphi \sqrt{\alpha_S t} - \frac{2h\alpha_S t}{k_S} \quad (28b)$$

Then the invariant form that modifies the proposed parabolic velocity profile is obtained from equation (28a); i.e.,

$$\frac{ds}{dt} = \varphi \sqrt{\frac{\alpha_S}{t}} - \frac{2h\alpha_S}{k_S} = \varphi \sqrt{\frac{\alpha_S}{t}} - \Omega \quad (28c)$$

For parabolic velocity,  $v = \frac{ds}{dt}$

$$\Omega = \frac{2h\alpha_S}{k_S} \quad (29d)$$

$$\frac{2\varphi^2 \alpha_S}{s} - \frac{2h\alpha_S}{k_S} = \frac{ds}{dt} - \Omega \quad (29e)$$

$$\frac{ds}{dt} - \Omega = \frac{1}{\rho_S L} \left[ k_S \frac{\partial T}{\partial x} \Big|_{x=s^-} - k_L \frac{\partial T}{\partial x} \Big|_{x=s^+} \right] \quad (29f)$$

Concerning the liquid phase, the proposed solution is given by

$$T_L(x, t) = A_L + B_L \left[ 1 - \operatorname{erf} \left( \frac{x}{2\sqrt{\alpha_L t}} \right) \right] \quad (30)$$

A relationship between the diffusivity of the solid and liquid phases is necessary to assess the similarity variable,

$$n = \sqrt{\frac{\alpha_S}{\alpha_L}} \quad (31)$$

Then, the solution becomes

$$T_L(x, t) = A_L + B_L \left[ 1 - \operatorname{erf} \left( \frac{nx}{2\sqrt{\alpha_S t}} \right) \right] \quad (32)$$

The substitution of initial and boundary conditions into the temperature profiles allows the constants  $A_L$  and  $B_L$  to be determined:

$$T_L(x = s(t), t) = T_F = A_L + B_L [1 - \operatorname{erf}(n\varphi)] \quad (33)$$

for  $A_L$  in  $x \rightarrow +\infty$ , when  $t > 0$ ,

$$T_L(x \rightarrow +\infty, t) = T_P = A_L + 0 \therefore A_L = T_P \quad (34)$$

$$T_F = T_P + B_L [1 - \operatorname{erf}(n\varphi)] \quad (35)$$

The constant  $B_L$  can be determined as

$$B_L = \frac{T_F - T_P}{1 - \operatorname{erf}(n\varphi)} \quad (36)$$

Finally, after the substitution of constants in the liquid-phase temperature profile gives

$$\begin{aligned} & \rho_S L \left( \frac{2\varphi^2 \alpha_S}{s} - \Omega \right) \\ &= k_S \frac{(T_F - T_\infty)}{\psi(s, \varphi)} \left\{ \frac{h}{k_S} \exp \left( \frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2} \right) \operatorname{erfc} \left( \varphi + \frac{hs}{2\varphi k_S} \right) + \frac{2\varphi}{\sqrt{\pi} s \exp(\varphi^2)} \right. \\ & \quad \left. - \frac{2\varphi}{\sqrt{\pi} s \exp \left[ \left( \varphi + \frac{hs}{2\varphi k_S} \right)^2 \right]} \exp \left( \frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2} \right) \right\} + k_L \frac{2\varphi n}{\sqrt{\pi} s} \cdot \frac{(T_P - T_F)}{\operatorname{erfc}(n\varphi)} \\ & \quad \cdot \exp(-n^2 \varphi^2) \end{aligned} \quad (43)$$

Rearranging the terms in a form for representing heat conduction parameters,

$$T_L(x, t) = T_P + \frac{T_F - T_P}{1 - \operatorname{erf}(n\varphi)} \cdot \left[ 1 - \operatorname{erf} \left( \frac{nx}{2\sqrt{\alpha_S t}} \right) \right] \quad (37)$$

However, by knowing that,

$$\frac{1}{2\sqrt{\alpha_S t}} = \frac{\varphi}{s} \quad (38a)$$

$$\frac{x}{2\sqrt{\alpha_S t}} = \varphi \frac{x}{s} \quad (38b)$$

and combining Eq. (37) and Eq. (38) results in

$$\frac{T_L(x, t) - T_P}{T_F - T_P} = \theta_L(x, t) = \frac{1}{1 - \operatorname{erf}(n\varphi)} \cdot \left[ 1 - \operatorname{erf} \left( \frac{nx}{2\sqrt{\alpha_S t}} \right) \right] \quad (39a)$$

$$\frac{T_L(x, s) - T_P}{T_F - T_P} = \theta_L(x, s) = \frac{1}{1 - \operatorname{erf}(n\varphi)} \cdot \left[ 1 - \operatorname{erf} \left( n\varphi \frac{x}{s} \right) \right] \quad (39b)$$

The derivative of  $T_L(x, s)$  with respect to  $x$  at  $x = s^+$  furnishes the temperature gradient for the liquid phase at the moving interface,

$$\frac{\partial T_L}{\partial x} \Big|_{x=s^+} = -\frac{1}{\sqrt{\pi}} \cdot \frac{T_P - T_F}{[1 - \operatorname{erf}(n\varphi)]} \cdot n \cdot \frac{1}{\sqrt{\alpha_S t}} \cdot \exp(-n^2 \varphi^2) \quad (40)$$

By inserting the similarity variable  $\varphi$  in Eq. (38),

$$\frac{\partial T_L}{\partial x} \Big|_{x=s^+} = -\frac{2\varphi n}{\sqrt{\pi} s} \cdot \frac{(T_P - T_F)}{\operatorname{erfc}(n\varphi)} \cdot \exp(-n^2 \varphi^2) \quad (41)$$

It is important to mention that sometimes the thermal gradient is a function of both the interface position and time, as presented in Eq. (40):

$$\frac{\partial T_L}{\partial x} \Big|_{x=s^+} = -\frac{2\varphi n}{\sqrt{\pi} s} \cdot \frac{(T_P - T_F)}{\operatorname{erfc} \left( n \frac{s}{2\sqrt{\alpha_S t}} \right)} \cdot \exp(-n^2 \frac{s^2}{4\alpha_S t}) \quad (42)$$

By combining Eq. (20), Eq. (27), Eq. (38), and Eq. (42), the similarity variable can be found:

$$\varphi = \frac{C_{PS}(T_F - T_\infty)}{L \psi(s, \varphi)} \left\{ \frac{hs}{2\varphi k_S} \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2}\right) \operatorname{erfc}\left(\varphi + \frac{hs}{2\varphi k_S}\right) + \frac{1}{\sqrt{\pi} \exp(\varphi^2)} \right. \\ \left. - \frac{1}{\sqrt{\pi} \exp\left[\left(\varphi + \frac{hs}{2\varphi k_S}\right)^2\right]} \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2}\right) \right\} \\ + \frac{C_{PL}(T_P - T_F)}{L} \frac{\alpha_L \rho_L}{\alpha_S \rho_S} \frac{n}{\sqrt{\pi} \operatorname{erfc}(n\varphi) \exp(n^2 \varphi^2)} + \frac{hs}{\varphi k_S} \frac{\sqrt{\alpha_S}}{\sqrt{t}}$$

and,

$$\varphi = \frac{C_{PS}(T_F - T_\infty)}{L \psi(s, \varphi)} \left\{ \frac{hs}{2\varphi k_S} \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2}\right) \operatorname{erfc}\left(\varphi + \frac{hs}{2\varphi k_S}\right) + \frac{1}{\sqrt{\pi} \exp(\varphi^2)} \right. \\ \left. - \frac{1}{\sqrt{\pi} \exp\left[\left(\varphi + \frac{hs}{2\varphi k_S}\right)^2\right]} \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2}\right) \right\} \\ + \frac{C_{PL}(T_P - T_F)}{L} \frac{\alpha_L \rho_L}{\alpha_S \rho_S} \frac{n}{\sqrt{\pi} \operatorname{erfc}(n\varphi) \exp(n^2 \varphi^2)} + \frac{hs}{\varphi k_S} \frac{\sqrt{\alpha_S}}{\sqrt{t}}$$

$$\varphi = \frac{C_{PS}(T_F - T_\infty)}{L \psi(s, \varphi)} \left\{ \frac{hs}{2\varphi k_S} \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2}\right) \operatorname{erfc}\left(\varphi + \frac{hs}{2\varphi k_S}\right) + \frac{1}{\sqrt{\pi} \exp(\varphi^2)} \right. \\ \left. - \frac{1}{\sqrt{\pi} \exp\left[\left(\varphi + \frac{hs}{2\varphi k_S}\right)^2\right]} \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2}\right) \right\} \\ + \frac{C_{PL}(T_P - T_F)}{L} \frac{\alpha_L \rho_L}{\alpha_S \rho_S} \frac{n}{\sqrt{\pi} \operatorname{erfc}(n\varphi) \exp(n^2 \varphi^2)} + \Omega$$

in which

$$N = \frac{\alpha_L \rho_L}{\alpha_S \rho_S} \tag{44}$$

$$\varphi = \frac{Ste_S}{\psi(s, \varphi)} \left\{ \frac{Biot}{2\varphi} \exp\left(Biot + \frac{Biot^2}{4\varphi^2}\right) \operatorname{erfc}\left(\varphi + \frac{Biot}{2\varphi}\right) + \frac{1}{\sqrt{\pi} \exp(\varphi^2)} \right. \\ \left. - \frac{1}{\sqrt{\pi} \exp\left[\left(\varphi + \frac{Biot}{2\varphi}\right)^2\right]} \exp\left(Biot + \frac{Biot^2}{4\varphi^2}\right) \right\} \\ + Ste_L N \frac{n}{\sqrt{\pi} \operatorname{erfc}(n\varphi) \exp(n^2 \varphi^2)} + \Omega^* \tag{45}$$

where  $St_{eL} = \frac{c_{PL}(T_P - T_F)}{\rho_S L}$  is the Stefan number considering the liquid phase and,  $\Omega^* = \frac{L Biot}{\phi}$  is the dimensionless velocity  $\Omega = \frac{2h\alpha_S}{k_S}$ .

**Solidification time**

The prediction of time for a given solidified layer can be expressed as

$$t = \gamma s^2 + \delta s \tag{46}$$

where  $\gamma$  is

$$\gamma = \frac{1}{4\alpha_S \phi^2} \tag{47}$$

and  $\delta$  is given as

$$\delta = \frac{1}{\rho_S L \left( k_S \frac{\partial T_S}{\partial x} \Big|_{x=S^-} - k_L \frac{\partial T_L}{\partial x} \Big|_{x=S^+} \right)} - 2\gamma s \tag{48}$$

**Solid-liquid interface velocity**

The interface velocity can be directly derived from the moving boundary differential equation,

By making,

$$\frac{s}{2\sqrt{\alpha_S t}} + \frac{h\sqrt{\alpha_S t}}{k_S} = \phi \tag{49}$$

and, to find the invariable form of velocity correction, we write  $s$  as

$$s = 2\phi\sqrt{\alpha_S t} - \frac{2h\alpha_S t}{k_S} \tag{50}$$

Deriving  $s$  with respect to time  $t$  gives,

$$\frac{ds}{dt} = \phi \frac{\alpha_S}{t} - \frac{2h\alpha_S}{k_S} = \frac{2\phi^2 \alpha_S}{k_S} - \Omega \tag{51}$$

$$v = \frac{ds}{dt} = \frac{1}{\rho_S L} \left( k_S \frac{\partial T_S}{\partial x} \Big|_{x=S^-} - k_L \frac{\partial T_L}{\partial x} \Big|_{x=S^+} \right) + \Omega \tag{52}$$

The growth rate  $v$  written in terms of  $\gamma$  and  $\delta$  provide

$$v = \frac{1}{2\gamma s + \delta} \tag{53}$$

**Thermal gradient of the liquid**

The thermal gradients of the solid and liquid phase are

$$\frac{\partial T_S(x, s)}{\partial x} \Big|_{x=S^-} = \frac{(T_F - T_\infty)}{\psi(s, \phi)} \left\{ \frac{h}{k_S} \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\phi^2 k_S^2}\right) \operatorname{erfc}\left(\phi + \frac{hs}{2\phi k_S}\right) + \frac{2\phi}{\sqrt{\pi} s \exp(\phi^2)} - \frac{2\phi}{\sqrt{\pi} s \exp\left[\left(\phi + \frac{hs}{2\phi k_S}\right)^2\right]} \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\phi^2 k_S^2}\right) \right\} \tag{54}$$

and,

$$\frac{\partial T_L}{\partial x} \Big|_{x=S^+} = -\frac{1}{\sqrt{\pi}} \cdot \frac{T_P - T_F}{[1 - \operatorname{erf}(n\phi)]} \cdot \frac{n}{\sqrt{\alpha_S t}} \cdot \exp(-n^2 \phi^2) \tag{55}$$

respectively.

**Cooling rate**

The cooling rate can be expressed in terms of the thermal gradient  $\frac{\partial T(x, t)}{\partial x} \Big|_{x=S^+}$  of the liquid phase Eq. (55) and the interface velocity  $v$ , Eq. (52),

$$\dot{T}_L = G_L v = \frac{\partial T(x, t)}{\partial x} \Big|_{x=S^+} \frac{ds}{dt} = -\frac{1}{\sqrt{\pi}} \cdot \frac{T_P - T_F}{[1 - \operatorname{erf}(n\phi)]} \cdot \frac{n}{\sqrt{\alpha_S t}} \cdot \exp(-n^2 \phi^2) \left[ \frac{1}{\rho_S L} \left( k_S \frac{\partial T_S}{\partial x} \Big|_{x=S^-} - k_L \frac{\partial T_L}{\partial x} \Big|_{x=S^+} \right) + \Omega \right] \tag{56}$$

The similarity variable is calculated from the solid-liquid interface thermal balance as,

$$\phi = \frac{C_{PS} (T_F - T_\infty)}{L \psi(s, \phi)} \left\{ \frac{hs}{2\phi k_S} \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\phi^2 k_S^2}\right) \operatorname{erfc}\left(\phi + \frac{hs}{2\phi k_S}\right) + \frac{1}{\sqrt{\pi} \exp(\phi^2)} - \frac{1}{\sqrt{\pi} \exp\left[\left(\phi + \frac{hs}{2\phi k_S}\right)^2\right]} \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\phi^2 k_S^2}\right) \right\} + \frac{C_{PL}(T_P - T_F)}{L} \frac{\alpha_L \rho_L}{\alpha_S \rho_S \sqrt{\pi}} \frac{n}{\operatorname{erfc}(n\phi) \exp(n^2 \phi^2)} + \Omega \tag{57}$$

The set of equations from the analytical solution for transient solidification proposed by Clyne et al. [26] necessary to calculate the thermal variables is the following:

**Solidification time**

The prediction of time for a given solidified layer can be expressed as

$$t = \alpha s^2 + \beta s \tag{58}$$

where  $\alpha$  and  $\beta$  are defined as

$$\alpha = \frac{1}{4\alpha_S \phi^2} \tag{59}$$

and

$$\beta = \frac{c_{PS} L}{\sqrt{\pi} \phi \exp(\phi^2) [M + \operatorname{erf}(\phi)] h_i} \tag{60}$$

respectively. In Eq. (59),  $\alpha_S$  represents the diffusivity of the solid, and  $\phi$  the similarity variable used in Garcia et al.'s model. When the mold is not considered, as in this study, where  $M = 0$ , the mean interfacial heat transfer coefficient  $h_i$  becomes equal to the mean global heat transfer coefficient  $h$ , i.e.,  $h = h_i$ . The specific heat and density of the solid phase are denoted by  $c_{PS}$

and  $c_{PS}$ , respectively.

### Solid-liquid interface velocity

The solid-liquid interface velocity can be directly derived from the moving boundary differential equation, Eq. (7) or by the derivative of Eq. (8), as deduced by Garcia et al. [24-26],

$$\frac{1}{v} = \frac{dt}{dS} = 2\alpha S + \beta \quad (61)$$

and, by  $v$  provides,

$$v = \frac{dS}{dt} = \frac{1}{2\alpha S + \beta} \quad (62)$$

### Thermal gradient of the liquid

One simple form to compute the thermal gradient is by taking the temperature profile of the liquid and derive it with respect to  $G_L = \left. \frac{\partial T(x,t)}{\partial x} \right|_{x=S^+}$ ,

$$G_L = \left. \frac{\partial T(x,t)}{\partial x} \right|_{x=S^+} = \frac{2n\phi(T_P - T_F)}{\sqrt{\pi} \operatorname{erfc}(n\phi) \exp(n^2\phi^2)(S+S_0)} \quad (63)$$

### Cooling rate

The cooling rate can be expressed in terms of the thermal gradient  $\left. \frac{\partial T(x,t)}{\partial x} \right|_{x=S^+}$  and the interface velocity  $v$ ,

$$\dot{T}_L = G_L v = \left. \frac{\partial T(x,t)}{\partial x} \right|_{x=S^+} \frac{dS}{dt} = \frac{2n\phi(T_P - T_F)}{\sqrt{\pi} \operatorname{erfc}(n\phi) \exp(n^2\phi^2)(S+S_0)} \frac{1}{2\alpha S + \beta} \quad (64)$$

The similarity variable is calculated from solid-liquid interface thermal balance as,

$$\frac{\exp(-\phi^2)}{M + \operatorname{erf}(\phi)} - \frac{m(T_V - T_F) \exp(-n^2\phi^2)}{(T_F - T_P)[1 - \operatorname{erf}(n\phi)]} - \sqrt{\pi} \phi \frac{L}{c_{PS}(T_F - T_0)} = 0 \quad (65)$$

### 3. Experimental Procedure

The eutectic alloy was prepared from commercially pure solvent Al  $\cong 99.7\%$  and solute Si  $\cong 99.5\%$ , determined through a stoichiometric calculation based on the desired eutectic

composition (Al-12.6 wt.%Si), and on the volume of the mold. The checking of the nominal compositions of Al and Si elements was carried out utilizing a thermal characterization which consisted of the insertion in the liquid metal of type K thermocouples connected to a temperature recorder. The resulting experimental curve furnishes the eutectic temperature ( $T_{\text{Eut}} = 577^\circ\text{C}$ ). A comprehensive description of the experimental procedure can be found in [40,41,43].

Figure 2 shows a scheme of the upward unsteady directional solidification device used in the experiment to obtain the thermal data and as-cast ingot. The thermocouples were positioned at 5, 10, 15, 20, 30, 50, 70 and 90 mm from the heat-extracting surface and calibrated at the melting point of aluminium. Solidification occurred primarily through a water-cooled bottom, driving upward directional growth, as shown in Figure 3. A stainless steel mold, with 60 mm internal diameter, 160 mm height, 5 mm wall thickness, was employed. An insulating alumina layer covered the inner vertical surface to minimize radial heat loss, while an insulated top cover reduced heat transfer from the metal to air, minimizing both radiation and convection. The bottom of mold was sealed with a thin (3 mm) carbon steel sheet featuring a roughness of approximately  $35 \mu\text{m}$ . The investigated alloy was melted in situ and lateral electric heaters' power were precisely controlled to achieve the target superheat at the 5 mm thermocouple. Solidification commenced upon disconnecting the electric heaters and simultaneously initiating water flow of 7 l/s at 298.15K.

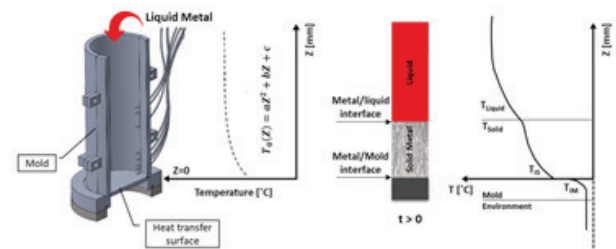


Figure 2. Schematic representation of upward-directional solidification mold and thermocouple positions.

### 4 Results and Discussion

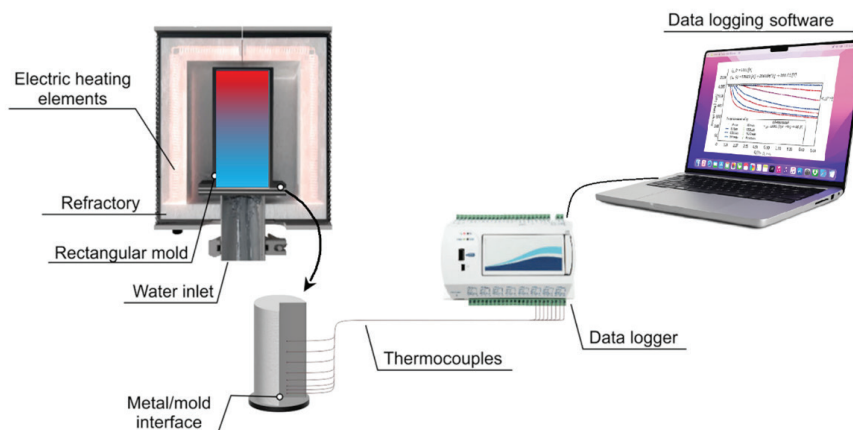


Figure 3. Schematic representation of upward-directional solidification apparatus.

The thermal variables are calculated for Al, Cu, Fe, Pb, Sn, and Ni with the aim of analyzing the results obtained by a classical [26] and a recently published analytical model for solidification [37]. The comparison was made by evaluating isothermal position, velocity, thermal gradient, and cooling rate for a set of Biot numbers, considering 4% melt superheat.

The analytical model is initially compared against the numerical model for transient multicomponent alloy solidification [36,42,43] and experimental data from [40]. The numerical model was used to find solutions for all available thermocouple positions. Figure 4 presents the numerical simulation of Al-12.6 wt%Si, illustrating key kinetic variables including temperature profiles, solid-liquid interface position versus time, velocity, thermal gradient, and cooling rate. During external calculation of the global mean heat transfer coefficient,  $\bar{h}$ , using integral methods, we have integrated  $h(t)$  to obtain its mean integral

value:  $\bar{h} = \frac{1}{t_{\infty}} \int_0^{t_{\infty}} h(t) dt$ , where  $t_{\infty} \rightarrow +\infty$  is significantly greater than the process time  $t=400$  s, i.e.,  $t_{\infty} = 60000000$  s is enough to converge the thermal gradient and cooling rate. In the case of Clyne and Garcia's solution,  $t_{\infty} = 400$  s.

Figure 5 shows the solidification related thermal variables solid-liquid interface velocity, cooling rate, and thermal gradient plotted versus the distance from the chill for the analytical solution, the experimental data reported in [40], and the numerical simulation. The excellent agreement between the experimental results and the analytical solution provides strong validation of the analytical model. Notably, the numerical simulation shows improved agreement with the experiments, especially concerning the solid-liquid interface velocity. Although the overall model is validated, additional experimental data would be valuable for further refining our understanding of this interfacial behaviour.

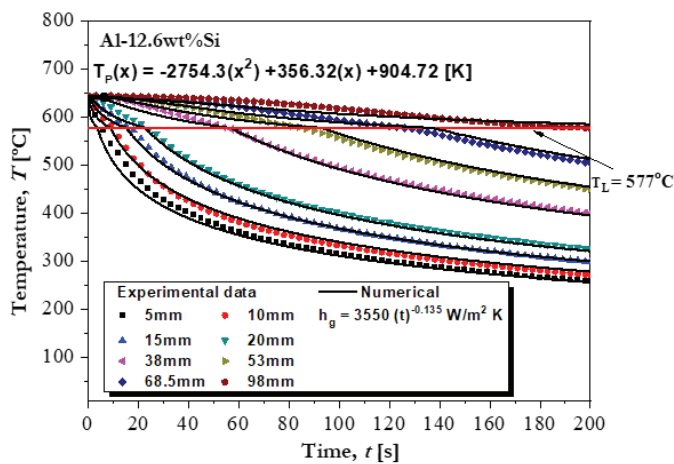


Figure 4(A)

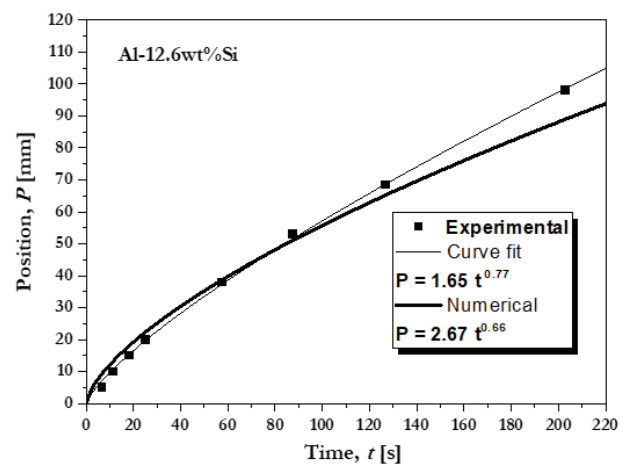


Figure 4(B)

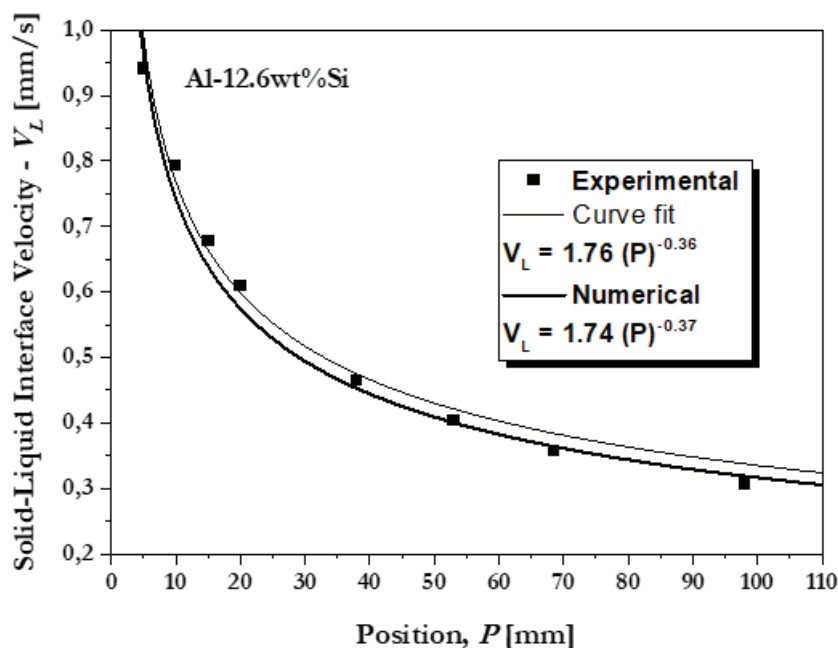


Figure 4(C)

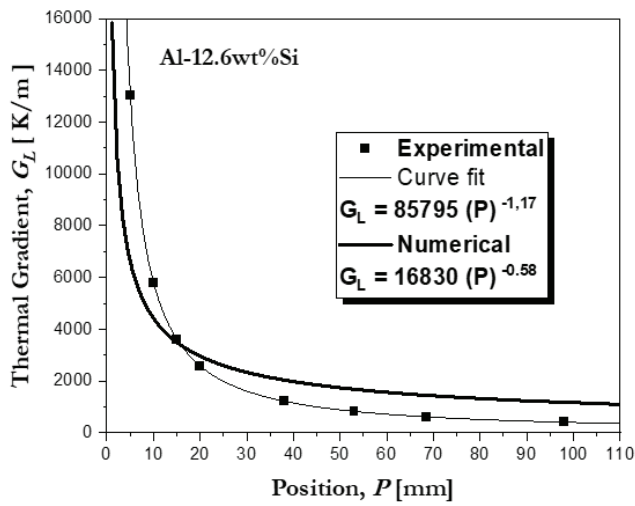


Figure 4(D)

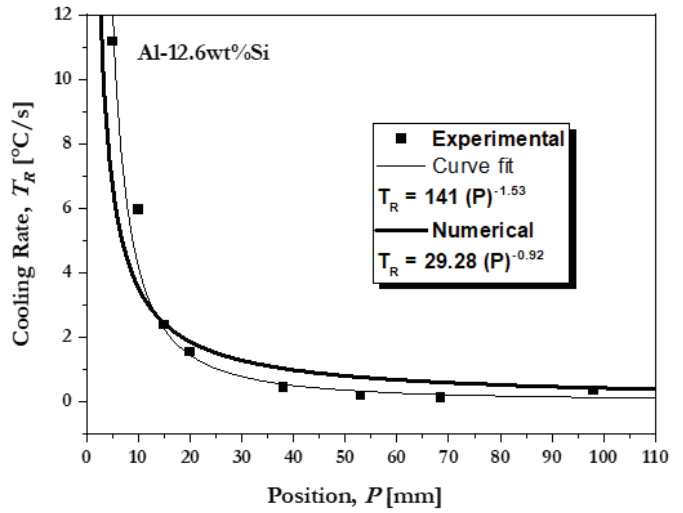


Figure 4(E)

Figure 4. Numerical predictions against experimental data for (A) cooling curves, (B) position versus time, (C) solid/liquid interface velocity, (D) cooling rate, and (E) thermal gradient.

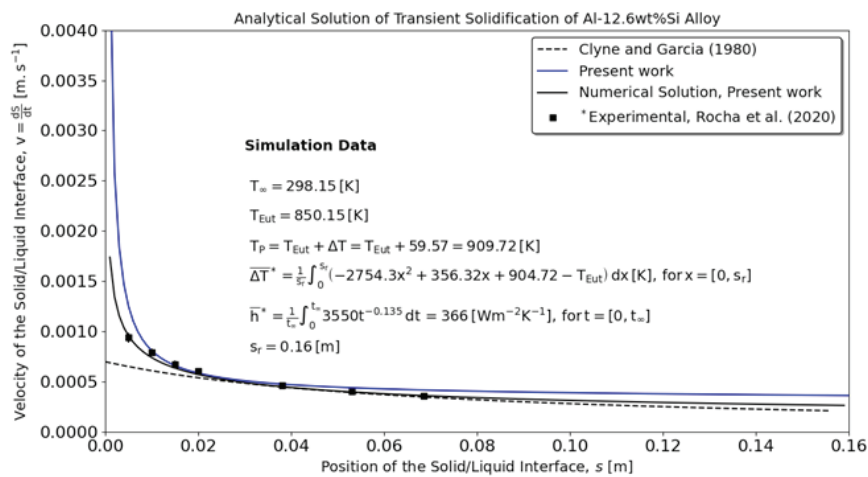


Figure 5(A)

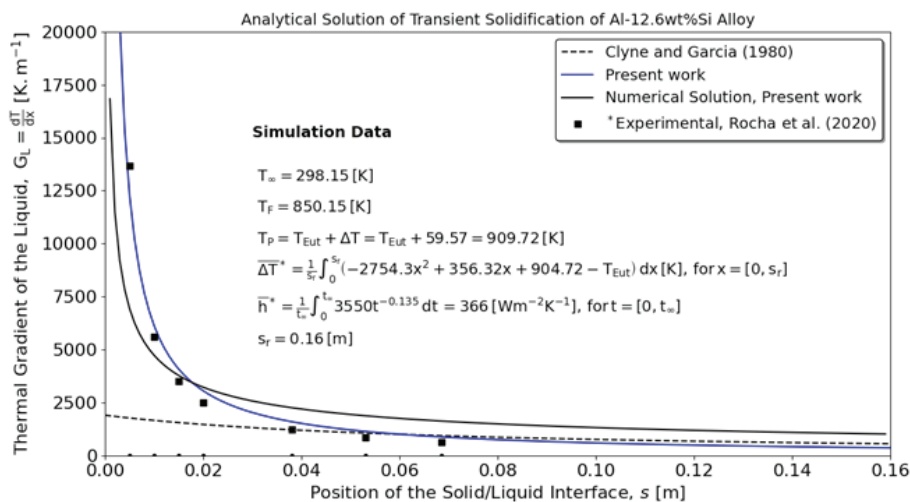


Figure 5(B)

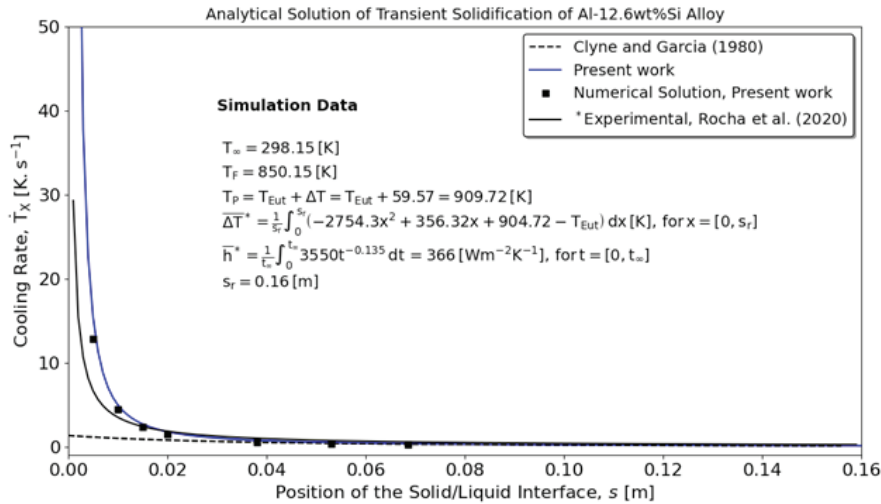


Figure 5(C)

Figure 5. Analytical and numerical predictions compared to experimental data for thermal variables as a function of position from the chill: (A) solid/liquid interface velocity, (B) cooling rate, and (C) thermal gradient.

Figure 6 shows the solid–liquid interface velocity (growth rate) as a function of position. Both models produce very similar predictions over the whole range of Biot numbers considered, accurately capturing the interface velocity for all of the investi-

gated materials. However, the new model predicts steeper interface velocities than the classical solution in regions of high Biot number and fast flow, where the classical solution yields smoother curves. Equation (52) employs a liquid thermal gradient that is similar to the one used in Equation (62), but it also incorporates a second term representing the solid thermal gradient. This additional term, which uses a new similarity variable, generates a steeper thermal gradient.

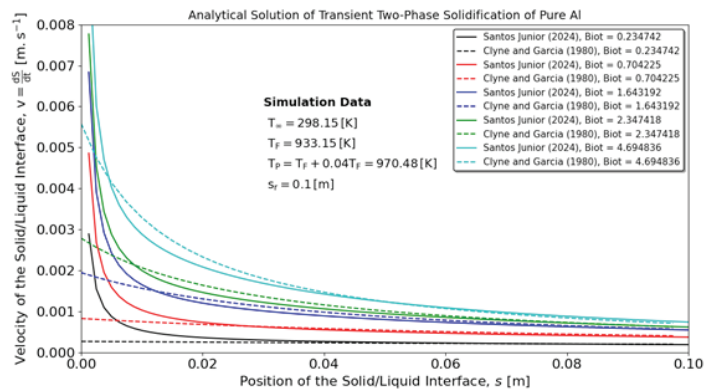


Figure 6(A)

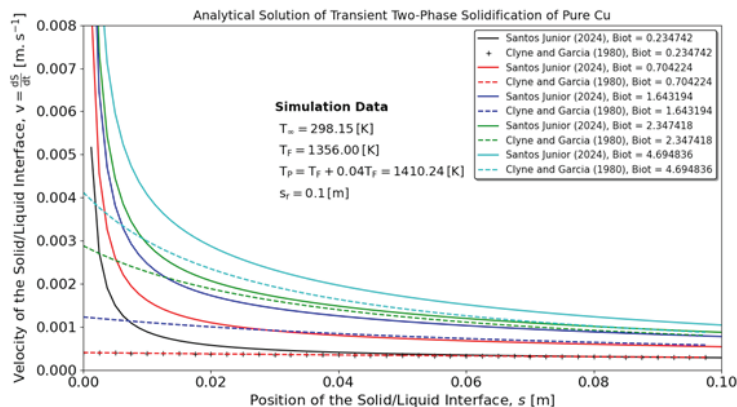


Figure 6(B)

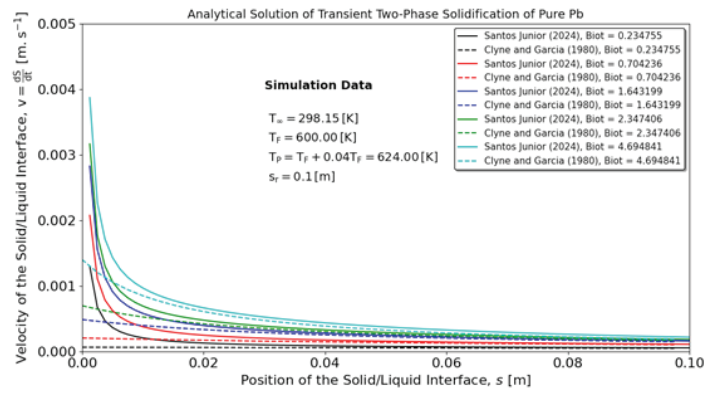


Figure 6(C)

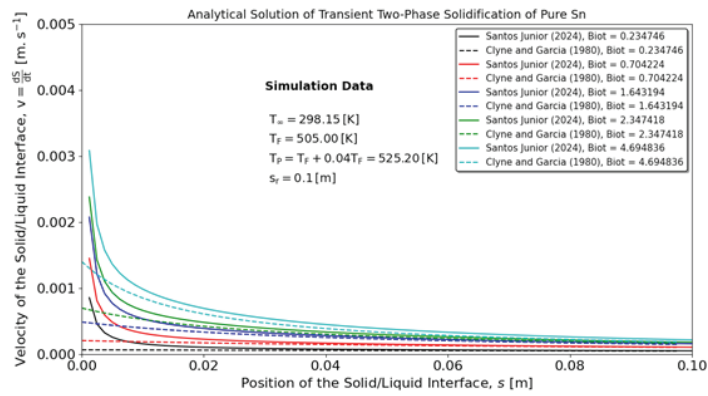


Figure 6(D)

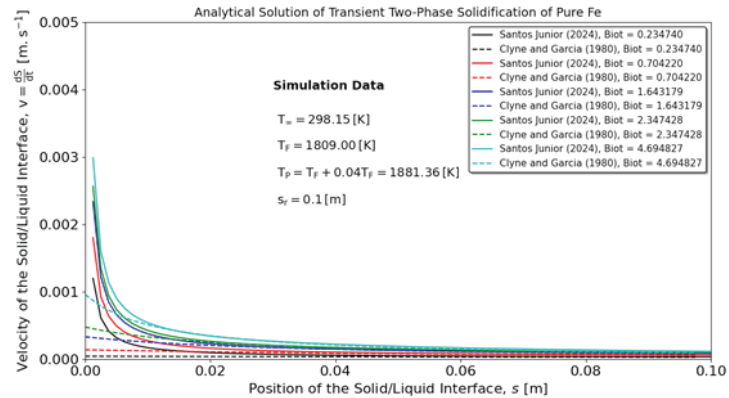


Figure 6(E)

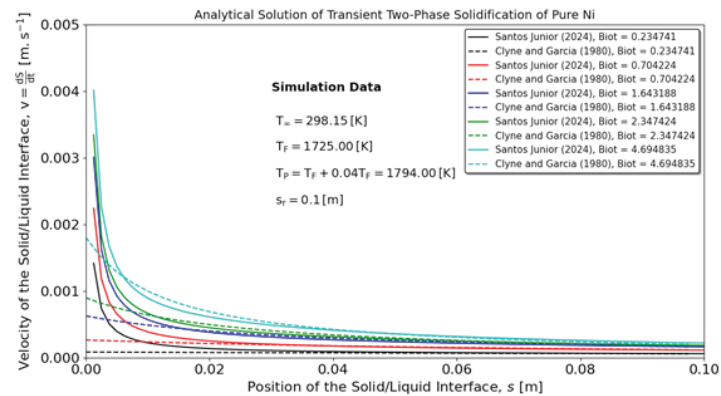


Figure 6(F)

Figure 6. Analytical predictions for the solid-liquid interface velocity versus time for pure: (A) Al, (B) Cu, (C) Pb, (D) Sn, (E) Fe, and (F) Ni.

The thermal gradient of the liquid phase is plotted against the solid-liquid interface position, as shown in Figure 7. For all cases analyzed, the predicted thermal gradient by the new approach is steeper than that furnished by the classical model, whose differences can be achieved up to 8 times. As thermal gradients are inherently steeper in nature, this can also be observed in experimental transient solidification studies (e.g., [40]). Consequently, it appears that the classical model may not be as accurate for calculating the thermal gradient. The differences in solutions arise from the combined effect of the new similarity variable, which accounts for parabolic and linear profiles calculated at the moving boundary interface via energy balance. While this approach provides valuable insights, a general solution for this type of problem might be based on a

full quadratic profile.

Figure 7 shows the liquid phase thermal gradient plotted as a function of the solid-liquid interface position. For every case examined, the gradient predicted with the new approach is noticeably steeper than that given by the classical model up to eight fold larger in some instances. Because thermal gradients are intrinsically steep, this behaviour is also observed in experimental transient solidification studies (e.g., [40]). Consequently, the classical model may be insufficiently accurate for calculating the thermal gradient.

The disparity between the two solutions stems from the new similarity variable, which incorporates both parabolic and linear temperature profiles at the moving interface as imposed by the energy balance condition. Although this approach yields valuable insight, a more general solution for this class of problems could be obtained by adopting a full quadratic temperature profile.

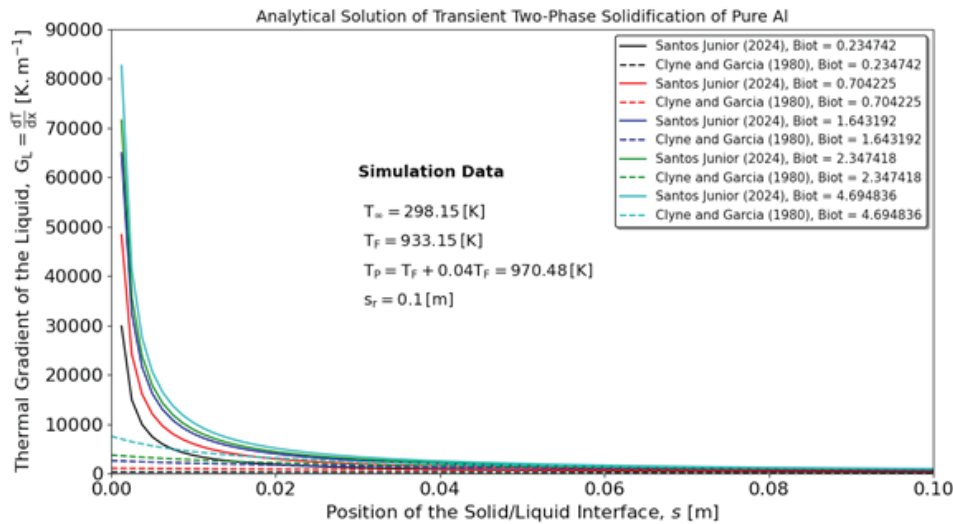


Figure 7(A)

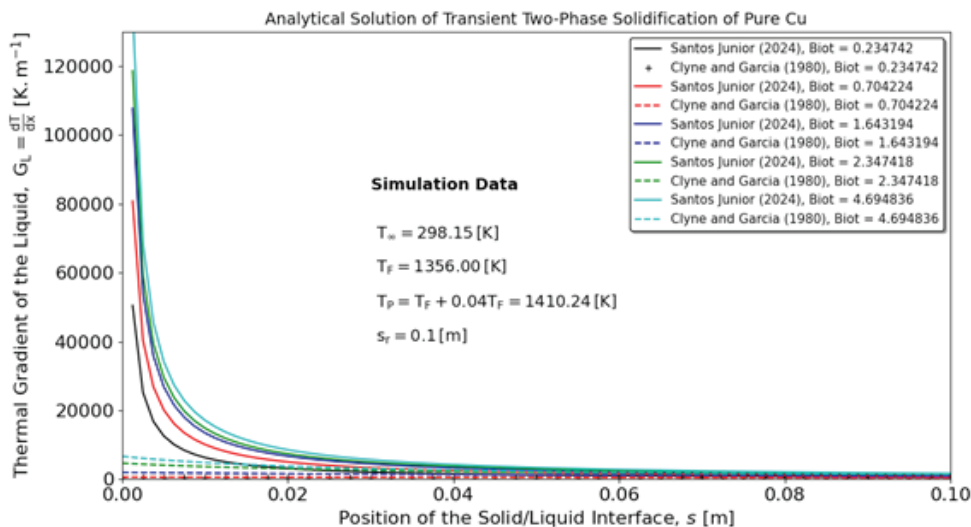


Figure 7(B)

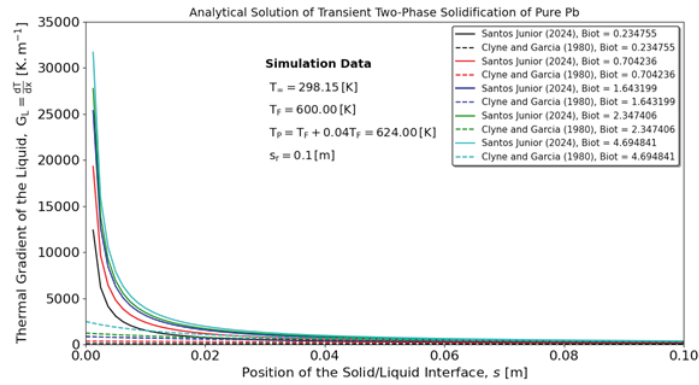


Figure 7(C)

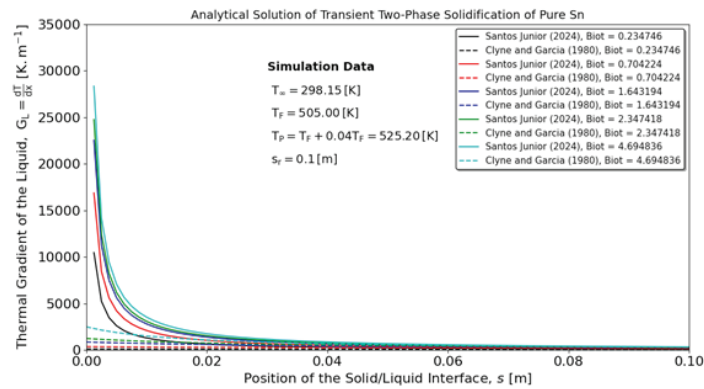


Figure 7(D)

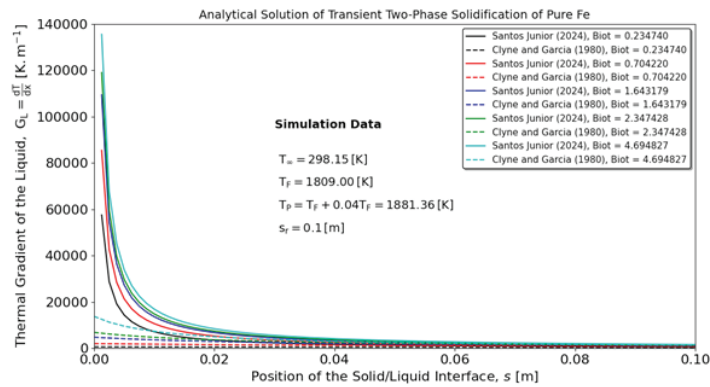


Figure 7(E)

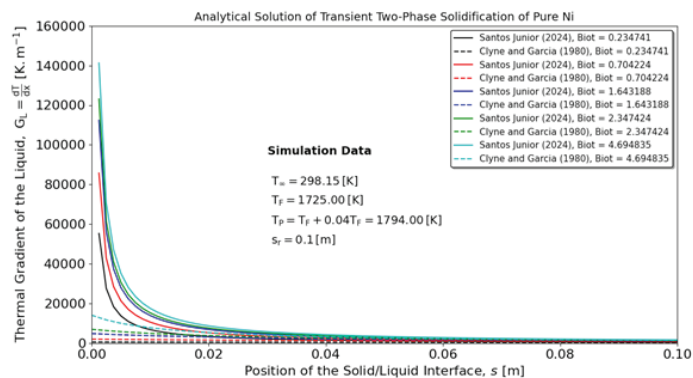


Figure 7(F)

Figure 7. Analytical predictions of the thermal gradient of the liquid phase versus time for pure: (A) Al, (B) Cu, (C) Pb, (D) Sn, (E) Fe, and (F) Ni.

Figure 8 presents the cooling rate as a function of the solid–liquid interface position for several Biot numbers. All cases display a comparable trend, indicating that the classical model underestimates the steepness of the cooling rate when compared with the experimental measurements reported in [40].

Equation (64) for transient solidification,  $\dot{T}_L = \frac{dx}{dt} v_L$ , shows that the cooling rate scales with the interface velocity; therefore a steep cooling rate is expected for the velocities observed. Although the solid–liquid interface velocities predicted by the classical and the new models are essentially identical, the new formulation through its modified treatment of the temperature gradient produces a markedly steeper cooling rate, in line with the experimental data.

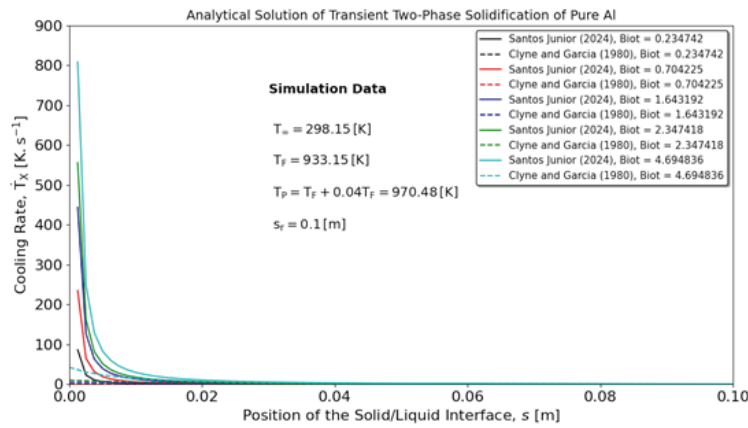


Figure 8(A)

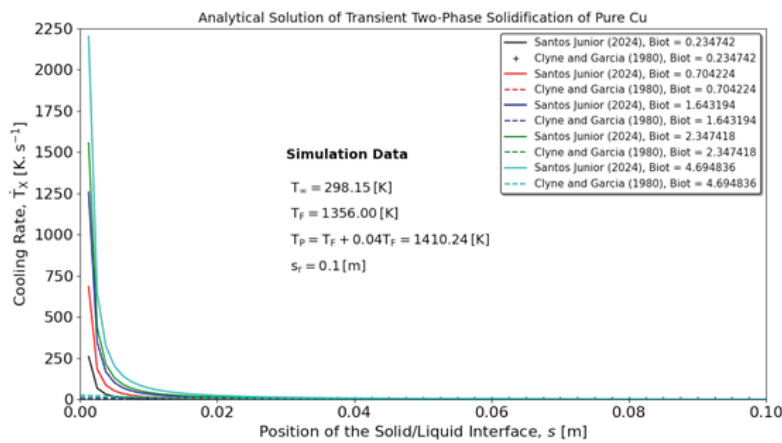


Figure 8(B)

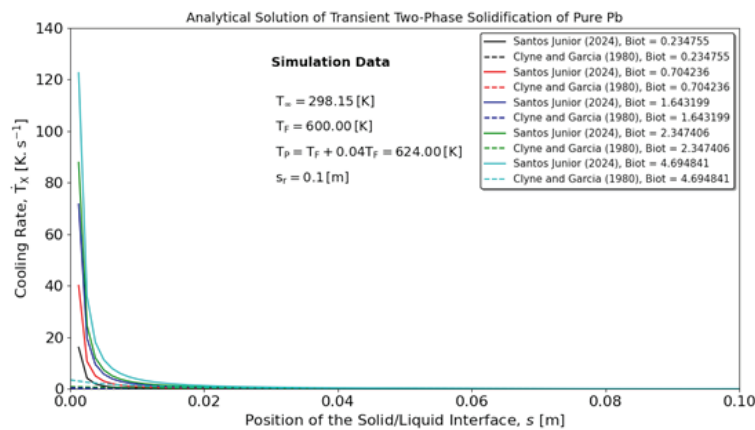


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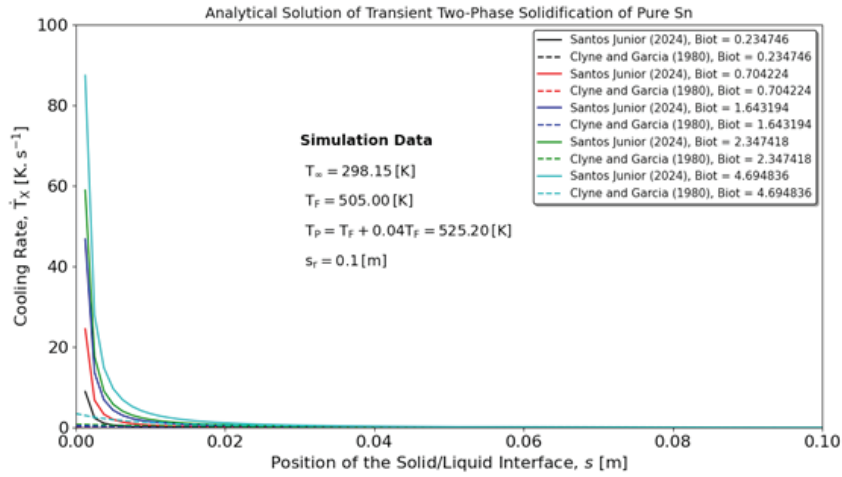


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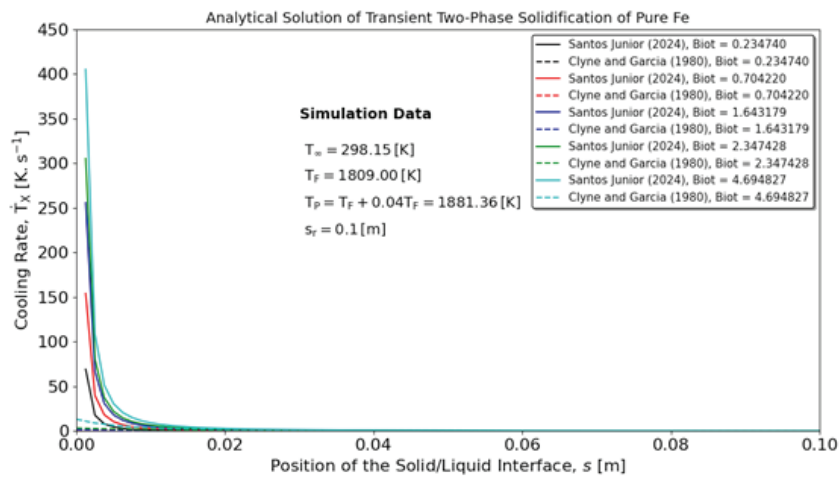


Figure 8(E)

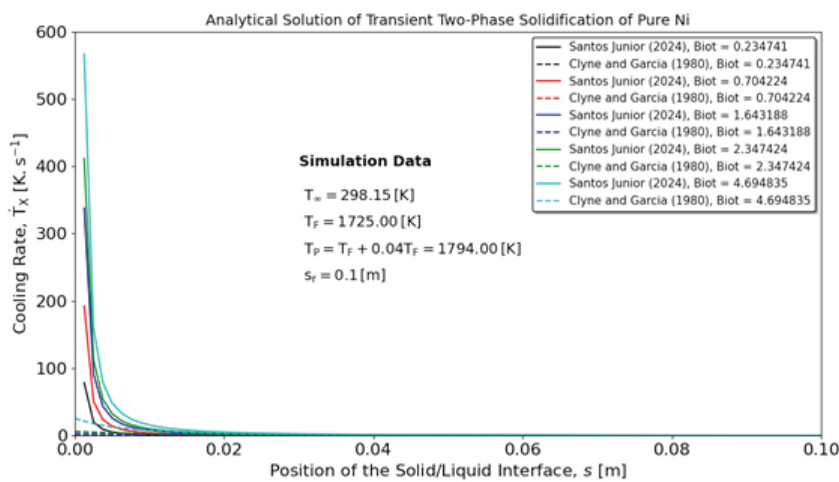


Figure 8(F)

Figure 8. Analytical predictions of the cooling rate against time for pure: (A) Al, (B) Cu, C(C) Pb, (D) Sn, (E) Fe, and (F) Ni.

The final application of this analytical model is a comparison with a classical solidification model for pure and eutectic materials

[25,26]. This analysis involves freezing water at an altitude of 5000 m to capture the surface thermal gradient. The present model can accommodate a wide range of Biot numbers, as shown in Figures 9-11.

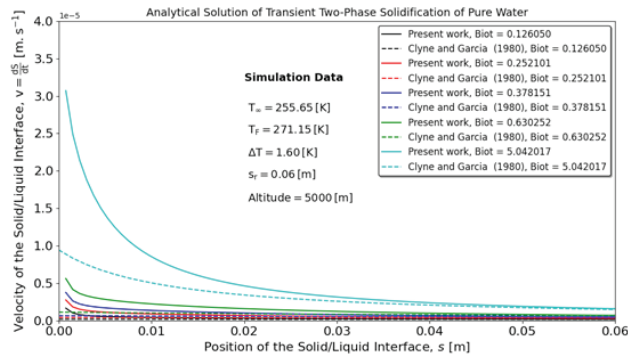


Figure 9(A)

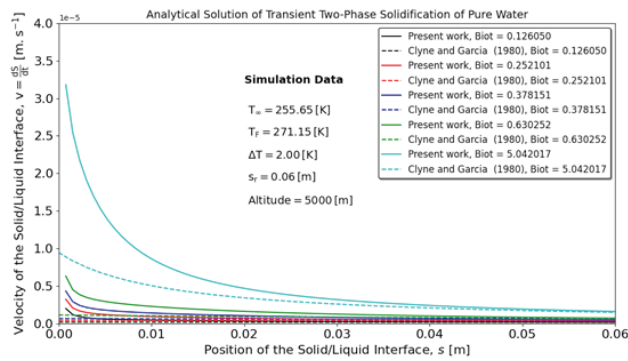


Figure 9(B)

Figure 9 Comparison of analytical solutions for one-dimensional water freezing under solid-liquid interface velocities, considering (A) 1.6 K and (B) 2.0 K superheat.

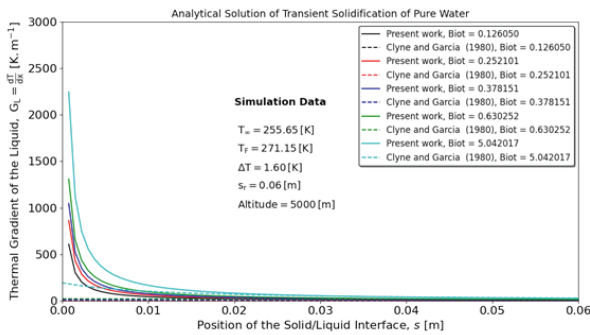


Figure 10(A)

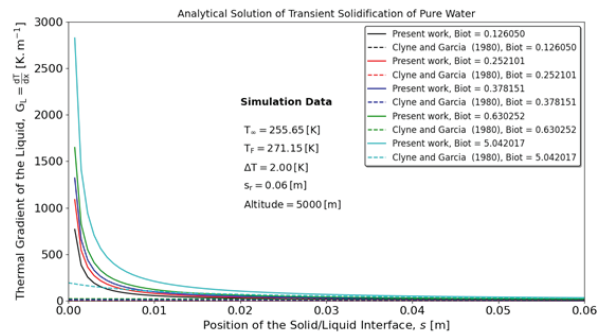


Figure 10(B)

Figure 10 Comparison of analytical solutions for one-dimensional water freezing under thermal gradients, considering (A) 1.6 K and (B) 2.0 K superheat.

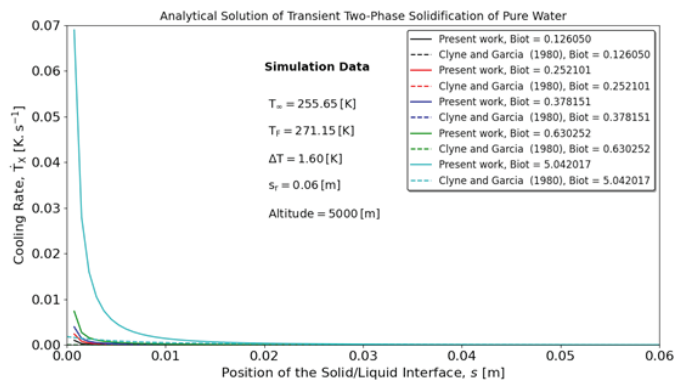


Figure 11(A)

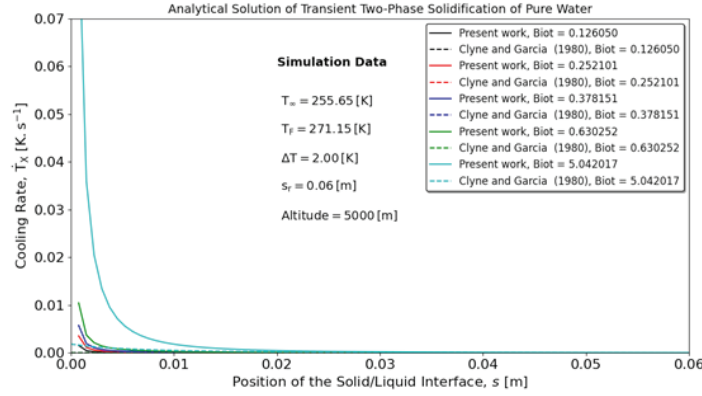


Figure 11(B)

Figure 11 Comparison of analytical solutions for one-dimensional water freezing under cooling rate, considering (A) 1.6 K and (B) 2.0 K superheat.

### 5. An Important Solution for Melt Convection

An important solution, normally applied for horizontal transient solidification is those with melt convection. In this case, the governing equations are the following:

$$\frac{\partial^2 T_S}{\partial x^2} = \frac{1}{\alpha_S} \frac{\partial T}{\partial t} \quad 0 < x < s(t) \quad (66)$$

$$\frac{\partial^2 T_L}{\partial x^2} = \frac{1}{\alpha_L} \frac{\partial T}{\partial t} \quad s(t) < x < +\infty \quad (67)$$

$$t = 0, \quad 0 < x < +\infty, \quad T = T_P \quad (68)$$

$$\frac{T_S(x, t) - T_F}{T_\infty - T_F} = \frac{\left\{ \operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha_S t}}\right) - \exp\left(\frac{hx}{k_S} + \frac{h^2 \alpha_S t}{k_S^2}\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha_S t}} + \frac{h\sqrt{\alpha_S t}}{k_S}\right) - \operatorname{erfc}(\varphi) + \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2}\right) \operatorname{erfc}\left(\varphi + \frac{hs}{2\varphi k_S}\right) \right\}}{\left\{ 1 - \operatorname{erfc}(\varphi) + \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2}\right) \operatorname{erfc}\left(\varphi + \frac{hs}{2\varphi k_S}\right) \right\}} \quad (73)$$

In similar way, we can write,

$$\frac{T_S(x, t) - T_F}{T_\infty - T_F} = \frac{\left\{ \operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha_S t}}\right) - \exp\left(\frac{hx}{k_S} + \frac{h^2 \alpha_S t}{k_S^2}\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha_S t}} + \frac{h\sqrt{\alpha_S t}}{k_S}\right) + \zeta(s, t) \right\}}{\psi(s, t)} \quad (74a)$$

$$\frac{T_S(x, s) - T_F}{T_\infty - T_F} = \frac{\left\{ \operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha_S t}}\right) - \exp\left(\frac{hx}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2}\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha_S t}} + \frac{hs}{2\varphi k_S}\right) + \zeta(s, \varphi) \right\}}{\psi(s, \varphi)} \quad (74b)$$

The thermal gradient  $T_S(x, t)$  in the vicinity of boundary  $x = s$  is found by deriving the temperature profile with respect to  $x$ , which has the following form:

$$\frac{\partial T_S(s, t)}{\partial x} \Big|_{x=s^-} = \frac{(T_F - T_\infty)}{\psi(s, t)} \left\{ \frac{h}{k_S} \exp\left(\frac{hs}{k_S} + \frac{h^2 \alpha_S t}{k_S^2}\right) \exp\left(\varphi + \frac{h\sqrt{\alpha_S t}}{k_S}\right) + \frac{2\varphi}{\sqrt{\pi} s \exp(\varphi^2)} - \frac{2\varphi}{\sqrt{\pi} s \exp\left[\left(\varphi + \frac{h\sqrt{\alpha_S t}}{k_S}\right)^2\right]} \exp\left(\frac{hs}{k_S} + \frac{h^2 \alpha_S t}{k_S^2}\right) \right\} \quad (75a)$$

$$\frac{\partial T_S(s,\varphi)}{\partial x}\Big|_{x=s^-} = \frac{(T_F-T_\infty)}{\psi(s,\varphi)} \left\{ \frac{h}{k_S} \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2}\right) \exp\left(\varphi + \frac{hs}{2\varphi k_S}\right) + \frac{2\varphi}{\sqrt{\pi} s \exp(\varphi^2)} - \frac{2\varphi}{\sqrt{\pi} s \exp\left[\left(\varphi + \frac{hs}{2\varphi k_S}\right)^2\right]} \exp\left(\frac{hs}{k_S} + \frac{h^2 s^2}{4\varphi^2 k_S^2}\right) \right\} \quad (75b)$$

$$\frac{\partial T_S(s,\varphi)}{\partial x}\Big|_{x=s^-} = \frac{(T_F-T_\infty)}{\psi(s,\varphi)} \frac{2\varphi}{s} \left\{ \frac{Biot_{Env}}{2\varphi} \exp\left(Biot_{Env} + \frac{Biot_{Env}^2}{4\varphi^2}\right) \exp\left(\varphi + \frac{Biot_{Env}}{2\varphi}\right) + \frac{1}{\sqrt{\pi} \exp(\varphi^2)} - \frac{1}{\sqrt{\pi} \exp\left[\left(\varphi + \frac{Biot_{Env}}{2\varphi}\right)^2\right]} \exp\left(Biot_{Env} + \frac{Biot_{Env}^2}{4\varphi^2}\right) \right\} \quad (75c)$$

The liquid phase profile and its gradient can be deduced as follows,

$$\frac{T_L(x,t)-T_P}{T_F-T_P} = \frac{1}{\psi(s,t)} \left\{ \operatorname{erfc}\left(\frac{s+x}{2\sqrt{\alpha_L t}}\right) - \exp\left(\frac{h_i(s+x)}{k_L} + \frac{h^2 \alpha_L t}{k_L^2}\right) \operatorname{erfc}\left(\frac{s+x}{2\sqrt{\alpha_L t}} + \frac{h_i \sqrt{\alpha_L t}}{k_L}\right) \right\} \quad (76a)$$

$$\frac{T_L(x,t)-T_P}{T_F-T_P} = \frac{1}{\psi(s,t)} \left\{ \operatorname{erfc}\left(\frac{s+x}{2\sqrt{\alpha_L t}}\right) - \exp\left(\frac{h_i(s+x)}{k_L} + \frac{h^2 \alpha_L t}{k_L^2}\right) \operatorname{erfc}\left(\frac{s+x}{2\sqrt{\alpha_L t}} + \frac{h_i \sqrt{\alpha_L t}}{k_L}\right) \right\} \quad (76b)$$

The thermal gradient  $T_L(x,t)$  in the vicinity of boundary  $x=s^+$  is found by deriving the temperature profile with respect to  $x$ , which has the following form:

$$\frac{\partial T_L(s,t)}{\partial x}\Big|_{x=s^+} = \frac{(T_F-T_P)}{\psi_L(s,t)} \left\{ \frac{h_i}{k_L} \exp\left(\frac{h_i s}{k_L} + \frac{h_i^2 \alpha_L t}{k_L^2}\right) \operatorname{erfc}\left(n\varphi + \frac{h_i \sqrt{\alpha_L t}}{k_L}\right) + \frac{2n\varphi}{\sqrt{\pi} s \exp(n^2 \varphi^2)} - \frac{2n\varphi}{\sqrt{\pi} s \exp\left[\left(n\varphi + \frac{h_i \sqrt{\alpha_L t}}{k_L}\right)^2\right]} \exp\left(\frac{h_i s}{k_L} + \frac{h_i^2 \alpha_L t}{k_L^2}\right) \right\} \quad (77a)$$

$$\frac{\partial T_L(s,\varphi)}{\partial x}\Big|_{x=s^+} = \frac{(T_F-T_P)}{\psi_L(s,\varphi)} \left\{ \frac{h_i}{k_L} \exp\left(\frac{h_i s}{k_L} + n^2 \frac{h_i^2 s^2}{4\varphi^2 k_L^2}\right) \operatorname{erfc}\left(n\varphi + n \frac{h_i s}{2\varphi k_L}\right) + \frac{2n\varphi}{\sqrt{\pi} s \exp(n^2 \varphi^2)} - \frac{2n\varphi}{\sqrt{\pi} s \exp\left[\left(n\varphi + n \frac{h_i s}{2\varphi k_L}\right)^2\right]} \exp\left(\frac{h_i s}{k_L} + n^2 \frac{h_i^2 s^2}{4\varphi^2 k_L^2}\right) \right\} \quad (77b)$$

$$\frac{\partial T_L(s,\varphi)}{\partial x}\Big|_{x=s^+} = \frac{(T_F-T_P)}{\psi_L(s,\varphi)} \frac{2\varphi}{s} \left\{ \frac{Biot_i}{2\varphi} \exp\left(Biot_i + n^2 \frac{Biot_i^2}{4\varphi^2}\right) \operatorname{erfc}\left(n\varphi + n \frac{Biot_i}{2\varphi}\right) + \frac{n}{\sqrt{\pi} \exp(n^2 \varphi^2)} - \frac{n}{\sqrt{\pi} \exp\left[\left(n\varphi + n \frac{Biot_i}{2\varphi}\right)^2\right]} \exp\left(Biot_i + n^2 \frac{Biot_i^2}{4\varphi^2}\right) \right\} \quad (77c)$$

Substituting the thermal gradient of the solid phase  $k_S \frac{\partial T}{\partial x}\Big|_{x=s^-}$  and temperature profil  $T_L(x = s^-, t)$  derived in Eq. (72) into the moving boundary interface,

$$\rho_S L \left(\frac{ds}{dt} - \Omega\right) = k_S \frac{\partial T}{\partial x}\Big|_{x=s^-} - h_i(T_L(x = s^-, t) - T_F)$$

provides,

$$\begin{aligned} & \rho_S L \left( \frac{2\varphi^2 \alpha_S}{s} - \Omega \right) \\ &= k_S \frac{(T_F - T_\infty)}{\psi(s, \varphi)} \left\{ \frac{h}{k_S} \exp \left( \frac{h s}{k_S} + \frac{h^2 s^2}{4 \varphi^2 k_S^2} \right) \operatorname{erfc} \left( \varphi + \frac{h s}{2 \varphi k_S} \right) + \frac{2 \varphi}{\sqrt{\pi} s \exp(\varphi^2)} \right. \\ & \quad \left. - \frac{2 \varphi}{\sqrt{\pi} s \exp \left[ \left( \varphi + \frac{h s}{2 \varphi k_S} \right)^2 \right]} \exp \left( \frac{h s}{k_S} + \frac{h^2 s^2}{4 \varphi^2 k_S^2} \right) \right\} - h_i (T_L(x = s^-, t) - T_F) \end{aligned} \quad (78a)$$

Rearranging Eq.(47) and substituting Eq. (46),

$$\begin{aligned} & \frac{L}{c_{PS}(T_F - T_\infty)} \left( \varphi - \frac{h s}{k_S} \right) \\ &= \frac{1}{\psi(s, \varphi)} \left\{ \frac{h s}{k_S 2 \varphi} \exp \left( \frac{h s}{k_S} + \frac{h^2 s^2}{4 \varphi^2 k_S^2} \right) \operatorname{erfc} \left( \varphi + \frac{h s}{2 \varphi k_S} \right) + \frac{1}{\sqrt{\pi} \exp(\varphi^2)} \right. \\ & \quad \left. - \frac{1}{\sqrt{\pi} \exp \left[ \left( \varphi + \frac{h s}{2 \varphi k_S} \right)^2 \right]} \exp \left( \frac{h s}{k_S} + \frac{h^2 s^2}{4 \varphi^2 k_S^2} \right) \right\} \\ & \quad - \frac{k_L}{k_S (T_F - T_\infty)} \frac{h_i s}{k_L 2 \varphi} (T_L(x = s^-, t) - T_F) \end{aligned} \quad (78b)$$

$$\begin{aligned} & \frac{1}{Ste} \left( \varphi - \frac{Biot_{Env}}{\varphi} \right) \\ &= \frac{1}{\psi(s, \varphi)} \left\{ \frac{Biot_{Env}}{2 \varphi} \exp \left( Biot_{Env} + \frac{Biot_{Env}^2}{4 \varphi^2} \right) \operatorname{erfc} \left( \varphi + \frac{Biot_{Env}}{2 \varphi} \right) \right. \\ & \quad \left. + \frac{1}{\sqrt{\pi} \exp(\varphi^2)} - \frac{1}{\sqrt{\pi} \exp \left[ \left( \varphi + \frac{Biot_{Env}}{2 \varphi} \right)^2 \right]} \exp \left( Biot_{Env} + \frac{Biot_{Env}^2}{4 \varphi^2} \right) \right\} \\ & \quad - \frac{1}{N} \frac{Biot_i (T_L(x = s^-, t) - T_F)}{2 \varphi (T_F - T_\infty)} \end{aligned} \quad (78c)$$

$$\begin{aligned} & \frac{1}{Ste} \left( \varphi - \frac{Biot_{Env}}{\varphi} \right) \\ &= \frac{1}{\psi(s, \varphi)} \left\{ \frac{Biot_{Env}}{2 \varphi} \exp \left( Biot_{Env} + \frac{Biot_{Env}^2}{4 \varphi^2} \right) \operatorname{erfc} \left( \varphi + \frac{Biot_{Env}}{2 \varphi} \right) \right. \\ & \quad \left. + \frac{1}{\sqrt{\pi} \exp(\varphi^2)} - \frac{1}{\sqrt{\pi} \exp \left[ \left( \varphi + \frac{Biot_{Env}}{2 \varphi} \right)^2 \right]} \exp \left( Biot_{Env} + \frac{Biot_{Env}^2}{4 \varphi^2} \right) \right\} \\ & \quad - \frac{1}{N} \frac{Biot_i (T_P - T_F)}{2 \varphi (T_F - T_\infty)} \left( \frac{2 \varphi}{Biot_i \psi_L(s, \varphi)} f(Biot_i, \varphi) \right) \end{aligned} \quad (78d)$$

Where,  $f(Biot_i, \varphi)$  is given by the following derivation: For determining the temperature at the liquid region  $s^+$ ,

$$-k_L \frac{\partial T}{\partial x} \Big|_{x=s^+} = -h_i(T_L(x = s^+, t) - T_F) \tag{79}$$

and, by expressing these equations in terms of dimensionless numbers, by writing,  $N = \frac{k_S}{k_L}$ ,  $Ste = \frac{c_P(T_F - T_\infty)}{L}$ ,  $\Theta_0 = \frac{(T_P - T_F)}{(T_F - T_\infty)}$ ,  $Biot_{Env} = \frac{h_i s}{k_S}$ ,  $Biot_i = \frac{h_i s}{k_L}$ , and from Eq. (29f),  $\Omega^* = \frac{Biot_{Env}}{\varphi Ste}$ , which provides

$$\frac{h_i s}{2\varphi} [T_L(x = s^+, t) - T_F] = \frac{s}{2\varphi} k_L \frac{\partial T}{\partial x} \Big|_{x=s^+} = \frac{s}{2\varphi} k_L \frac{(T_P - T_F)}{\psi_L(s, \varphi)} \left\{ \frac{h_i}{k_L} \exp\left(\frac{h_i s}{k_L} + n^2 \frac{h_i^2 s^2}{4 \varphi^2 k_L^2}\right) \operatorname{erfc}\left(n\varphi + n \frac{h_i s}{2\varphi k_L}\right) + \frac{2n\varphi}{\sqrt{\pi} s \exp(n^2 \varphi^2)} - \frac{2n\varphi}{\sqrt{\pi} s \exp\left[\left(n\varphi + n \frac{h_i s}{2\varphi k_L}\right)^2\right]} \exp\left(\frac{h_i s}{k_L} + n^2 \frac{h_i^2 s^2}{4 \varphi^2 k_L^2}\right) \right\} \tag{80a}$$

$$\frac{h_i s}{k_L 2\varphi} [T_L(x = s^+, t) - T_F] = \frac{(T_P - T_F)}{\psi_L(s, \varphi)} \left\{ \frac{h_i s}{2\varphi k_L} \exp\left(\frac{h_i s}{k_L} + n^2 \frac{h_i^2 s^2}{4 \varphi^2 k_L^2}\right) \operatorname{erfc}\left(n\varphi + n \frac{h_i s}{2\varphi k_L}\right) + \frac{n}{\sqrt{\pi} \exp(n^2 \varphi^2)} - \frac{n}{\sqrt{\pi} \exp\left[\left(n\varphi + n \frac{h_i s}{2\varphi k_L}\right)^2\right]} \exp\left(\frac{h_i s}{k_L} + n^2 \frac{h_i^2 s^2}{4 \varphi^2 k_L^2}\right) \right\} \tag{80b}$$

$$\frac{Biot_i}{2\varphi} [T_L(x = s^+, t) - T_F] = \frac{(T_P - T_F)}{\psi_L(s, \varphi)} \left\{ \frac{Biot_i}{2\varphi} \exp\left(Biot_i + n^2 \frac{Biot_i^2}{4 \varphi^2}\right) \operatorname{erfc}\left(n\varphi + n \frac{Biot_i}{2\varphi}\right) + \frac{n}{\sqrt{\pi} \exp(n^2 \varphi^2)} - \frac{n}{\sqrt{\pi} \exp\left[\left(n\varphi + n \frac{Biot_i}{2\varphi}\right)^2\right]} \exp\left(Biot_i + n^2 \frac{Biot_i^2}{4 \varphi^2}\right) \right\} \tag{80c}$$

$$f(Biot_i, \varphi) = \left\{ \frac{Biot_i}{2\varphi} \exp\left(Biot_i + n^2 \frac{Biot_i^2}{4 \varphi^2}\right) \operatorname{erfc}\left(n\varphi + n \frac{Biot_i}{2\varphi}\right) + \frac{n}{\sqrt{\pi} \exp(n^2 \varphi^2)} - \frac{n}{\sqrt{\pi} \exp\left[\left(n\varphi + n \frac{Biot_i}{2\varphi}\right)^2\right]} \exp\left(Biot_i + n^2 \frac{Biot_i^2}{4 \varphi^2}\right) \right\} \tag{80d}$$

$$T_L(x = s^+, t) = T_F$$

$$+ \frac{(T_P - T_F)}{\psi_L(s, \varphi)} \frac{2\varphi}{Biot_i} \left\{ \frac{Biot_i}{2\varphi} \exp\left(Biot_i + n^2 \frac{Biot_i^2}{4 \varphi^2}\right) \operatorname{erfc}\left(n\varphi + n \frac{Biot_i}{2\varphi}\right) + \frac{n}{\sqrt{\pi} \exp(n^2 \varphi^2)} - \frac{n}{\sqrt{\pi} \exp\left[\left(n\varphi + n \frac{Biot_i}{2\varphi}\right)^2\right]} \exp\left(Biot_i + n^2 \frac{Biot_i^2}{4 \varphi^2}\right) \right\} \tag{80e}$$

$$\frac{Biot_i}{2\varphi} [T_L(x = s^+, t) - T_F] = \frac{(T_P - T_F)}{\psi_L(s, \varphi)} f(Biot_i, \varphi) \tag{81}$$

gives,

$$T_L(x = s^+, t) = T_F + \frac{2\varphi (T_P - T_F)}{Biot_i \psi_L(s, \varphi)} f(Biot_i, \varphi) \tag{82}$$

Substituting the thermal gradient of the solid phase  $k_S \frac{\partial T}{\partial x} \Big|_{x=s^-}$  and temperature profile  $T_L(x = s^+, t)$  derived in Eq. (80e) into the moving boundary interface,

$$\begin{aligned} & \frac{1}{Ste} \left( \varphi - \frac{Biot_{Env}}{\varphi} \right) \\ &= \frac{1}{\psi(s, \varphi)} \left\{ \frac{Biot_{Env}}{2\varphi} \exp \left( Biot_{Env} + \frac{Biot_{Env}^2}{4\varphi^2} \right) \operatorname{erfc} \left( \varphi + \frac{Biot_{Env}}{2\varphi} \right) \right. \\ &+ \frac{1}{\sqrt{\pi} \exp(\varphi^2)} - \frac{1}{\sqrt{\pi} \exp \left[ \left( \varphi + \frac{Biot_{Env}}{2\varphi} \right)^2 \right]} \exp \left( Biot_{Env} + \frac{Biot_{Env}^2}{4\varphi^2} \right) \left. \right\} \\ &- \frac{1}{N} \frac{(T_P - T_F)}{(T_F - T_\infty)} \left( \frac{1}{\psi_L(s, \varphi)} \left\{ \frac{Biot_i}{2\varphi} \exp \left( Biot_i + n^2 \frac{Biot_i^2}{4\varphi^2} \right) \operatorname{erfc} (n\varphi \right. \right. \\ &+ n \frac{Biot_i}{2\varphi} \left. \left. \right) + \frac{n}{\sqrt{\pi} \exp(n^2\varphi^2)} \right. \\ &\left. \left. - \frac{n}{\sqrt{\pi} \exp \left[ \left( n\varphi + n \frac{Biot_i}{2\varphi} \right)^2 \right]} \exp \left( Biot_i + n^2 \frac{Biot_i^2}{4\varphi^2} \right) \right\} \right) \end{aligned} \tag{83}$$

An evaluation of the present solution, could be determination of heat transfer coefficients., i.e.,  $h_i$  and  $h$ , respectively. The liquid interface temperature for a set of interface and environment thermophysical data can be found in Table 1.

Table 1 = Thermophysical properties of pure Al

Property	Symbol	Unit	Value
Thermal conductivity of the solid	$k_S$	$W.m^{-1} K^{-1}$	213.0
Thermal conductivity of the liquid	$k_L$	$W.m^{-1} K^{-1}$	91.0
Specific heat of the solid	$c_{PS}$	$J.kg^{-1} K^{-1}$	1181.0
Specific heat of the liquid	$c_{PL}$	$J.kg^{-1} K^{-1}$	1086.0
Density of the solid	$\rho_S$	$kg.m^{-3}$	2550.0
Density of the liquid	$\rho_L$	$kg.m^{-3}$	2368.0
Thermal diffusivity of the solid	$\alpha_S$	$m^2.s^{-1}$	$7.073 \times 10^{-5}$
Thermal diffusivity of the liquid	$\alpha_L$	$m^2.s^{-1}$	$3.539 \times 10^{-5}$
Latent heat	$L$	$J.kg^{-1}$	397500.0
Parameter	$n$	-	1.41377
Parameter N	$N$	-	2.34066
Fusion temperature	$T_F$	$K$	933.15
Pouring temperature	$T_P$	$K$	970.48
Environment Temperature	$T_\infty$	$K$	298.15
Environment heat transfer	$h$	$W.m^{-2} K^{-1}$	400
Interface heat transfer coefficient 1	$h_{i,1}$	$W.m^{-2} K^{-1}$	1800
Interface heat transfer coefficient 2	$h_{i,2}$	$W.m^{-2} K^{-1}$	1600
Interface heat transfer coefficient 3	$h_{i,3}$	$W.m^{-2} K^{-1}$	1400
Interface heat transfer coefficient 4	$h_{i,4}$	$W.m^{-2} K^{-1}$	800
Interface heat transfer coefficient 5	$h_{i,5}$	$W.m^{-2} K^{-1}$	500

The results for liquid domain solid-liquid interface temperature calculations are provided in Table 2. As can be observed the interface temperature  $T_L(x=s^-)$  increases as interface heat transfer coefficients  $h_{i,j}$  decreases.

Table 2 – Calculation of liquid-domain temperature at the solid-liquid interface.

Interface heat transfer coefficient, $h_i$	Temperature at $x = s^-$ , $T_L(x = s^-, t)$
$h_{i,1}$	949.18 K
$h_{i,2}$	950.74 K
$h_{i,3}$	952.57 K
$h_{i,4}$	960.31 K
$h_{i,5}$	963.69 K

## 6. Conclusions

- The results obtained with both the classical and the new transi-ent solidification analytical solutions for the set of pure metals studied lead to the following conclusions:
- Both models predict virtually identical interface velocities for all of the investigated materials.
- The agreement seen for the velocity does not extend to the thermal gradient and the cooling rate values. The new model treats the Biot number rigorously, based on fundamental mathematical and physical principles that explicitly account for the convective nature of the problem; consequently it yields steeper and more accurate gradients and cooling rates.
- Classical literature solutions for the similarity variable usually assume a pure quadratic temperature profile and rely on a single function the error function  $\text{erf}(x)$  for the solid phase. In contrast, the present solution contains both a quadratic and a linear component in the similarity variable. The solid phase solution therefore employs the complementary error function  $\text{erfc}(x)$  and the exponential of the complementary error function,  $\exp(x) \text{erfc}(x)$ , which enables it to capture the steep gradients and high cooling rates observed experimentally.
- The core formulation of the new model incorporates convective boundary conditions by using first and second order Biot numbers within the solidified layer. Adding convection to the classical solidification solution for a prescribed temperature, on the other hand, is essentially a mathematical artifice a useful approximation that does not fully satisfy the convective boundary condition.
- Overall, the new analytical framework provides a more physically consistent description of transient solidification under convective heat transfer than the classical approach.

## Declarations

### Competing interests:

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Authors' contributions:

Conceptualization, I.L. Ferreira; methodology, I.L. Ferreira;

software, I.L. Ferreira, and G.E.M Santos Júnior; validation, G.E.M. dos Santos Júnior, A.B.S. Silva, D.A.R. Carmo, M. O. Silva and F.S. Rocha; formal analysis, I.L. Ferreira; investigation, I.L. Ferreira, and G.E.M. Santos Júnior; resources, I.L. Ferreira; data curation, A.B.S. Silva, D.A.R. Carmo, M. O. Silva, and F.S. Rocha; writing original draft preparation, I.L. Ferreira; writing review and editing, and I.L. Ferreira; visualization, G.E.M. Santos Júnior, F.S. Rocha, and I.L. Ferreira; supervision, I.L. Ferreira; project administration, I.L. Ferreira; funding acquisition, I.L. Ferreira. All authors have read and agreed to the published version of the manuscript.

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### Availability of data and materials:

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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