Multi-mode heat transfer analysis during freezing of an encapsulated storage medium

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Abstract

Simultaneous conduction, convection and thermal radiation have been analyzed during the freezing of a non-opaque, non-gray phase change material (PCM) encapsulated in a closed spherical container and heated at relatively high temperatures ($250 \leq T \leq 325^\circ\text{C}$). In contrast to the well-known conduction-dominated model of the single phase Stefan problem, in the present study the influence of the participating thermal radiation and the buoyancy induced natural convection within the melt layer is highlighted and analyzed. A two-dimensional, axisymmetric, transient model has been solved numerically. The discrete ordinate method was used to solve the equation of radiative transfer and the finite volume scheme was used to solve the equations for mass, momentum and energy conservation. The effect of additional parameters like the shell size and the external heat transfer coefficient imposed on the outer shell surface as a boundary condition have also been analyzed. It was found that the contribution of thermal radiation on the solidification process of NaNO_3 is to reduce the solidification time by 17% as compared with the limiting case where thermal radiation is neglected.

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1. Introduction

Assessment of the fundamental thermal energy transport mechanisms during phase change in materials at relatively high operating temperatures has recently gained considerable attention in the solar energy research community because the urgent need to explore and develop advanced energy storage systems [1, 2, 3] based on latent heat storage in solar thermal power plants. Special attention has been devoted to the melting and freezing of thermal storage media confined in spherical or cylindrical containers to be used in packed bed and shell and tube heat exchangers respectively [4, 5]. The ability to quantify and appropriately predict, from a theoretical perspective, the energy contributions from conduction, convection and thermal radiation and their influence on the melting and freezing is necessary to evaluate the thermal performance and obtain accurate thermal designs of the aforementioned systems [6, 7, 8, 9].

An extensive literature review of the reported solutions of the PCM solidification problem reveals that the most commonly analyzed model assumes that the medium is initially at the phase change temperature. Therefore, no heat transfer is allowed across the liquid phase, and the heat only flows in the solid portion. This simplified model is known as the single phase Stefan problem. Closed-form, semi-analytical solutions of the aforementioned problem has been presented by [10, 11, 12, 13, 14, 15, 16, 17] based on the similarity variable approach, asymptotic theory and parameter-perturbation methods. Tao [18] reported a numerical solution of the single phase Stefan problem. The formulation in which the presence of temperature gradients across the liquid phase is considered has been termed the two phase Stefan problem and has been experimentally and numerically analyzed, during freezing in vertical tubes, by Sparrow and Broadbent [19] and Sparrow and Ohkubo [20] respectively. The studies conclude that initial superheating of the liquid moderately diminishes the frozen mass and the associated latent energy extraction at small times, but has a small effect on these quantities at large times. Also, good agreement was found between the numerical predictions and the experimental results.

An extension of the single phase Stefan problem has been presented by McCue et al. [21]. In the model, the initial temperature of the system was above the phase change temperature. However, only heat

conduction was taken into account through the liquid phase. The study concludes that for small Stefan number conditions, the temperature within the inner liquid phase rapidly decreases to the phase change temperature. Consequently, heat conduction within the liquid does not affect the solidification process. Ismail and Henriquez [22] performed a parametric analysis on the single phase Stefan problem for water confined in a spherical shell. They discussed the influence of the capsule size, shell material, shell thickness and outer surface boundary condition on the PCM solidification rate. The study concludes that an increase of the Biot number at the external surface of the shell decreases the solidification time. Although the domain geometry and the boundary conditions are the same in the present analysis and the study reported in [22], the present analysis expands the previous one by including the contributions of thermal radiation and natural convection within the PCM on the net energy transport. These contributions were included in the equation of energy conservation and present a more realistic physical description of the problem.

Freezing experiments of n-hexadecane encapsulated in spherical shells have been reported by Chan and Tan [23]. The evolution of the solidification phase via visualization front is presented for different outer surface and initial temperatures. The study concludes that the solidification phase front progresses concentrically inwards from the colder outer surface of the sphere. Regin et al. [24] presented a numerical analysis on the solidification process of paraffin wax within a horizontal cylindrical capsule externally heated by a convection boundary condition.

The influence of the PCM volume reduction during the solidification in a partially filled spherical shell has been studied by Assis et al. [25]. In the model, the domain was initially partially filled with liquid paraffin wax, with air in the remaining volume. Numerical results and experimental observations show that an upper void space is created inside the capsule due to the PCM volume reduction during the solidification process. The study also concludes that natural convection heat transfer in the liquid phase is negligible for Stefan numbers below 1. Diffusion-controlled freezing of a micro encapsulated PCM has been analyzed by Yang and Zhao [26]. The influence of thermal radiation on the single phase Stefan problem for non-opaque media have been largely limited to planar systems [27, 28, 29, 30, 31, 32] while

the problem in spherical media has received little attention; especially when all the fundamental heat transfer modes are simultaneously present.

The objective of the present work is to examine the influence of simultaneous conduction, convection and thermal radiation on the freezing dynamics of a non-opaque media, with spectral dependence on its optical properties, encapsulated in a closed spherical shell at relatively high temperatures, in order to estimate the induced error in the solutions where participating thermal radiation within the PCM has been omitted. To accomplish that, a two-dimensional, axisymmetric, transient model has been solved numerically. The primary motivation of this investigation is to provide additional information about the key elements in any phase change problem, i.e., solid-liquid interface position and phase distribution at a given time after the application of a thermal driving force. Particularly under operating thermal conditions related to thermal energy storage for concentrating solar power plants.

2. Heat transfer analysis

The considered system is schematically shown in a cross sectional view in Figure 1. It consists of an opaque, gray and a diffuse spherical shell of inner radius R_i and wall thickness δ . Initially the shell inner volume is completely filled with liquid PCM at temperature T_o , which is higher than the storage material melting temperature T_m . At time $t > 0$, the outer boundary surface, whose emissivity was set to unity, is subjected to a convective boundary condition characterized by a heat transfer coefficient h_∞ and a free stream temperature T_∞ , which is lower than T_m . The PCM is treated as a semitransparent, non-gray, medium being emitting and absorbing. Uniform and equal index of refraction of each phase has been assumed. The scattering of thermal radiation has been neglected in this study because of the lack of the PCM property data.

Multiple physical assumptions have been considered in the mathematical model and attention will now be turned to discuss their applicability. Experimental observations on the freezing of a low temperature PCM [23] and the natural convection heat transfer to a fluid contained in spherical containers [33] suggest that both the phase change process and the buoyancy induced fluid motion can be modeled

as axisymmetric. It was also reported by Chow and Akins [33] that for Rayleigh numbers below 10^7 , laminar flow was found to exist. In the present study the range of the examined Rayleigh numbers was $7.92 \times 10^4 \leq Ra \leq 2.0 \times 10^7$. Therefore the process has been modeled as axisymmetric and laminar flow has been assumed for the fluid motion within the liquid phase. In order to account for the natural convection, temperature dependent density within the liquid phase has been defined only in the body force terms of the momentum equations based on the Boussinesq approximation.

The PCM is assumed to be a continuous, homogeneous and isotropic substance and its thermo-physical properties have been taken from [34]. The melting of $NaNO_3$ takes place in the interval between 306.3°C and 306.8°C and the wall thickness used in all the study cases was 1 mm. The equations that characterized the previously described problem consist of continuity, momentum and energy. For a two-dimensional, viscous Newtonian flow with no viscous dissipation in a polar and radial coordinate system, the governing equations may be written as:

$$\frac{\partial \rho}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (\rho v_r r^2) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (\rho v_\theta \sin \theta) = 0 \quad (1)$$

$$\rho \left(\frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_r}{\partial \theta} - \frac{v_\theta^2}{r} \right) = -\frac{\partial P}{\partial r} + \eta \left[\nabla^2 v_r - \frac{2v_r}{r^2} - \frac{2}{r^2 \sin \theta} \frac{\partial (v_\theta \sin \theta)}{\partial \theta} - \frac{2v_\theta \cot \theta}{r^2} \right] - \rho g_r \beta (T - T_m) \quad (2)$$

$$\rho \left(\frac{\partial v_\theta}{\partial t} + v_r \frac{\partial v_\theta}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{v_r v_\theta}{r} \right) = -\frac{1}{r} \frac{\partial P}{\partial \theta} + \eta \left[\nabla^2 v_\theta + \frac{2}{r^2} \frac{\partial v_r}{\partial \theta} - \frac{v_\theta}{r^2 \sin^2 \theta} \right] - \rho g_\theta \beta (T - T_m) \quad (3)$$

$$\frac{\partial h}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 v_r h) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (v_\theta \sin \theta h) = \alpha \nabla^2 h - \frac{1}{\rho c_p} \left(\frac{\partial \lambda}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 v_r \lambda) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (v_\theta \sin \theta \lambda) \right) - \nabla \cdot q_r \quad (4)$$

The last term on the right-hand side of the energy equation accounts for the thermal radiation contribution, and it is coupled with the radiation intensity via the equation of radiative transfer (RTE). For diffuse radiation and isotropic scattering in a spherically symmetric medium the RTE [35] can be written as:

$$\frac{\mu}{r^2} \frac{\partial [r^2 I(r, \mu)]}{\partial r} + \frac{1}{r} \frac{\partial [(1 - \mu^2) I(r, \mu)]}{\partial \mu} + \kappa_a I(r, \mu) = \kappa_a I_b(T) \quad (5)$$

where $I(r, \mu)$ is the radiation intensity, which is a function of the position and direction, μ is the cosine of the angle between the direction Ω of the beam and the extension of the radius vector r , $I_b(T)$ is the intensity of a black body radiation at the temperature of the medium. In the discrete ordinate method, the RTE is approximated by discretizing the entire incident solid angle using a finite number of ordinate directions [36, 37, 38, 39]. Therefore, the equation [5] is written for each ordinate and reduces to a discrete system of differential equations, sufficient to solve for radiation intensity (I_i) at every location within the medium. The set of the equation results in:

$$\frac{\mu_i}{r^2} \frac{\partial [r^2 I_i]}{\partial r} + \frac{1}{r} \frac{\partial [(1 - \mu^2) I]_{\mu=\mu_i}}{\partial \mu} + \kappa_a I_i = \kappa_a I_b \quad (6)$$

where the subscript i denotes the ordinate directions. Once the radiation intensity is known, the local radiative heat flux (q_r) can be determined based on the following expression:

$$q_r = 2\pi \int_{-1}^1 I(r, \mu) \mu d\mu = 2\pi \sum_{i=1}^n \mu_i w_i I_i \quad (7)$$

The control volume technique, which employs an implicit scheme based on the SIMPLE (Semi-Implicit Method for Pressure-Linked Equations) algorithm [40], has been used to solve the governing equations. The computational domain has been discretized based on a structured grid consisting of 5580 quadrilateral cells with refined mesh distribution in the vicinity of the inner wall of the shell. Commercially available software Ansys/Fluent v12 was employed for the calculations. The details of the employed numerical procedure have been described in reference [41].

Two different properties have been selected to evaluate the effect of the mesh grid size on the solution of the model. The mass average solid fraction and the dimensionless temperature (Θ_n) of a node located at the horizontal axis of the domain have been plotted as a function of the dimensionless time (as seen in Figure 2) for different grid densities on the study case with $R_i = 15\text{mm}$, $T_o - T_m = 20^\circ\text{C}$, and $T_m - T_\infty = 20.5^\circ\text{C}$. It may be seen from Figure 2 that for the given conditions, additional refining of the grid from 1400 to 10400 elements has no influence on the freezing rate. No significant difference is observed in the solidification dynamics with the freezing time approximately to 28.33 minutes. The same trend is observed in the dimensionless temperature response during the liquid phase sensible cooling and phase transition process $0 \leq t \leq 13.1\text{min}$. However, some minor differences are observed at the beginning of the solid phase sensible cooling process with slightly faster temperature response

with the increase of the element size. A grid distribution with 5580 elements, where the minimum and maximum element sizes are $0.29 \times 0.15 \text{ mm}$ and $0.15 \times 0.55 \text{ mm}$ (width x height) respectively, was found sufficient to achieve independence of the solution.

The time step (t_{sp}) used in the present study was 0.008sec and it was selected based on the results of the time step independent analysis reported by the authors at [34] for a similar problem. In the range of $0.002 \leq t_{sp} \leq 0.009 \text{ s}$, It was concluded that the solution is independent of the time step. The proposed numerical model has been validated against the semi-analytical solution of the single phase Stefan problem, in the absence of thermal radiation, reported by Hill and Kucera [16]. A comparison is provided in Figure 3 which illustrates the variation of the dimensionless solid/liquid interface with respect to the dimensionless time for parametric values of the Stefan and Biot number equal to 0.5 and 1 respectively. Reasonably good agreement is observed between the numerical and the analytical results. However, as it was mentioned in the introduction section, the proposed model also incorporates the participating thermal radiation within the PCM during the phase change process, which is missing in the simplified Stefan problem where the heat of fusion is assumed to be removed by conduction only. Therefore a second validation test has been performed in order to verify the thermal response of the one dimensional transient solidification problem of a semitransparent planar medium in the presence of simultaneous conduction and thermal radiation. Figure 4 shows the solid fraction distribution along the characteristic length of the slab for different dimensionless time (ξ). The figure also includes a comparison between the results reported by Parida et al. [42] and the predictions obtained from our simulation of the same problem. The general trends for both simulations are the formation of a mushy zone that extends into the slab early in the process and the propagation of the solid phase into the slab as the freezing proceeds. Reasonably good agreement is observed.

3. Results and discussion

The parameters analyzed during the course of this investigation are the melt degree of superheat ($T_o - T_m$), the external heat transfer coefficient that characterizes the outer shell wall boundary condition, the size of the shell and the participating thermal radiation within the PCM. These parameters have been selected based on a practical point of view of the possible use of NaNO_3 for storage of thermal energy in concentrating solar power plants. Eight different study cases have been defined to identify the

aforementioned parameters and are presented in table 1. Under the present conditions, the liquid phase degree of superheat will activate the natural convection energy transport and consequently affect the freezing dynamic of the PCM, at least during the early periods of the process, as reported by Sparrow and Broadbent [19] for the solidification in vertical cylinders. Four superheating conditions were considered, 1, 5, 10 and 20°C above the PCM melting temperature respectively. Study cases 1-3 and 5 represent this effect. As it was mentioned before, a uniform convective thermal boundary condition was imposed at the outer wall of the capsule in order to represent the discharging process in a packed bed system.

The Biot number ($Bi = h_{\infty}R_i/\kappa_{sol}$) has been used to characterize this effect where three different heat transfer coefficients (h_{∞}) have been evaluated and their influence on the thermal behavior of the system was analyzed. Study cases 4-6 describe this effect. Three different shell sizes have been analyzed in this study with inner radius of 15, 25 and 35mm respectively. These conditions are represented by study cases 6-8. In order to account for the participating thermal radiation, the PCM has been modeled as a semitransparent, non-gray medium in all the study cases presented in table 1. A seven-band model, based on the experimental results reported by Ramdas [43] has been used to account for the spectral dependence of the PCM optical properties. A limiting case in which the PCM has been treated as a non-attenuating and non-emitting medium with shell inner surface emissivity equal to zero has been also included in the analysis, in order to provide a reference condition in which the thermal radiation does not play any role. The shell size and thermal conditions of the limiting case have been selected to be exactly the same as the used in the study case 5. Further, in this section a discussion about the relevant radiant properties is also included.

Predictions of the evolution of the solidification process at various time instants are presented in Figure 5. Each plot is composed of two separate halves divided by the symmetry line of the domain which is used as the ordinate in the defined radial and axial (Z) coordinate system. Isotherms are presented in the left half while the streamline contours and solid fraction distribution are shown in the right half.

As the cooling process begins, a buoyancy-induced force drives the molten PCM located at the central core of the capsule upward. The ascending fluid transfers its heat to the adjacent cooler fluid near

the inside wall. It is cooled down and descends nearby the inner shell wall. Hence an unsteady, clockwise circulating flow is formed in the melt layer which is characterized by the closed streamline maps observed on the right side of Figures 5a and 5b. This recirculation pattern delivers relatively hot liquid to the upper region of the capsule, where its presence retards the cooling process.

During this short time scale (relative to the period to complete the PCM freezing), the hot fluid continuously arrives into this region, impinges on the inner wall and displaces the cooler fluid down. Inspection of the temperature contours of Figures 5a and 5b reveals a stratified temperature field with the highest temperature in the upper zone. During its travel along the inner wall, the displaced fluid is being cooled by the outer wall and descends toward the lower portion of the capsule where the temperature drops below the melting point and therefore inward solidification begins. A closer view of the right hand side of Figures 5a and 5b illustrates the formation of the first PCM solid layer at the bottom of the shell. During this time scale the buoyancy induced flow pattern in the melt layer is characterized by a thin layer of liquid PCM flowing downward and a large core of fluid moving upward. The thickness of the down-flow fell in the range of 12 to 18.7% of the inner radius of the shell at early times. These findings are in agreement with the experimental observations of the natural convection flow inside spherical enclosures reported by Chow and Akins [33].

In order to complete the analysis of the physical events that characterize the early periods of freezing ($0 \leq t \leq 150s$) where natural convection is believed to be the dominant energy transport mechanism, the temperature profile at the horizontal radius is presented in Figure 6 for different times. Sharp temperature gradients are developed in the fluid adjacent to the inner wall while uniform temperature is observed across the thickness of the PCM liquid layer. This trend is associated with the formation of the thermal boundary layer near the inner shell wall. Similar results were reported by Sparrow et al. [44] for the melting problem in vertical cylinders.

Inspection of the left hand side of Figure 5c shows that the temperature gradient within the melt layer that was responsible for the natural convection motion is no longer in evidence, therefore, a significant reduction of the streamline contour intensity is also observed as compared with the previous

time instant. Another important observation of Figure 5c is that the temperature within the melt layer is slightly above the phase change temperature, meaning that during the first 240s of the process the temperature has dropped approximately 20°C. With the absence of the hot flow at the top of the shell the inward solidification proceeds and solid PCM is observed in the vicinity of all the inner shell.

Figures 5d to 5i illustrate the freezing dynamics of the PCM with almost concentric ring shape for the isotherms as well as the solid/liquid interface. The absence of the temperature gradients within the melt layer is the reason why the streamlines contours are not included in figures 5d to 5i.

To place these findings in perspective, the events that occur during the presented freezing process can be divided into two different time scales. A short time scale $0 \leq t \leq 150s$ in which natural convection plays a first order role, but rapidly terminated because of the sharp decrease of the liquid core temperature. On the other hand, a second and larger time scale (relative to the period to complete the PCM freezing) that shows solid-phase isotherms close to the solution of the Laplace equation, where it is assumed that the leading energy transport mechanisms are conduction and radiation. In that context the simultaneous interaction between the conductive and the radiative transfer provides a more effective mechanism to transport the liberated latent heat of fusion from the solid/liquid interface to the outer shell wall.

It has been previously reported [45] that the presence of thermal radiation significantly improves the heating or cooling rates as compared with the pure conduction systems. Based on that, a spectral absorption coefficient has been defined for both solid and liquid PCM phases in order to account for the participating thermal radiation that may occur during the freezing process. Figure 7 shows the experimental measurements of the near infrared transmittance of $NaNO_3$, reported by Ramdas [43] and the approximate seven band model that was used during the calculation process. For each band, a uniform absorption coefficient has been estimated while the contribution of scattering to the extinction of thermal radiation has been neglected.

Even though in this study, emphasis has been placed on Sodium Nitrate as a PCM, no further difficulties are anticipated to analyze other PCMs in the presented model. For instance, the influence of thermal radiation on the melting of NaCl with enhanced radiative properties was reported by [46].

Recent experimental contributions on the radiative properties of high-temperature eutectic systems reported by Myers et al. [47] can be utilized to extend and compare the results reported in this investigation. The predicted variation of the solid fraction with time for the limiting case and the study case 5 is presented in Figure 8. It may be seen that faster solidification is achieved when thermal radiation is considered. The solidification time decreases 17% when thermal radiation is included in the model. A closer look of the solid fraction curves reveals that during the early times, the solid fraction is equal to zero, indicating the existence of the pure natural convection motions within the liquid PCM.

As the freezing initiates, a small difference is observed between the curves with study case 5 predicting a slightly faster solidification. As the solid layer increases in size, the contribution of thermal radiation becomes more significant in the presence of conduction, resulting in a more pronounced difference. In the absence of radiation heat transfer, the rate of heat transfer decreases as the solid layer thickness increases, since conduction is the only mode of heat transfer through the solid PCM. However, the presence of radiation allows the heat transfer from the inner liquid core to the shell walls through the solid layer attenuated only by the absorption and scattering by the solid PCM layer. Consequently, radiant heat transfer increases the cooling rate from the liquid core to the outer surface of the shell, resulting in a faster freezing process.

The predicted energy transfer interactions at the inner shell wall are also included in Figure 8 and are displayed in broken lines. In order to appropriately correlate the heat transfer data, two different dimensionless parameters have been defined, the Nusselt number (Nu) which is estimated based on the conductive and the convective heat fluxes (q_{cd} and q_{cv}) and the dimensionless radiative flux (Ψ) which has been calculated based on the radiation heat flux (q_r). It should be noticed that the limiting case is only characterized by the Nusselt number because of the absence of thermal radiation while the case 5 accounts for all the energy transport modes. Both curves are multiplied by the Stefan number in order to

accommodate them in the solid fraction plot. A sharp decrease is initially observed in the heat transfer curves during the pure natural convection period. A change in slope in both of the curves is found to be coincident with the starting of the freezing process as may be seen from the solid fraction curves. As expected the contribution of thermal radiation enhances the energy interaction at the inner shell wall.

In order to provide a quantitative notion of the velocity magnitudes and the flow patterns developed in the melt layer during the early periods of the process, the axial velocity distribution along the horizontal radius of the capsule at different times is presented in Figure 9. The flow structure can be described as follows. A thin layer of fluid flows downward in the vicinity of the inner shell wall, where the maximum velocity is attained, and an upward flow characterizes the fluid in the center of the capsule. As the driving temperature difference within the melt layer decreases with time (see Fig. 6) the natural convection flow loses its strength and consequently the downward and inward velocities also decrease. A closer view of Figure 9 reveals that the thickness of both flows increases as the process proceeds. At 180s, the velocity magnitude was found to be significantly smaller as compared to the values at 60s.

The effects of the initial superheating temperature on the solid fraction and the dimensionless energy transfer at the inner shell wall are presented in Figure 10. It may be seen from the bottom of the solid fraction curves that the larger the degree of superheating the longer to start the freezing. Even though, the liquid superheat clearly affects the freezing dynamics early in the process. Once the energy transfer from the liquid phase to the solid/liquid interface has ceased, the remaining energy transport mechanisms are radiation and conduction within the solid phase which essentially remain unchanged under the analyzed thermal conditions of cases 1-3 and 5. This fact could be responsible for the small differences observed in all of the curves at the latest stages of the process.

The influence of the external heat transfer coefficient on the solid fraction rate is depicted in Figure 11. The heat transfer coefficient values of 45.4, 226.7 and 453.5 W/m^2K have been evaluated which correspond to Biot numbers equal to 1, 5 and 10 respectively. As expected a reduction in the solidification time was found with the increase of the Biot number. However the time reduction was more pronounced in the case where $Bi=1$ as compared with the study cases where the Biot number was 5 and

10. No attempt to analyze the influence of the free stream temperature on the thermal dynamics of the process has been made in this investigation. The reason is because the trend that characterizes the sub-cooling degree is fully expected and has been previously discussed.

The effect of the shell size on the solidification rate is presented in Figure 12. Three different shell sizes have been analyzed with inner radius varying from 15 to 35mm. It may be observed that the smaller the capsule the faster the solidification. As shown in Figure 13, the predicted solid fraction for all the study cases, except for the study case 4, has been plotted as a function of a dimensionless group ($FoSte_L^a Gr_R^b Bi^c$) that takes into consideration the controlling parameters analyzed in this investigation. The following equation is proposed to be used to correlate the solid fraction of the analyzed cases:

$$SF = 1.017 \operatorname{erf} [0.1 (FoSte_L^a Gr_R^b Bi^c)^{1.04}] \quad (8)$$

It was found that, for the exponents $a=-0.18$, $b=0.13$, $c=0.31$, all the data merged together in a single line. A small deviation from the proposed correlation is observed in the early stages of the process in study cases 5, 6 and 7 and it is related to the wide range considered for the Biot number, which controls the cooling rate at the beginning of the freezing. The proposed correlation seems valid in the following range of the controlling parameters:

$$\begin{aligned} 0.0096 &\leq Ste_L \leq 0.195 \\ 8.77 \times 10^3 &\leq Gr_R \leq 2.42 \times 10^6 \\ 5 &\leq Bi \leq 23.34 \\ Pr &\cong 9.0 \end{aligned}$$

4. Summary and conclusions

The numerical solution of the solidification problem of a semitransparent, non-gray PCM confined in a spherical shell has been presented. In contrast to the well-known conduction-dominated model of the single phase Stefan problem, the present study has taken into consideration the energy contributions due to simultaneous convection, radiation and conduction during the solidification at relatively high temperature. The discrete ordinate method was used to solve the equation of radiative transfer, and the finite volume scheme was used to solve the equations for mass, momentum and energy

conservation. Based on the numerical analysis of the governing equations, the results may be summarized as:

- In the presence of all the fundamental heat transfer mechanisms, it was found that the contribution of thermal radiation on the solidification process of NaNO_3 is to reduce the solidification time by 17% as compared with the limiting case where thermal radiation has been neglected.
- During the early periods of the process, an increase of the initial liquid-phase superheating degree was found to accelerate the freezing. Once the natural convection which is induced by the temperature differences within the liquid phase is terminated, the remaining energy transport mechanisms take control of the process until the final stages, attenuating in this way, the initial effect of the natural convection. It was also shown that the presence of natural convection induces the initial formation of an asymmetrical solid PCM layer from the bottom of the capsule. It is believed that this factor is responsible for the slight variation in the solid layer thickness along the shell symmetry line, with the smallest layer thickness at the top and the greatest layer thickness at the bottom.
- It was shown that as the Biot number decreases from 5 to 1, the freezing time increases from 28.5 to 57.8min. However, a significantly smaller difference in the freezing times was observed when the Biot number decreases from 10 to 5.
- For a fixed thermal boundary condition, the solidification time decreases 60.92% and 21.23% as R_i decreases from 35mm to 15 and 25mm respectively.
- An expression was obtained for the solid fraction as a function of the controlling parameters of the process. This can be readily used to estimate the PCM phase distribution at a given time when solving problems of latent heat thermal energy storage contained in a packed bed heat exchanger.

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Nomenclature

c_p	specific heat at constant pressure (J/kg K)
$ Fo$	Fourier number $(\kappa/\rho c_p)(t/R_i^2)$
g	gravitational acceleration (m/s ²)
Gr_R	Grashof number $(g\beta\Delta TR_i^3\rho^2/\eta^2)$
h_∞	external heat transfer coefficient (W/m ² K)
h	sensible enthalpy (J/kg)
L	Latent heat of fusion (J/kg)
Nu	Nusselt number $(q_{cd} + q_{cv})R_i/\kappa(T_m - T_\infty)$

P	pressure (Pa)
Pr	Prandtl number of the fluid ($\eta c_p/k$)
q_{cd}	conductive heat flux at the inner shell wall (W/m^2)
q_{cv}	convective heat flux at the inner shell wall (W/m^2)
q_r	radiative heat flux at the inner shell wall (W/m^2)
R_i	inner radius of the capsule (m)
Ra	Rayleigh number (GrPr)
Ste_L	liquid phase Stefan number ($c_{pL}(T_o - T_m)/L$)
Ste_s	solid phase Stefan number ($c_{pS}(T_m - T_\infty)/L$)
t	time (s)
T	temperature ($^{\circ}C$)
T_∞	free stream temperature ($^{\circ}C$)
ϑ	velocity (m/s)

Greek Symbols

α	Thermal diffusivity (m^2/s)
β	thermal expansion coefficient ($1/K$)
δ	shell wall thickness (m)
η	dynamic viscosity ($kg/m\ s$)
κ	thermal conductivity ($W/m\ K$)
κ_a	absorption coefficient (m^{-1})
λ	latent heat (J/kg)
ρ	density (kg/m^3)
σ	Stefan-Boltzmann constant, $\sigma = 5.67 \times 10^{-8} W/m^2 K^4$

Subscripts

m	melting
o	initial
r	radial direction
s	solid
w	wall
θ	angular direction
Ψ	dimensionless radiative flux at the inner shell wall $q_r/\sigma(T_m^4 - T_\infty^4)$

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Figure 1. Schematic representation of the physical domain.

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Figure 2 Influence of the grid size on the solidification rate and node temperature.

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Figure 3 Evolution of the solid/liquid interface during single phase Stefan problem.

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Figure 4 Solid fraction distribution along the slab.

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Figure 5 Predicted evolution of the solidification process for case5.

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Figure 6 Temperature distribution along the shell horizontal radius.

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Figure 7 Spectral transmittance of Sodium Nitrate.

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Figure 8 Influence of radiative energy transfer on the thermal dynamics of the process.

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Figure 9 Velocity distribution along the horizontal radius of the shell for study case 5.

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Figure 10 Influence of the liquid superheating on the thermal dynamics of the process.

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Figure 11 Influence of the Biot number on the solid fraction rate.

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Figure 12 Influence of the shell size on the solid fraction rate.

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Figure 13 Solid fraction as a function of the controlling parameters.

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Table 1 Geometrical and thermal parameters.

<i>case</i>	$R_i(m)$	$T_o - T_m(^{\circ}C)$	Gr_R	Bi	Ste_{Liq}
1	0.015	1	8.77×10^3	5	0.0096
2	0.015	5	4.46×10^4	5	0.048
3	0.015	10	9.09×10^4	5	0.096
4	0.015	20	1.90×10^5	1	0.195
5	0.015	20	1.90×10^5	5	0.195
6	0.015	20	1.90×10^5	10	0.195
7	0.025	20	8.81×10^5	16.67	0.195
8	0.035	20	2.42×10^6	23.34	0.195

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427 **Figure captions.**

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