



# ANALYSIS OF HEAT TRANSFER DURING SOLIDIFICATION OF PHASE CHANGE MATERIALS USING BIOT'S VARIATIONAL METHOD

V. Sarath Chandra Varma

Department of Mechanical Engineering  
ANITS, Visakhapatnam, Andhra Pradesh,  
India

V. V. Narayana Reddy

Department of Mechanical Engineering  
ANITS, Visakhapatnam, Andhra Pradesh,  
India

D. Srinivasa Rao

Department of Mechanical Engineering  
ANITS, Visakhapatnam, Andhra Pradesh,  
India

M. Rama Krishna

Department of Mechanical Engineering  
ANITS, Visakhapatnam, Andhra Pradesh,  
India

**ABSTRACT - Thermal energy recovered during solidification of a Phase Change Materials (PCM) can be used in variety of applications specially in providing heated water to power plants, air conditioning systems, and process heat utility systems and in many thermal storage devices integrated with solar systems. In practise, when a PCM is brought to the temperature sufficiently lower than its solidification temperature it begins to solidify and releases thermal energy. During solidification, several PCM exhibit change in their densities that possibly has significant effect upon the design parameters of thermal energy storage devices, which cannot be ignored.**

The present work enables an analytical investigation of the thermal energy gain in the form of latent heat during solidification of PCM due to uniform temperature heat rejection. The governing energy equations with associated initial and boundary conditions have been developed and solved using Biot's Complimentary Variational method. The closed-form solutions that include the parameters like modified Stephen number, phase-change parameters and ratio of densities of PCM in two phases (solid and liquid), have been obtained. It is observed that PCM having smaller value of modified Stephen number release large amount of thermal energy. The change in density of PCM changes the phase-

change depth but appears not to alter the release of thermal energy.

*Keywords:* Biot's Variational method, Phase Change materials, Latent heat, Modified Stefan number, Density ratio, Lagrangian equation.

## I. INTRODUCTION

The thermal energy storage due to solidification of phase change materials (PCM) is one of the important ways to store thermal energy. The phase change materials are solidified at a uniform temperature heat rejection that leads to release of thermal energy. In this process, the devices store the energy directly in the energy form. The thermal energy recovered from the phase change materials during solidification process can be used in variety of applications, such as in providing feed water to power plants, air conditioning systems, process heat utility system [1,2,3,6,9] and in many thermal storage devices related to solar systems [5,10]. For analysis of recovery of this thermal energy from PCM, it is necessary to have the knowledge of temperature distribution, location and movement of phase change boundary surface, mode of heat transfer and desired thermo-physical properties of the phase change materials. The phase change material releases thermal energy, when temperature of the material is sufficiently lower than its

solidification temperature and then it starts solidifying.

In solidification process, the change in density of phase change materials may have significant effect upon the design parameters of the thermal energy storage devices and hence it cannot be ignored. Therefore the design plays an important role in latent heat storage system for improving the heat transfer. In such type of problem, due to the presence of a moving phase change boundary surface, the heat transfer problem becomes non-linear in a mathematical model and due to this, its exact solution is not possible to obtain unless a semi-analytical method is used which often becomes capable of providing a closed-form solution [2]. For such type of problems, Biot's Complementary Variation method [7] is applied to solve several phase change problems and for some of them the closed forms of solutions have been reported [1-3]. This method is one of the approximate methods that has been applied to solve phase change problems.

Based on the study of previous research papers, it is observed that various researchers have worked for thermal energy storage in the form of sensible heat, latent heat, thermo-chemical heat and their combinations. The latent heat thermal storage system is based on some of the vital properties like melting temperature, latent heat of fusion, conductivity and density of PCM. But it is found that no significant work has been done for the situation involving density variation during solidification of PCM by Biot's variation method in which density ratio  $\rho_{12}$  is less than or greater than 1.

## II. MATHEMATICAL MODELING

Considering a Phase Change Material in a cylindrical container having an initial temperature  $T_i$  which is greater than its freezing temperature  $T_f$ . The PCM starts to solidify and at any instant the temperature of the outer surface of the cylinder is reduced to  $T_o$ . This surface is kept at this temperature  $t > 0$  which results in heat rejection from the surface and solidification starts at the surface ( $r = 0$ ), such that the interface between solid and liquid phase moves in a radially inward direction. The diagrammatical representation of such a one-dimensional solidification problem is shown in Fig-1.

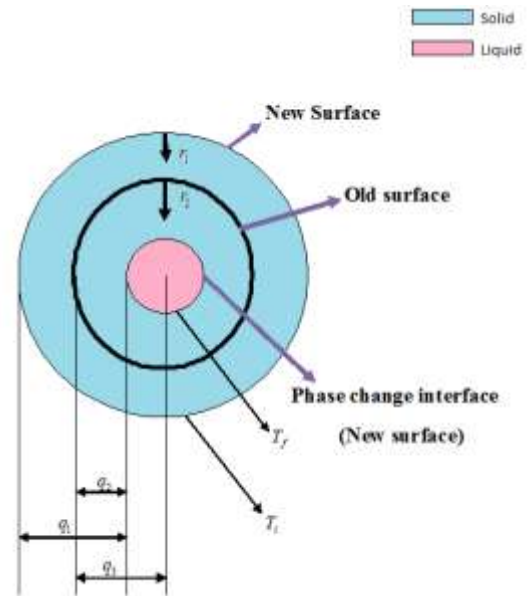


Figure-1: Front view of cylinder with PCM.

## III. GOVERNING EQUATIONS & BOUNDARY CONDITIONS

The governing equations of one-dimensional heat conduction in cylindrical coordinates in the solidified region (new phase) are given as

$$\frac{1}{r_1} \cdot \frac{\partial}{\partial r_1} \left( r_1 \frac{\partial T_1}{\partial r_1} \right) = \frac{1}{\alpha_1} \cdot \frac{\partial T_1}{\partial \tau} \quad (1)$$

for  $0 \leq r_1 \leq q_1$ , at  $t > 0$

Boundary conditions:-

$$\text{At } t = 0, T_1 = T_i, q_1 = 0$$

$$\text{At } t > 0, T_1 = T_o, r_1 = 0$$

$$K_1 \frac{\partial T_1}{\partial r_1} = j, T_1 = T_s, r_1 = 0, t > 0$$

Similarly, the governing equation of one-dimensional heat conduction in the liquid region (old phase) is given as

$$\frac{1}{r_2} \cdot \frac{\partial}{\partial r_2} \left( r_2 \frac{\partial T_2}{\partial r_2} \right) = \frac{1}{\alpha_2} \cdot \frac{\partial T_2}{\partial \tau} \quad (2)$$

for  $q_2 \leq r_2 \leq q_3$ , at  $t > 0$

Boundary conditions:-

$$\text{At } t = 0, T_2 = T_f, q_2 = 0$$

$$\text{At } t > 0, T_2 = T_i, r_2 = q_3$$

$$\text{At } t > 0, r_2 = q_3, \frac{\partial T_2}{\partial r_2} = 0$$

In order to apply Biot's variational method, the energy balance and mass balance equations can be given as.



$$H_{1_{r_1=q_1}} = H_{2_{r_2=q_2}} - \rho_1 L q_1 \quad (3)$$

$$\rho_1 q_1 = \rho_2 q_2 \quad (4)$$

#### IV. SOLUTION USING BIOT'S VARIATIONAL METHOD

Assuming a linear temperature profile for solid region and parabolic profile for liquid region because in general case the temperature distribution in solid is linear and in liquid is parabolic as given in equations (5) and (6) respectively in order to apply Biot's Variational method. The choice of such profiles is realistic since in the earlier studies [1-3], these profiles have provided appropriate results.

$$\theta_1 = T_1 - T_f = (T_s - T_f) \left(1 - \frac{r_1}{q_1}\right) \quad (5)$$

$$\theta_2 = T_2 - T_i = (T_f - T_i) \left(1 - \frac{r_2 - q_2}{q_3 - q_2}\right)^2 \quad (6)$$

The related boundary conditions are

$$\text{At } r_1 = 0, T_1 = T_s$$

$$\text{At } r_1 = q_1, T_1 = T_f$$

$$\text{At } r_2 = q_2, T_2 = T_f$$

$$\text{At } r_2 = q_3, T_2 = T_i$$

The conservation of the energy representing equations (1), (2) and (3) yields equation (7).

$$\text{Div}(H) = -C\theta$$

By combining the equations (3), (5) and (7) the heat flow equation in the solidified region becomes

$$H_1 = \frac{1}{2} C_1 q_1 (T_s - T_f) \left(1 - \frac{r_1}{q_1}\right)^2 + \frac{1}{3} C_2 (T_f - T_i) (q_3 - q_2) - \rho_1 L q_1 \quad (8)$$

The thermal potential, dissipative function and the thermal force of the solidified region is given by equation (9), (10) and (11) respectively

$$V_1 = \frac{1}{2} C_1 \iiint_{\tau} \theta_1^2 \cdot d\tau \quad (9)$$

$$D_1 = \frac{1}{2K_1} \iiint_{\tau} \dot{H}_1^2 d\tau \quad (10)$$

$$Q_{11} = \iint \theta_1 \frac{\partial H_1}{\partial q_1} dA \quad \text{at } r_1 = 0 \quad (11)$$

Lagrangian equation for the solidified region can be given as

$$\frac{\partial V_1}{\partial q_1} + \frac{\partial D_1}{\partial \dot{q}_1} = Q_{11} \quad (12)$$

By combining the equations (9), (10), (11) and (12) the non dimensional Lagrangian equation for solidified region is obtained as given below

$$m \left[ \frac{1}{12} (St^*)^2 + \frac{1}{4} St^* + 1 \right] + St^* \left[ \frac{1}{30} St^* + \frac{1}{24} \right] \frac{m^2 \dot{\varphi}}{\varphi} - m (\dot{\eta} - l) \left[ \frac{1}{12 C_{12}} St + \frac{1}{6 C_{12} \varphi} \right] St^* = St^* \left[ \frac{1}{4} St^* + 1 \right] \quad (13)$$

Similarly, the non dimensional Lagrangian equation for liquid region is obtained as

$$\alpha_{12} (\eta - l) \left[ \eta (63 \dot{\eta} + 5 \dot{l}) + l (20 \dot{\eta} - 95 \dot{l}) \right] = 375 \eta + 1848 l \quad (14)$$

#### V. DETERMINATION OF PHASE CHANGE DEPTH AND TEMPERATURE PENETRATION DEPTHS DURING PHASE CHANGE FOR UNIFORM TEMPERATURE (ISOTHERMAL) CONDITION. (7)

For isothermal condition the temperature  $T_s$  at the free surface ( $r = 0$ ) remains constant and is not a function of time. Consequently,  $\dot{T}_s = 0$  i.e.  $\dot{\varphi} = 0$  and  $\varphi$  becomes unknown. Using continuity equation, if there is no change in volume.

$$\rho_{12} = \frac{l}{m} \quad (15)$$

$$\rho_{12} = \frac{\dot{l}}{\dot{m}} \quad (16)$$



Introducing a parameter  $\beta$  such that  $\eta = \beta l$  and  $\dot{\eta} = \beta \dot{l}$  into equation (13) in order to get the equation in terms of  $\beta$ .

$$\beta = 6C_{12}\rho_{12}\varphi \left( l \dot{l} \right)^{-1} \left( \frac{1 - St^*}{\frac{St^*}{4} + 1} \right)^{-1} - 6C_{12}\varphi \left[ \frac{\frac{1}{12}(St^*)^2 + \frac{1}{4}St^* + 1}{St^* \left( \frac{St^*}{4} + 1 \right)} \right] \left( \rho_{12} \left( \frac{1 - St^*}{\frac{St^*}{4} + 1} \right) \right)^{-1} - 1$$

Combination of equations (14) and (17)

leads to a third order equation with  $l \dot{l}$  as variable to get  $l$ . We get the dimensionless phase change depth with the change in density and temperature penetration depth from equations (18) and (19).

$$m = \frac{l}{\rho_{12}} \quad (18)$$

$$\eta = \beta l \quad (19)$$

#### Time rate of heat flow

The rate of heat flow during phase change is obtained by differentiating the equation (8) resulting the equation in non-dimensional form.

$$\dot{Q} = -\frac{\dot{m}}{St} \left( \frac{St^*}{2} + 1 \right) + \frac{\dot{\eta} - \dot{l}}{3C_{12}} \quad (20)$$

Integrating equation (20) to get the time rate of heat flow.

$$Q_\tau = m \left[ \varphi \left( \frac{1}{2} + \frac{1}{St^*} \right) + \frac{\rho_{12}}{C_{12}} (\beta - 1) \right] \quad (21)$$

## VI. RESULTS & DISCUSSIONS

The various parameters like phase change depth ( $l$  and  $m$ ) with and without density variation respectively, temperature penetration depth ( $\eta$ ) and time rate of heat flow ( $Q_\tau$ ) were calculated with respect to different parameters for water-ice phase change combination by using a suitable MATLAB code for the obtained above equations.

a) Variation of  $l, m$  and  $\eta$  with  $\tau$ : The variations of phase change depths  $l$  and  $m$

due to freezing and the temperature penetration depth  $\eta$  with non dimensional time  $\tau$  for different values of  $\rho_{12}$  and fixed values of parameters  $St^*$  and  $\varphi$  are shown in Figure-2.

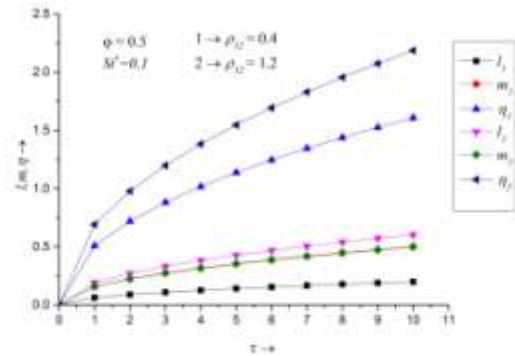


Figure-2: Variation of  $l, m$  and  $\eta$  with  $\tau$ .

b) Variation of  $l, m$  and  $\eta$  with  $\rho_{12}$ : The effect of density variation ( $\rho_{12}$ ) on  $l, m, \eta$  at  $\tau = 4$ , for  $\varphi = 0.5$  and  $St^* = 0.1$  are given in Figure-3.

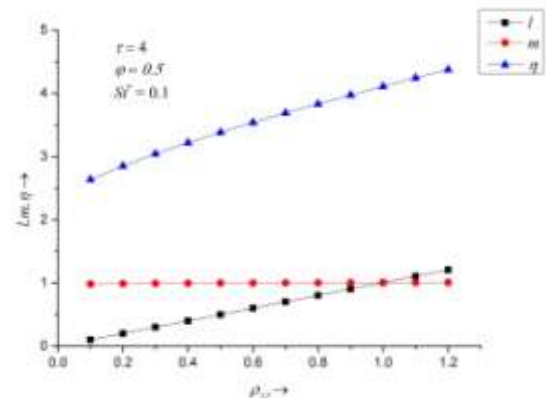


Figure-3: Variation of  $l, m$  and  $\eta$  with  $\rho_{12}$ .

From figure-3 it is found that penetration depth without density variation ( $m$ ) is greater than penetration depth with density variation ( $l$ ) for  $\rho_{12} < 1$ , higher for  $\rho_{12} > 1$  and equal for  $\rho_{12} = 1$ . This appears due to the fact that phase change interface moves in radial direction, when  $\rho_{12} < 1$ , as a result the solidified portion expands on freezing as in case of water. It is noted that temperature penetration depth ( $\eta$ ) has the highest value among  $l$  and  $m$  at all  $\rho_{12}$ . It is observed that  $l$  and  $\eta$  are constant for different values of  $\varphi$  but its value is



increasing with increase in  $\rho_{12}$  at particular  $\varphi$  and it is observed that  $m$  are constant for different values of  $\varphi$  and  $\rho_{12}$ .

c) Variation of  $l, m$  and  $\eta$  with  $St^*$ : The effect of variation in  $St^*$  on  $l, m, \eta$  at  $\tau = 1$  and  $\tau = 3$  for,  $\varphi = 0.5, \rho_{12} = 0.9$  are given in Figure -4.

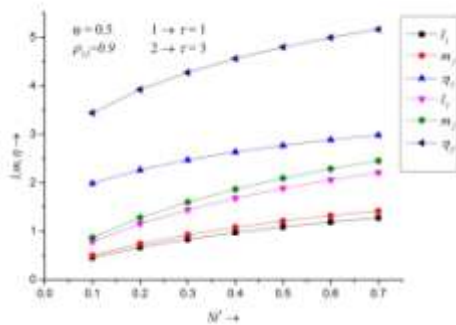


Figure-4: Variation of  $l, m$  and  $\eta$  with  $St^*$ .

It is found from Figure-4 that  $l, m$  and  $\eta$  decrease with decrease in  $St^*$ . Such predictions appear to be realistic because the PCM of smaller  $St^*$  has larger heat of fusion and for the same heat release a smaller phase change depth with a smaller penetration depth is required.

d) Variation of  $l, m$  and  $\eta$  with  $\varphi$ : The effect of variation in  $\varphi$  on  $l, m, \eta$  at  $\rho_{12} = 0.4$  and  $\rho_{12} = 1.2$  for  $\tau = 1$  and  $St^* = 0.1$  are shown in Figure- 5.

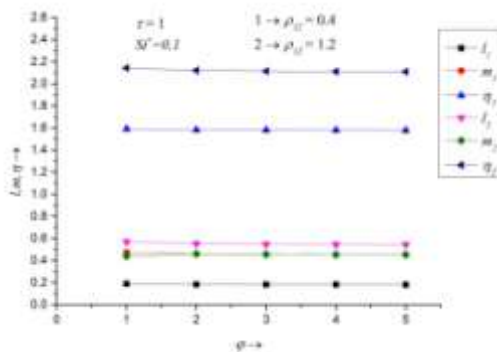


Figure-5: Variation of  $l, m$  and  $\eta$  with  $\varphi$

It is found that  $l, m$  are less than  $\eta$  for all density ratios. The trend of the plot reveals that

$l, m$  and  $\eta$  are almost constant with the variation of  $\varphi$  but with the increase in density ratio,  $l$  and  $\eta$  values are increased whereas  $m$  remains unchanged.

e) Variation of  $Q_\tau$  with  $St^*$ : The effect of variation in modified Stephen number ( $St^*$ ) on thermal energy ( $Q_\tau$ ) at  $\varphi = 0.5, \varphi = 1$  and  $\varphi = 1.5$  for  $\tau = 1$  and  $\rho_{12} = 0.9$  are given in Figure- 6. It is observed that  $Q_\tau$  decreases with  $St^*$  for different values of  $\varphi$ . The trend of plot reveals that a PCM releases larger amount of thermal energy at lower value of  $St^*$ . The rate of heat release is larger at  $\varphi = 1.5$  as compared to the value at  $\varphi = 0.5$  and  $\varphi = 1$ .

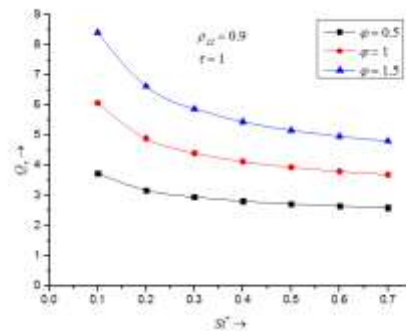


Figure-6: Variation of  $Q_\tau$  with  $St^*$ .

f) Variation of  $Q_\tau$  with  $\rho_{12}$ : The effect of variation in  $\rho_{12}$  on  $Q_\tau$  at  $\tau = 1, \tau = 3$  and  $\tau = 5$  for  $\varphi = 0.5$  and  $St^* = 0.1$  are given in Figure- 7.

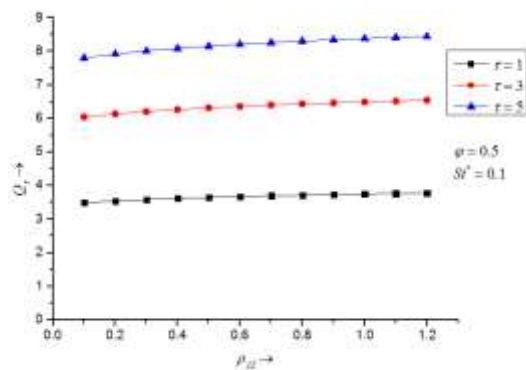


Figure-7: Variation of  $Q_\tau$  with  $\rho_{12}$ .

It is found that there is no considerable effect of change in density upon the heat released {Figure-7}.





g) Variation of  $Q_\tau$  with  $\tau$ : The effect of variation in  $\tau$  on  $Q_\tau$  at  $\rho_{12} = 0.4$ ,  $\rho_{12} = 0.9$  and  $\rho_{12} = 1.2$  for  $\phi = 0.5$  and  $St^* = 0.1$  are given in Figure- 8. It is found that  $Q_\tau$  is increasing at any  $\tau$  with increase in  $\rho_{12}$  which is realistic in general case.

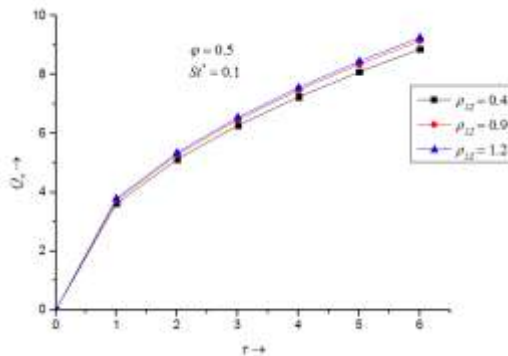


Figure-8: Variation of  $Q_\tau$  with  $\tau$ .

h) Variation of  $Q_\tau$  with  $\phi$ : The variation of  $Q_\tau$  with change in  $\phi$  at  $\rho_{12} = 0.4$ ,  $\rho_{12} = 0.9$  and  $\rho_{12} = 1.2$  for  $\tau = 1$  and  $St^* = 0.1$  are given in Figure- 9. The trend of plot reveals that  $Q_\tau$  is increasing with increase in  $\phi$  but remains constant at any  $\phi$  for different  $\rho_{12}$  it seems that  $Q_\tau$  doesn't depend on density variation.

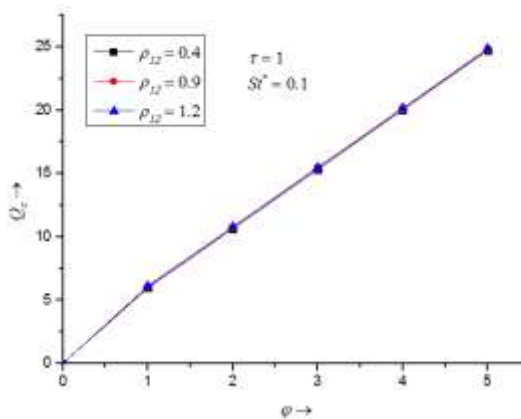


Figure-9: Variation of  $Q_\tau$  with  $\phi$ .

## VII. CONCLUSION

1. A closed form solution for the present nonlinear problem is obtained by the use of Biot's variational method.
2. At small values of  $St^*$  the larger amount of energy is gained from PCM.
3. The quantity of thermal energy released is increasing with increase in time.
4. The change in density changes the phase-change depth but does not alter the quantity of the thermal energy released.

## Nomenclature

$b$	Reference depth of the material, m
$t$	Time, s
$C$	Heat capacity of the material, $J/m^3K$
$C_{12} = \frac{C_1}{C_2}$	Ratios of heat capacities of solid and liquid
$K$	Thermal conductivity of the material, $W/mK$
$\rho$	Density of solid & liquid materials, $kg/m^3$
$\rho_{12} = \frac{\rho_1}{\rho_2}$	Ratio of densities of solid and liquid
$\alpha$	Thermal diffusivity of the materials, $m^2/s$
$\alpha_{12} = \frac{\alpha_1}{\alpha_2}$	Thermal diffusivity ratio of solid and liquid
$L$	Latent heat of solidification, $J/kg$
$T_o$	Surrounding temperature, $K$
$T_s$	Temperature at the heat rejection surface, $K$
$T_i$	Initial temperature of PCM inside cylinder, $K$
$T_f$	Freezing temperature of PCM, $K$
$H_1$	Heat flow in solidified region, $J/m^3K$
$\dot{Q} = \frac{\dot{H}_1 b}{K_1 (T_f - T_i)}$	Dimensionless rate of heat flow
$Q_\tau$	Total heat rejected, $J/m^2$



$j$	Heat flux, $W/m^2$
$St = \frac{c_1(T_f - T_i)}{\rho_1 L}$	Stefan number
$\varphi = \frac{T_s - T_f}{T_f - T_i}$	Dimensionless surface temperature
$St^* = -St\varphi$	Modified Stephan number
$\theta$	Temperature distribution, K
$\beta$	Dimensionless parameter
$m = \frac{q_1}{b}$	Dimensionless phase-change depth with the change in density
$l = \frac{q_2}{b}$	Dimensionless phase-change depth without change in density
$\eta = \frac{q_3}{b}$	Dimensionless temperature penetration depth
$\dot{q}_1 = \frac{\alpha_1}{b} \dot{m}$	Rate of change of penetration depth of solidified region, m/s
$\dot{q}_2 = \frac{\alpha_1}{b} \dot{l}$	Rate of change of penetration depth of solidified region from old surface, m/s
$\dot{q}_3 = \frac{\alpha_1}{b} \dot{\eta}$	Rate of change of penetration depth of liquid region from old surface, m/s
$\tau = \frac{\alpha_1 t}{b^2}$	Dimensionless time
$\dot{T}_s = (T_f - T_i)\varphi \frac{\alpha_1}{b^2}$	Rate of change of temperature at the heat rejection surface, K/s

VIII. REFERENCES

[1] Prasad, A., “Unidirectional Phase-Change Energy Storage with Uniform Temperature Heat Rejection,” J. Energy Heat Mass Transfer, Vol. 7(2), PP. 121-128, (1985).

[2] Prasad, A., “Latent heat of Fusion Energy Storage with Convective Heat Injection,” J. Energy Heat Mass Transfer, vol. 8(3), PP. 173-181, (1986).

[3] Kumar, A., Prasad, A., and Upadhaya, S.N., “Spherical Phase-Change Energy Storage with Constant Temperature Heat Rejection,” J. of Energy Resources Technology, Vol. 109, PP. 101-104, (1987).

[4] Lunardini, V.J., “Approximate Solution to Conduction Freezing with Density Variation,” J. Energy Resources Technology, Vol. 105, PP. 43-45, (1983).

[5] Abhat, A., “Low Temperature Latent Heat Thermal Energy Storage: Heat Storage Materials,” Solar Energy, Vol. 30(4), PP.313-332, (1983).

[6] Atul Sharma, V.V. Tyagi, C.R.Chen, D. Buddhi, “Review on Thermal Energy Storage with Phase-Change Materials and Applications,” J. of Renewable and Sustainable Energy Reviews 13, PP. 318-345, (2009)

[7] Biot, M.A., “Variation Principle in Heat Transfer, Clarendon Press, Oxford UK, (1970)”.

[8] Ozisik, M.N., “Heat Conduction, John Willey & Sons, Inc., New York, (1993)”.

[9] Demirbas, M.F., “Thermal Energy Storage and Phase Change Materials: An Overview,” J. of Researcher of Energy Technology, Trabzon, Turkey Part B, PP. 85-95, (2006).

[10] Velraj, r., and Seeniraj, R.V., “Latent Heat Thermal Storage for Solar Applications,” Proceedings of the 21<sup>st</sup> National Solar Energy Convection, Chennai, India, PP. 333-342 (1997).

[11] Belen Zalba, Jose M. Marin, Luisa F. Cabeza, Harald Mehling, “Review on Thermal Energy Storage with Phase Change: Materials, Heat Transfer Analysis and Applications,” J. of Applied Thermal Engineering 23, PP. 251-283, (2003).