SHORTER COMMUNICATIONS

SOLIDIFICATION OF LOW CONDUCTIVITY MATERIAL CONTAINING DISPERSED HIGH CONDUCTIVITY PARTICLES

ROBERT SIEGEL

Lewis Research Center, Cleveland, OH 44135, U.S.A.

NOMENCLATURE

c_p, specific heat;
h, convective heat-transfer coefficient;
k_p, thermal conductivity of particle material;
k_s, thermal conductivity of phase change material;
k, thermal conductivity of mixture;
L, latent heat;
L_s, latent heat of phase change material without particles;
l, length of tube or flat plate;
Q_T, energy removed from storage element up to time τ;
q, heat flux;
r, radial coordinate;
t, temperature;
t_s, solidification temperature of phase change material;
W, thickness of plane wall;
w, width of plane wall.

Greek symbols

δ, thickness of solidifying plane layer;
ε, volume fraction of particles in mixture;
ρ_s, density of phase change material without particles;
τ, time.

Subscripts

c, fluid receiving energy from storage;
i, inside;
o, outside;
p, particulate phase (except in c_p);
s, solidifying phase;
w, wall;
δ, at solidifying interface.

INTRODUCTION

THE HEAT of fusion of molten salts can be used for energy storage at elevated temperatures. During energy extraction the salt will begin to solidify at the surface through which energy is being removed, and as extraction continues, the heat will have to be conducted through the already solidified salt. This will severely limit the extraction rate because of the low thermal conductivity of the solidified salt. To obtain a satisfactory removal rate it might be required to increase the temperature drop from the molten salt to the working fluid extracting the energy. However, decreasing the working fluid temperature reduces the thermodynamic efficiency which is undesirable.

The heat extraction from storage could be improved by increasing the thermal conductivity of the solidified material. A proposed method investigated here is to disperse fine particles of a high conductivity material in the salt. This will produce two somewhat compensating effects. The conductivity of the mixture will be higher than that of the salt alone, which will aid the solidification rate. However, some of the volume is now occupied by particles that do not

melt so the heat of fusion per unit volume is diminished. For a given quantity of heat removal the solidified layer thickness is increased and the heat flow has to traverse a longer conduction path; this tends to retard the solidification rate. There will be an optimum particle concentration that will provide maximum heat extraction in a given time, and this concentration will depend on the particle heat conductivity relative to that of the solidified salt. In this note a simplified analysis is made to determine if the heat removal rate can be appreciably enhanced by the addition of particles. Three geometries of practical interest are considered; solidification on a flat plate, inside a tube, and outside a tube.

ANALYSIS

In a heat storage device the difference between the fusion and working fluid temperatures must not be large in order to prevent degradation of the high temperature energy. Hence any energy associated with subcooling the solid phase will be small compared with the heat of fusion. From [1], for freezing a single phase substance a reasonable approximation is to neglect the energy of subcooling if the ratio of the heat of fusion to the maximum subcooling energy, $L/(t_s - t_c)c_p$, is larger than 1.5. For the present analysis the L and c_p would be for a salt-particle mixture, and the criterion may be more difficult to achieve because the L is reduced by part of the volume now being occupied by particles that are assumed not to melt. However, for a practical system the particle concentration would be moderate so that the criterion would generally be met and the subcooling energy can be neglected here. The advantage of this assumption is that it greatly simplifies the analysis and will permit an easy and yet realistic assessment of the effect of particle addition.

Another assumption is that during the freezing and melting cycles, the particles will remain uniformly suspended in the phase change material. This will probably require certain particle sizes and combinations of materials since during freezing there is a tendency at the moving interface to exclude foreign particles from the solidifying material; also settling of the particles must be kept small.

Following the type of analysis in [2], the heat balances governing the rates of solidification for the three geometries in Fig. 1 are

$$L_s\rho_s(1-\varepsilon)\frac{\mathrm{d}\delta}{\mathrm{d}\tau} = \frac{t_s - t_c}{\frac{1}{h_c} + \frac{W}{k_w} + \frac{\delta}{k}} \tag{1a}$$

$$L_s\rho_s(1-\varepsilon)2\pi r_\delta\frac{(-\mathrm{d}r_\delta)}{\mathrm{d}\tau} = \frac{2\pi(t_s - t_c)}{\frac{1}{h_c r_o} + \frac{1}{k_w}\ln\left(\frac{r_o}{r_i}\right) + \frac{1}{k}\ln\left(\frac{r_i}{r_\delta}\right)} \tag{1b}$$

$$L_s\rho_s(1-\varepsilon)2\pi r_\delta\frac{\mathrm{d}r_\delta}{\mathrm{d}\tau} = \frac{2\pi(t_s - t_c)}{\frac{1}{h_c r_i} + \frac{1}{k_w}\ln\left(\frac{r_o}{r_i}\right) + \frac{1}{k}\ln\left(\frac{r_\delta}{r_o}\right)} \tag{1c}$$
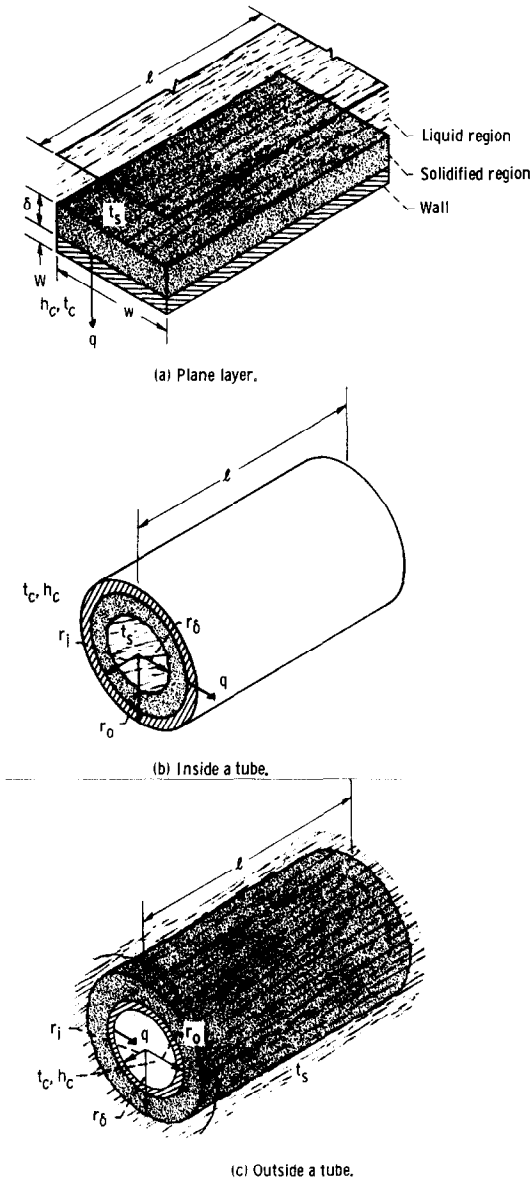
(a) Plane layer.

(b) Inside a tube.

(c) Outside a tube.

FIG. 1. Solidification during energy extraction.

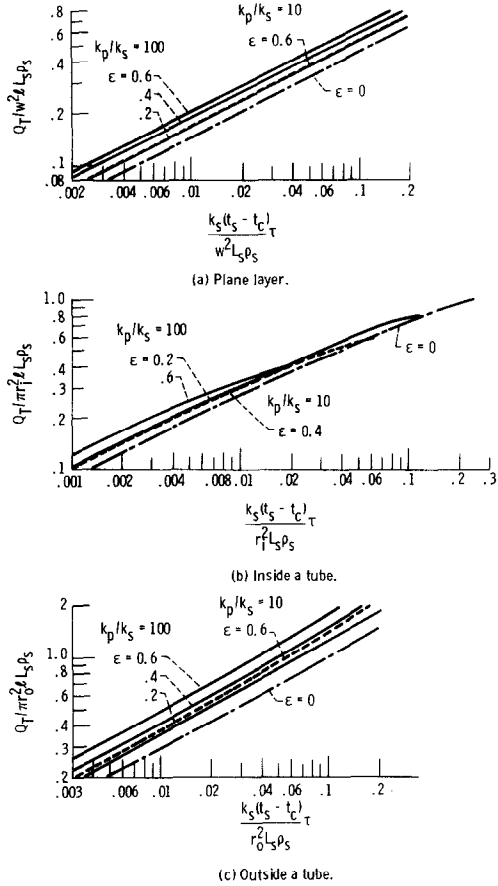(a) Plane layer.

(b) Inside a tube.

(c) Outside a tube.

FIG. 2. Total amount of energy removed from solidified region from zero time up to time τ.

The energy removed from storage from time 0 to τ is the heat of fusion in the solidified region which yields,

$$\frac{Q_T}{w^2 l L_s \rho_s} = (1 - \varepsilon) \frac{\delta}{w} \tag{3a}$$

$$\frac{Q_T}{\pi r_i^2 l L_s \rho_s} = (1 - \varepsilon)\left[1 - \left(\frac{r_\delta}{r_i}\right)^2 \right] \tag{3b}$$

$$\frac{Q_T}{\pi r_o^2 l L_s \rho_s} = (1 - \varepsilon)\left[\left(\frac{r_\delta}{r_o}\right)^2 - 1 \right] \tag{3c}$$

where the δ and r_δ as functions of time are obtained from equations (2). Equations (2) are the general solutions for the frozen layer growth, but they contain a number of parameters that will complicate discussing the results without aiding physical understanding. For simplicity the special case will be evaluated where the wall is thin and of high thermal conductivity, and the h_c is high enough to neglect the $1/h_c$ term; this is the same as imposing the condition that the cooled boundary is at t_c. Then equations (2) simplify to

$$\frac{\delta}{w} = \left\{ \frac{2(\bar{k}/k_s)}{1 - \varepsilon}\left[\frac{k_s(t_s - t_c)}{w^2 L_s \rho_s} \tau \right] \right\}^{1/2} \tag{4a}$$

$$-\left(\frac{r_\delta}{r_i}\right)^2 \ln\left(\frac{r_i}{r_\delta}\right) + \frac{1 - \left(\frac{r_\delta}{r_i}\right)^2}{2} = \frac{2(\bar{k}/k_s)}{1 - \varepsilon}\left[\frac{k_s(t_s - t_c)}{r_i^2 L_s \rho_s} \tau \right] \tag{4b}$$

$$\left(\frac{r_\delta}{r_o}\right)^2 \ln\left(\frac{r_\delta}{r_o}\right) - \frac{1}{2}\left[\left(\frac{r_\delta}{r_o}\right)^2 - 1 \right] = \frac{2(\bar{k}/k_s)}{1 - \varepsilon}\left[\frac{k_s(t_s - t_c)}{r_o^2 L_s \rho_s} \tau \right] \tag{4c}$$

where the term in brackets on the RHS is a dimensionless time.

where the molten phase change material is at temperature t_s. Using the initial condition of zero solidified thickness at $\tau = 0$, these equations are integrated to yield,

$$\frac{\delta}{w} = \left\{ \frac{2(\bar{k}/k_s)}{1 - \varepsilon}\left[\frac{k_s(t_s - t_c)}{w^2 L_s \rho_s} \tau \right] + \left(\frac{\bar{k}}{h_c w} + \frac{W\bar{k}}{w k_w} \right)^2 \right\}^{1/2}$$

$$- \left(\frac{\bar{k}}{h_c w} + \frac{W\bar{k}}{w k_w} \right) \tag{2a}$$

$$-\frac{r_\delta^2}{2} \ln\left(\frac{r_i}{r_\delta}\right) + \frac{(r_i^2 - r_\delta^2)}{4} + \bar{k}\left[\frac{1}{k_w} \ln\left(\frac{r_o}{r_i}\right) + \frac{1}{h_c r_o} \right] \frac{(r_i^2 - r_\delta^2)}{2}$$

$$= \frac{\bar{k}(t_s - t_c)}{L_s \rho_s (1 - \varepsilon)} \tau \tag{2b}$$

$$\frac{r_\delta^2}{2} \ln\left(\frac{r_\delta}{r_o}\right) - \frac{(r_\delta^2 - r_o^2)}{4} + \bar{k}\left[\frac{1}{k_w} \ln\left(\frac{r_o}{r_i}\right) + \frac{1}{h_c r_i} \right] \frac{(r_\delta^2 - r_o^2)}{2}$$

$$= \frac{\bar{k}(t_s - t_c)}{L_s \rho_s (1 - \varepsilon)} \tau. \tag{2c}$$

To evaluate equations (4) an expression is needed for $\bar{k}/k_s$. A simple expression for a dispersion of particles in a matrix is given in [3] as

$$\frac{\bar{k}}{k_s} = \frac{2 + \dfrac{k_p}{k_s} - 2\varepsilon\left(1 - \dfrac{k_p}{k_s}\right)}{2 + \dfrac{k_p}{k_s} + \varepsilon\left(1 - \dfrac{k_p}{k_s}\right)}. \qquad (5)$$

This is shown in [3] to agree well with experimental data for ε up to 0.6, and also goes to the limit $\bar{k} = k_p$ when $\varepsilon = 1$. The data were for combinations such as iron in lard and copper in water.

If equation (5) for $\bar{k}/k_s$ is substituted into equation (4a) and the result used to eliminate δ/w from equation (3a), the Q_T is then explicitly a function of ε. At any elapsed time τ, the ratio of Q_T with particles to that without is

$$\frac{Q_T(\varepsilon)}{Q_T(\varepsilon = 0)} = \left\{ \left[\frac{2 + \dfrac{k_p}{k_s} - 2\varepsilon\left(1 - \dfrac{k_p}{k_s}\right)}{2 + \dfrac{k_p}{k_s} + \varepsilon\left(1 - \dfrac{k_p}{k_s}\right)} \right] (1 - \varepsilon) \right\}^{1/2} . \qquad (6)$$

Values were specified for the ratio of particle to matrix conductivity k_p/k_s, and the volume concentration of particles, ε. Then equations (4) were evaluated for δ/w, r_δ/r_i and r_δ/r_o in terms of the dimensionless time and these quantities inserted into equations (3) to obtain the dimensionless heat withdrawal as a function of time. Results are shown in Fig. 2 for $k_p/k_s = 10$ and 100 for various ε values. The range of k_p/k_s was chosen because salt conductivities range from about 0.4 to 4 W/mK and the conductivities of various materials are: stainless steel, 15 W/mK; iron, 60 W/mK; aluminum, 204 W/mK; and copper, 386 W/mK.

DISCUSSION

Figure 2(a) shows the total heat removed from a solidifying plane layer from the onset of solidification up to the time given along the abscissa. From equations (4a) and (3a) the Q_T varies as $\tau^{1/2}$ and the lowest line in Fig. 2(a) is for $\varepsilon = 0$ (no particles). For a given τ the total heat removal is increased when particles are added. For example, if the thermal conductivity of the particles is 100 times that of the storage material, a particle concentration of 20 vol% increases the heat removal by about 17%; a concentration of 60% provides an increase of about 45%. From a practical viewpoint these increases may not be sufficiently helpful to justify the larger storage unit required to accommodate the volume occupied by the particles.

Equation (6) is plotted in Fig. 3 as a function of ε for $k_p/k_s = 10$ and 100. The curves show the existence of a maximum heat withdrawal as expected from the comments made in the Introduction. The maximum $Q_T(\varepsilon)$ is at an ε that is probably too large to be practical. At large ε the $\bar{k}$ in equation (5) may become somewhat inaccurate, as this
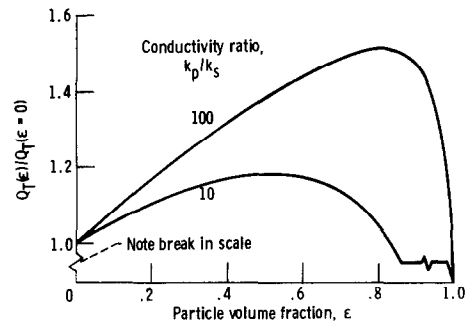

F IG. 3. Ratio of heat removal with particles to that without particles; plane layer geometry.

relation applies for completely dispersed particles while at large ε there can be appreciable particle contacts.

Figures 2(b) and (c) show the heat withdrawal for solidification inside or outside a tube and there is a pronounced geometric effect. The particles are much more effective for solidification outside a tube, as this geometry produces less increase in heat-conduction path length as a result of the volume occupied by the particles.

CONCLUSIONS

An analysis was made to determine how the solidification rate is influenced by the introduction of high conductivity particles into a solidifying low conductivity material. The particles increase the thermal conductivity of the solidified region so that heat can be more easily transported from the freezing front to the cooled surface. However, the particles also reduce the volume fraction occupied by phase change material so that for a given total heat removal the solidified region has a greater thickness and the energy must travel through a greater distance. This compensating effect yields a particle concentration that provides maximum heat removal; this particular concentration is usually too high to be practical. For reasonable concentrations such as 20% particles by volume, the heat removal rate for a plane geometry can be increased by 10–20% depending on the ratio of particle to matrix conductivity. Hence only moderate increases can be achieved by this technique. There is also a geometric effect; compared with a plane layer, the effect of the particles is less for solidification inside a tube, and somewhat greater for solidification outside a tube.

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