Mathematical model of solid-liquid phase transitions applied to thermal energy accumulators

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Abstract. The paper presents a mathematical model for the numerical calculation of the heat flow and the volumetric fraction of the liquid phase of phase change materials (PCM) in containers of thermal energy accumulators of spherical and cylindrical shape, used in air conditioning and ventilation systems. The comparison of the calculated and experimental values for n-octadecane showed good convergence of the results. When using in geometry optimization algorithms of containers and when choosing PCM, the model has an advantage due to the high speed of calculations on it.

1. Introduction

In modern cooling, air conditioning and ventilation systems, thermal energy accumulation is often used, this ensures reducing consumption of energy resources and peak consumption under variable loads [1–4]. An actively developing direction is the use of phase change materials (PCM) [5] using the latent heat of the phase transition for energy accumulation. The action mechanism of such substances consists in charging the accumulator during a liquid–solid phase transition and using the stored cold during a reverse solid–liquid phase transition [6].

Generally, thermal energy accumulators are containers where PCM with a circulating heat-transfer agent is located [5, 7–9]. The main difference in their design is the placement of PCM in the accumulator container. In one modification, PCM is placed in containers in the form of pipes of rectangular or circular cross-section, as well as in the form of balls. The heat carrier circulates in an accumulator container in the space between containers, as it is shown in Figure 1. In another design, PCM is placed in an accumulator container, and the heat carrier circulates inside the tubes of the heat exchanger placed in the tank.

Figure 1. The accumulator of cold in the spherical container: 1 – heat-transfer agent, 2 – container, 3 – liquid phase, 4 – solid phase, 5 – interphase boundary.
Air conditioning systems operate in different climatic conditions with variable loads, so it is very important to choose the optimal parameters of the containers and the substance for the technical design specification set. The choice can be made on the basis of numerical solutions of equations of mathematical models describing the processes in the container with PCM [10–14].

Such mathematical models are based on the solution of a system of equations for PCM [12] considered as an incompressible liquid. The system consists of equations:

continuity:

\[
\frac{\partial \rho}{\partial t} + \nabla (\rho v) = 0, \tag{1}
\]

momentum

\[
\frac{\partial (\rho v)}{\partial t} + \nabla (\rho v) = -\nabla P + \mu \nabla^2 v + \rho g \tag{2}
\]

and the energy equations written using the enthalpy approach

\[
\frac{\partial (\rho H)}{\partial t} + \nabla (\rho w H) = \nabla (k \nabla T) \tag{3}
\]

where \(v\) – the liquid velocity vector, \(\rho\) – the density, \(\mu\) – the dynamic viscosity, \(P\) – the pressure, \(g\) – the acceleration of gravity, \(k\) – the thermal conductivity, \(H\) – the enthalpy, \(T\) – the temperature, \(t\) – the time. The enthalpy is represented as the sum of the latent heat of phase transition and the enthalpy associated with the heat capacity of PCM.

The system (1) – (3) allows finding three-dimensional temperature field inside the container, however, it does not directly give such values as the charging-discharging time of the accumulator or the thermal flow absorbed by the container. And it is these values that are fundamental in optimizing the design. When solving the system, the approach described in [15] is also used. It considers the phase transition zone as a porous one of liquid and solid phases. Numerical solution of equations (1) – (3) is cost-based in terms of computational resources.

An alternative is considering models describing the motion of the phase transition boundary. They are based on the solution of the so-called the Stefan problem [5, 7]. It is formulated in the following way [16]. The phase transition is assumed to take place at a constant temperature \(T_m\) at the interface between solid and liquid phases (see Figure 1). The thermal conductivity equation for the solid phase is

\[
c_p \rho_s \frac{\partial T}{\partial t} = \text{div} \left( k_s \text{grad}(T) \right) + w_s \tag{4}
\]

where \(c\) – the specific heat capacity, \(w\) – the volumetric density of the power of heat sources. Index ‘s’ refers to the solid phase.

For the liquid phase, convective heat transfer is taken into account

\[
c_p \rho_f \left( \frac{\partial T}{\partial t} + v \text{grad}(T) \right) = \text{div} \left( k_i \text{grad}(T) \right) + w_i \tag{5}
\]

index ‘f’ refers to the liquid phase.

At the interface between the solid and liquid phases \(\partial \Omega_m\), the boundary conditions of Stephan are written. Namely, the temperature continuity condition

\[
T_l = T_s = T_m \tag{6}
\]

and condition for heat flow which is not continuous due to the release or absorption of the heat of phase transition \(L_m\) at the interface boundary

\[
k_s \frac{\partial T_s}{\partial n} - k_i \frac{\partial T_l}{\partial n} = L_m \nu_m \tag{7}
\]
where \( v_m \) – the movement velocity of the phase transition boundary in the direction of normal \( n \) to it.

The velocity of the moving boundary is considered as an unknown value.

Classical analytical solutions of the Stefan problem are obtained for one-dimensional linear cases of freezing, when there is no need to simulate the processes of convective heat transfer [16]. In [17], the assessment of convective heat exchange in the liquid phase is carried out by semi-empirical criterion equations substituted into the analytical solution. In this paper, a similar approach is applied, but a numerical solution is used allowing taking into account nonlinearities in the problem.

2. Mathematical model

The model being proposed considers the case of PCM melting in a long cylindrical or spherical container. In it, between the layer of PCM not yet melted and the container shell, there exists a layer of liquid substance where natural convection takes place. In experimental studies [11], it was shown that the process occurred asymmetrically along the vertical axis for a ball, but the shape of a solid PCM was close to a ball for a spherical container. In this case, we can consider a zero-dimensional model for melting the ball with calculating the integral heat flow through the layer by equations for ball or cylindrical layers.

In accordance with [18], the heat flow through the layer is calculated by the equations for conductive flow through the layer of the corresponding type with the replacement of thermal conductivity by the effective one being calculated by the equation

\[
k_{e} = \begin{cases} k_{i}, & \text{Pr} < 1000 \\ 0.18 \cdot \Pr^{0.25} \cdot \frac{Gr}{k_{i}}, & \text{Pr} \geq 1000 \end{cases}
\]  

(8)

where \( \text{Pr} \) is the Prandtl number for liquid PCM, \( \text{Gr} \) – Grashof’s criterion, calculated according to the equation

\[
\text{Gr} = b_{m} \cdot g (r_{c} - r_{m}(t)) \left( T_{c} - T_{m} \right) \frac{T_{c} - T_{m}}{\nu^{2}}
\]

(9)

\( b_{m} \) – the coefficient of volumetric expansion of PCM, \( r_{c} \) – the inner radius of the container, \( r_{m} \) – the radius at which the phase transition boundary is located, \( \nu \) – the kinematic viscosity of PCM, \( T_{c} \) – the temperature of the container.

The thermal resistances of a ball and cylindrical layer [16], respectively, also depend on the location of the phase transition boundary.

For a ball, the thermal resistance is

\[
R(t) = \frac{r_{c} - r_{m}(t)}{4\pi r_{m}(t) k_{e}}
\]

(10)

for a cylinder (per unit of length), the thermal resistance is:

\[
R(t) = \frac{1}{2\pi k_{e}} \ln \frac{r_{c}}{r_{m}(t)}
\]

(11)

Conditions (6) and (7) can be used to create an equation to calculate the location of the boundary as a function of time.

\[
v_{m} = \frac{dr_{m}(t)}{dt} = -\frac{T_{c} - T_{m}}{R(t)} \frac{1}{\rho_{l} \left[ L_{m} + c_{l} (T_{c} - T_{m}) A_{m}(t) \right]}
\]

(12)

where the surface area of the phase transition boundary (for a cylinder – per unit of length) is

\[
A_{m}(t) = \begin{cases} 4\pi r_{m}(t)^{2}, & \text{ball} \\ 2\pi r_{m}(t), & \text{cylinder} \end{cases}
\]

(13)
In equation (12), besides the layer resistance, the thermal resistance of the container shell and the resistance to the environment can be included in the thermal resistance $R(t)$ if there is specified not the shell temperature.

Nonlinear equation (12) is solved by numerical methods with respect to the position of the phase transition boundary with a given initial position of the boundary $r_m(0)$, usually $r_m(0) = r_c$. The heat flow being absorbed by the container with PCM is calculated by the equation 7.

3. Results and discussion
The numerical solution for equation (12), which has a high degree of nonlinearity, has been carried out in the Scilab environment with automatic switching between the non-rigid predictor-corrector Adams method and the method for solving rigid systems Backward Differentiation Formula (BDF) method in the course of solving this equation.

Using the presented model, comparison of the calculation results with experimental data is carried out in [19]. Namely, a spherical glass container with n-octodecane with an inner diameter of 101.66 mm and a thickness of 1.5 mm is considered. The temperature of the container outer surface is 40 °C, the melting point is 28.2 °C. At the initial moment of time, the container is completely filled with the substance in the solid state.

Comparison of calculation results with experimental data is shown in Figure 2. The calculation has been carried out for 7200 temporary nodes. One can see a very good agreement between the calculated and experimental data. The same data have been obtained when calculating in Fluent using the two-dimensional axisymmetric model described in [12]. However, the calculation time according to the two-dimensional model is more than 10,000 times longer than the calculation time for the developed zero-dimensional model on the same computer.

![Figure 2](image)

**Figure 2.** Dependence of the volumetric fraction of the liquid phase on time according to the results of calculations and experiments [19].

4. Conclusions
The model developed by the authors is based on the numerical solution of the Stefan problem of zero-dimensional spatial dimension. Reducing the dimension of the problem is achieved by including empirical formulas for convective heat exchange suitable for the case of a container with PCM in the model.

In contrast to the numerical one- two- and three-dimensional models, the model proposed immediately gives the integral characteristics necessary for optimizing air conditioning systems with cold accumulators, but with significantly lower computational resources – the volumetric fraction of the liquid phase and the heat flow to the container. This makes it very convenient for optimizing the sizes of containers and choosing the optimal PCM in the design tasks of new air-conditioning and
ventilation systems. On the example of PCM n-octodecane, the mathematical model proposed shows good agreement with the experimental data.

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