Chapter 2
Solidification of PCMs

2.1 Heat Storage Based on the Solidification Process

Heat storage is a subject of considerable importance in power engineering. The most common methods of heat storage exploit the thermal capacity, the latent heat, the heat of reaction and of photo chemical reaction and production of fuels. This work is concentrated on heat storage by exploiting the phenomenon of solidification as a special case of numerous phase changes occurring in reality.

The discussed heat storage and release system include a solidifying PCM (*phase-change material*), a reservoir and a heat-transporting medium. An example of heat storage and release is presented (Fig. 2.1). The PCM contained in a heat-isolated reservoir is successively subjected to melting when heat is stored and to solidification when it is released.

The agent acting as an intermediary in the storage or release of heat $\dot{Q}$ flows inside the channel or channels submerged in the material undergoing the phase change. The solidification process starts when PCM reaches the solidification temperature. In this phase very important for the process are thermophysical features of the material, its geometric shape, thermophysical features of the reservoir wall and the conditions of heat absorption. Equilibrium processes of solidification of different PCMs are presented (Fig. 2.2).

The process of solidification as it was discussed in Chap. 1 is the change of a liquid into a solid body with heat release at the same time. The phenomenon of equilibrium solidification of homogeneous bodies and compounds is presented (Fig. 2.2), where 1 and 2 appropriately mark the starting and the final points of the process. An interface between the solid and liquid parts of geometry depending on the heat transfer conditions separates a sharp solidification front of temperature T_F in case of homogeneous materials and a biphasic surface of temperature within liquidus T_L and solidus T_S interval in case of inhomogeneous ones. Within the not yet solidified liquid part, free or forced convection can still advance. Full

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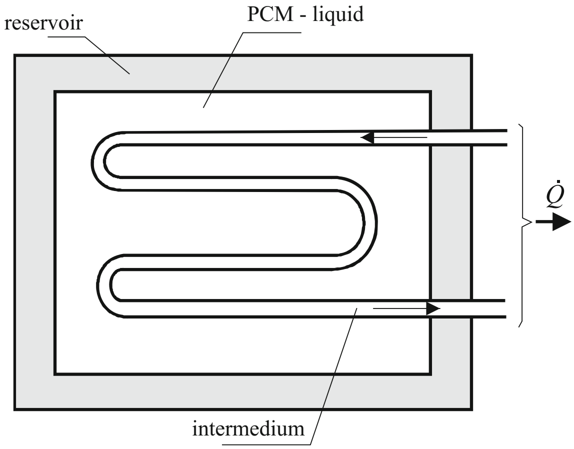

Fig. 2.1 Heat storage and release

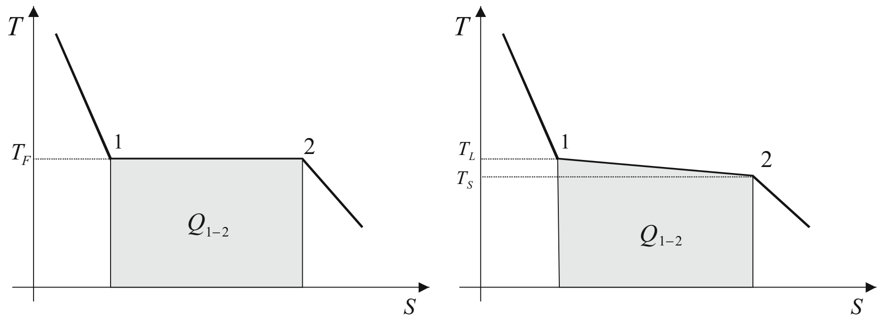

Fig. 2.2 PCM solidification processes

solidification is accompanied by the generation of heat Q_{1-2} and flow of entropy S to the heat receiver. A large field of research on the storage of heat or cold resulting from the phenomenon of solidification or melting was presented in the review works of Viskanta (1983), Zalb et al. (2003), Prashant et al. (2008) and Mehling and Cabez (2008). Examples of mathematic modelling of solidification processes are described among others in works: Mochnacki and Suchy (1993), and Alexides and Solomon (1993).

2.1.1 Multidimensional Solidification Heat Transfer

In practice, geometric shapes of applied PCMs are complex and multidimensional and depend on the shape of the reservoir (channel) in which they are contained.

Release of the accumulated heat from liquid PCMs during solidification is, as it has been already mentioned, a very complex phenomenon because of a movable surface called the solidification front (the case of movable boundary condition) of unknown shape separating the solid phase from the liquid one. Thus, a full description and a complete analytic solution are very difficult or even impossible.

In the solving of the two- or three-dimensional problems of heat transfer during a phase change, most helpful method is the numerical ones. With some chosen numerical methods and their review one, can get acquainted in works, among other of Shamsunder et al. (1975), Talmon et al. (1981), Viskanta (1983) and Mochnacki and Suchy (1993). Upon an analysis of presented work, the following main numerical methods applied in heat exchange during phase changes can be distinguished:

- Methods of finite differences (MRS) in regard to temperature as a definite parameter (method of finite explicit difference, method of infinite inexplicit difference, method of movable boundary immobilization, method of isotherm migration);
- Methods of finite differences (MRS) in regard to enthalpy, i.e. the enthalpy method;
- Methods of finite elements (MES).

Numerical methods are especially helpful in situations where analytic ones are not applicable, particularly in case of multidimensional phenomena. As particular errors of numerical methods can be listed those of process modelling (the applied mathematical model does not accurately reflect the reality, errors committed when tracing the original area by a computational one, errors of discretisation and those of rounding. The numerical methods are also disadvantageous because of the necessity to control the numerical error, the latter depending on net density and on temporal step. The analytic methods are free of numerical errors, and the solutions obtained are clearer in the form and easy to interpret.

2.1.2 Solutions of the Practical Solidification Problem

In practice, the attainable PCMs due to their temperature and the phase-change heat are characterized by a relatively small coefficient of heat transfer (Zalba 2003). To ensure effective storage of heat of high-thermal stream intensity, the volume of the heat accumulating materials should be small in relation to the boundary surface. However, to ensure storage of appropriately big amount of heat, the total volume of the material subjected to phase change should be also appropriately considerable. To make that discrepancy compatible, the total PCM volume should be divided into components of relatively small volume. Then, the time of charging and discharging of heat accumulators based on phase transition can be relatively short and regulated through appropriate construction of heat exchangers (heat accumulators).

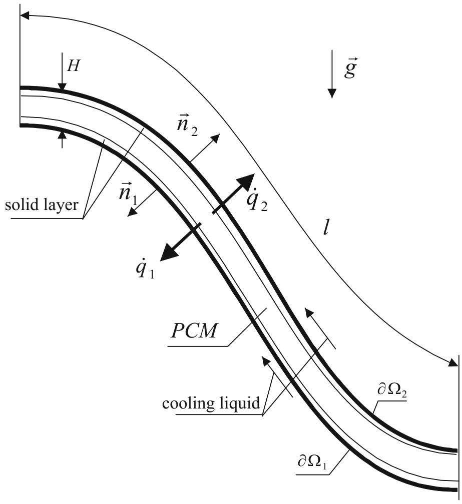

Fig. 2.3 Element of heat phase exchanger

The flow of heat in single elements can be modelled as one-dimensional heat flow. Then, a theoretical solution of such a fragmentary task is not theoretically difficult since there are simple analytical methods of solving this problem. Figure 2.3 shows an example of such element filled with PCM where H is the width of the channel and l its length. The width of the channel is assumed as small in relation to its length.

$$\frac{H}{l} \ll 1. \tag{2.1}$$

PCM is on both sides bounded by outer surfaces $\partial\Omega_1$ and $\partial\Omega_2$ being at the same time the channel walls marked by perpendicular $\vec{n}_1$ and $\vec{n}_2$ vectors, with intensities of the heat streams described by equations

$$\dot{q}_1 = -k_S \frac{\partial T}{\partial n_1}\bigg|_{\partial\Omega_1} \quad \text{and} \quad \dot{q}_2 = -k_S \frac{\partial T}{\partial n_2}\bigg|_{\partial\Omega_2}, \tag{2.2}$$

with T—the temperature and k_S—the coefficient of heat conductivity through a PCM.

When analysing the phenomenon occurring in simple geometric elements, some effects of free convection occurring within the liquid PCM in the result of the gravitation $\vec{g}$ as well as heat resistance of the contact layer formed between the solidified layer and the cool wall of the channel can be easily taken into consideration. The resistance of the contact layer is important for the construction aims.

Constructors of heat exchangers based on phase transition (solidifying and melting) and on PCM exploitation should aim at providing such construction solutions in which heat exchange is effective.

2.2 The Geometry of Outer PCMs

Generally, the geometry of PCMs is very complex. It is the main difficulty when theoretically describing the flow of heat which accompanies the transition phase occurring within the material considered. The radius of the wall curvature is of significant importance. A similar problem can be found in casting of alloys where in case of casts of different outer geometries, the problem of solidification is attempted to be considered irrespective of their shape by introducing a representative parameter, i.e. "*supplementary wall thickness*" (Braszczyński 1989), introduced by Chvorinov, expressing the relation of the cast volume to its outer surface. The cast solidification time is proportional to the square of the above-mentioned parameter.

Such a simple description of solidification is difficult to be accepted for PCMs since the latter are usually poor heat conductors. An attempt to overcome this inconvenience is the research on the phase change of PCM substances with added metallic supplements, thereby creating a unit of porous structure. Such research was conducted in the work of Weaver and Viskanta (1986). To improve the effectiveness of heat conductivity of the material undergoing the phase change, the above authors were sinking metal globules, aluminium or copper ones in its volume. Thus, created system was characterized by highly effective heat exchange. Theoretical research on similar porous medium was conducted in the work (Lipnicki and Weigand 2008).

Another way for the improvement of the heat exchange effectiveness is the choice of outer geometry of PCM. Figure 2.4 shows some examples of various shapes of materials undergoing phase changes. Each case requires an individual theoretical approach; however, theoretical difficulties rise proportionally to the outer geometry complexity.

The presented above particular cases of outer geometry of materials, i.e. a thin plate (*a*), a cylinder (*b*), a hollow cylinder (*c*) and a globe (*d*), in the case of heat accumulators can be of different degree of usability. An accurate identification of the most advantageous heat accumulator is determined by material, the geometry and outer conditions. Its construction is very complex because of a great number of

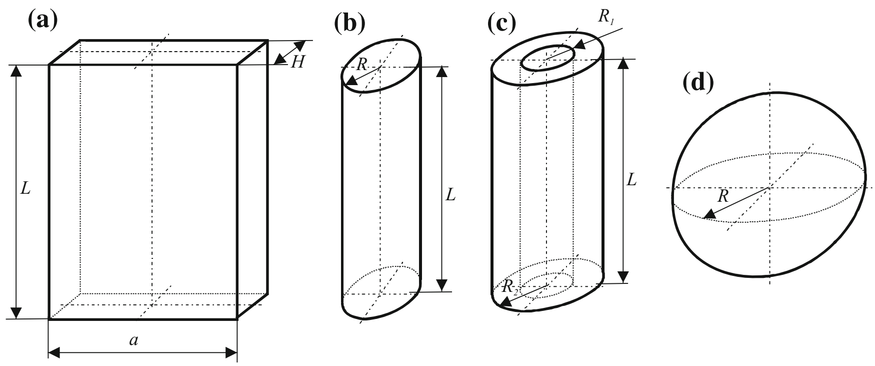

Fig. 2.4 Examples of outer geometry of PCMs

interrelation combinations between those factors. The outer conditions are defined among others by heat resistance of the layer near the contact surface. An accurate choice of the most preferable case requires lots of theoretical analyses. As it has been already mentioned, heat conductivity of the PCMs is very poor. This makes the time of heat release longer; i.e., the power of heat flow is relatively low. To increase the strength of the heat flow, one should attempt to enlarge the outer surface of the element, and in what follows, there is a need to divide the construction into several relatively thin components. The outer geometry of the element determines the process course. Usually, it is advised to obtain a relatively high power of the accumulator. To fulfil this task, the investigation of phenomena may be limited to some chosen shapes of elements of PCMs (Mehling and Cabeza 2008).

2.3 The Criterion for the Selection of Accumulator Design

The constructions of heat accumulators based on phase change of PCMs may differ in relation to their intended use, size and shape. The intended use of a heat accumulator, the method of heat delivery or removal directly influence the choice of geometry of PCMs and their outer sizes. The shape of elements of an accumulator and the method of heat absorption determine the phenomena indirectly realized during the process. Figure 2.5 shows various examples of profiles of phase changes in PCMs together

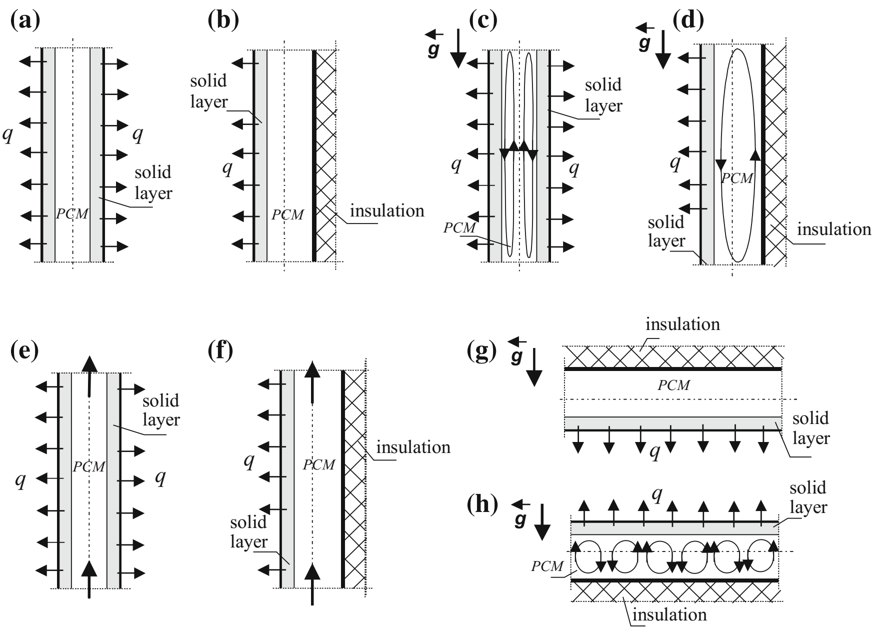

Fig. 2.5 Exemplary models of solidification of a flat liquid layer

with the direction of heat removal q. These are the models of solidification of a flat layer of a liquid in the case of two-sided cooling (a) and one-sided cooling (b); models of solidification of a vertical layer of liquid under the impact of free convection during two-sided cooling (c) and one-sided cooling (d); models of solidification of a liquid layer during forced flow at two-sided cooling (e) and one-sided cooling (f); and models of solidification of horizontal immovable layer of a solidifying liquid cooled from the bottom (g) and under free convection (h) cooled from above. During free convection, an important role is played by the orientation of the element of the heat accumulator to the gravitation vector $\vec{g}$. In a similar way, one can consider the models of solidification of elements constructed of PCMs of curved outer surfaces in which more complex phenomena of heat flow and exchange occur and their theoretical description is still more complex. Every one of the mentioned models should follow basic equations of mass conservation and those of momentum and energy if both the initial and boundary conditions have been fulfilled.

It remains to determine which of the above-presented theoretical models reflex the real phenomenon in the best way? An attempt to establish the choice criterion regarding the construction of a heat accumulator in view of its intended use is one of the aims of this work. To answer the question of the choice criterion for a heat accumulator, its main exploitation parameters, first of all capacity and thermal power, should be defined. The listed above features are derivatives of shape and of volume of the PCM, of geometric sizes and outer surface within which PCM is contained, of difference between the solidification and of cooling temperatures, solidification heat, specific heat, density, heat conductivity and viscosity. Introductory estimation of the amount of accumulated heat and the heat stream size in regard to the applied PCM and the type of construction requires an analysis and theoretical evaluation based on the accepted physical model. In other words, construction of a heat accumulator requires a complex theoretical analysis of the whole system of the heat accumulator and its elements.

To establish a general choice criterion for a heat accumulator considering its outer needs and as well as to choose the best solution in regard to the posed problem is a complex task requiring answers to a lot of elementary questions and joining them together.

The features of an accumulator are defined by heat power and capacity, geometry and thermal conductivity of material. The phenomena appearing in the process are the flow of heat in immobile material and free convection or the forced one. Outer conditions will define the boundary ones and the method of heat transfer. These factors should decide on the choice of the accumulator. The collection of the elements of a heat accumulator is a collection of various types, and some elements are interdependent what hinders their equal treatment.

The factors determining the features of a heat accumulator can be divided into the following groups:

- The factors deciding on free convection:
  - type of PCM,
  - spatial arrangement of the reservoir in which PCM is contained,

  - condition of heat absorption,
  - geometry of outer surface of the reservoir in which PCM is contained and
  - thermal resistance of the contact layer between PCM and the boundary wall.

- The factors deciding on the type of forced convection:
  - type of PCM,
  - geometry of the flow channel,
  - conditions of heat absorption from the flowing liquid and
  - thermal resistance of the contact layer between PCM and the boundary wall.

- The factors deciding on mixed convection and forced and free one:
  - type of PCM,
  - participation of factors influencing this kind of convection (pressure gradient, temperature gradient),
  - geometry of the flow channel,
  - conditions of the heat absorption from the flowing liquid and
  - thermal resistance of the contact layer between PCM and the boundary wall.

When considering the presented above models of the phenomena accompanying liquid solidification and the groups of factors deciding on the capacity and power of a heat accumulator, it can be seen that solidification of PCMs to release their earlier accumulated heat is a very complex problem. The author offers an individual approach to each particular case. Examples of such solutions are presented in the next parts of this work.

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