

Enhancing conduction heat transfer in phase change materials – graphite inserts

Bogdan Diaconu and Mihai Cruceru

Abstract — The availability of the renewable energy sources and systems – solar especially – is generally not synchronous with the demand. Therefore, methods to ensure the supply during the periods with no availability had to be implemented. Such method is represented by Phase Change Materials (PCMs) which are used in thermal systems where primary energy sources are available with intermittence. PCMs effect is based on storage and release of a significant amount of heat with a relatively small temperature variation – due to the latent heat of fusion/solidification. PCMs widely used in thermal systems are organic compounds with low thermal conductivity which is a major drawback in implementation of thermal systems with high efficiency. The paper describes a method of increasing significantly the thermal conductivity of PCMs by means of graphite inserts.

Keywords— Phase Change Materials, Graphite, Thermal conductivity.

I. PHASE CHANGE MATERIALS (PCMs) – MAIN PROPERTIES AND USES

PCMs are substances that undergo a phase change process – usually melting/solidification in a cyclical way such as they absorb and then release significant amounts of heat with little temperature variation. In theory any substance that undergoes a phase transition process at a temperature which is within the operating temperature range of the application can be used as PCM. In practice, only a few compounds fulfill the requirements, amongst which the most important is the latent heat of fusion/solidification. Latent heat can be achieved through various phase transition processes: liquid – solid, liquid – gas or gas – solid. However, the only process of practical importance is liquid – solid. Processes involving the

gas phase require large volumes and are consequently impractical.

PCMs classification. PCMs can be categorized in the following groups:

Organic PCMs. Usually paraffins, which are carbohydrate derived. Paraffins solidify with negligible subcooling, melt congruently, possess self-nucleating properties – which favors solidification, are compatible with most materials (especially building materials), do not manifest segregation, are chemically stable, have a high value of the latent heat of melting/solidification. Among the main disadvantages: low thermal conductivity in the solid state especially, volumetric latent heat storage capacity can be low due to the low density in the liquid phase, some compounds can be highly flammable. Another major disadvantage is the fact that obtaining reliable melting point values, most manufacturers use technical grade paraffins which are essentially paraffin mixture(s) and are completely refined of oil, resulting in high costs.

Inorganic PCMs. Usually salt hydrates, (MnH_2O), they have the following properties: High value of the volumetric latent heat storage capacity, low cost and widely available, very small deviation from the melting point, high value of the thermal conductivity, high value of the latent heat of solidification, not flammable. Salt hydrates have a number of disadvantages, such as: large volume change during the phase transition process, significant supercooling during liquid – solid transition, nucleation does not occur naturally requiring nucleating agents. After a number of cycles nucleating agents become inoperative.

Eutectics. Such compounds have very small deviations of the melting point similar to pure substance, volumetric storage density is slightly above organic compounds, extra water principle can be used to avoid phase change degradation, involving dissolving the anhydrous salt during melting to result in a thickening of the liquid material so that it melts to a gel form. Eutectics are however new to heat storage applications.

The key parameters of the PCMs are the melting point and the latent heat of fusion. The applicability area is given mainly by these two parameters. In addition to the latent heat of fusion and melting point, other consideration must be taken into account before deciding the suitability of a given PCM for a heat storage application, such as: cost, chemical stability, chemical interaction with other heat storage system components and pipelines, fluid flow properties of the fluid phase, phase equilibrium, supercooling effects, non-sliding melting/solidification point, long term stability of the thermo-

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B. Diaconu is with the Department of Automation, Energy, Environment and Sustainable Development, Faculty of Engineering, University “Constantin Brancusi” from Targu-Jiu, Eroilor 30, Targu Jiu, Gorj, RO 210152, Romania

M. Cruceru is with the Department of Automation, Energy, Environment and Sustainable Development, Faculty of Engineering, University “Constantin Brancusi” from Targu-Jiu, Eroilor 30, Targu Jiu, Gorj, RO 210152, Romania, (phone: +40 766567521, fax: +40 253 218222, e-mail: cruceru.mihai@gmail.com)

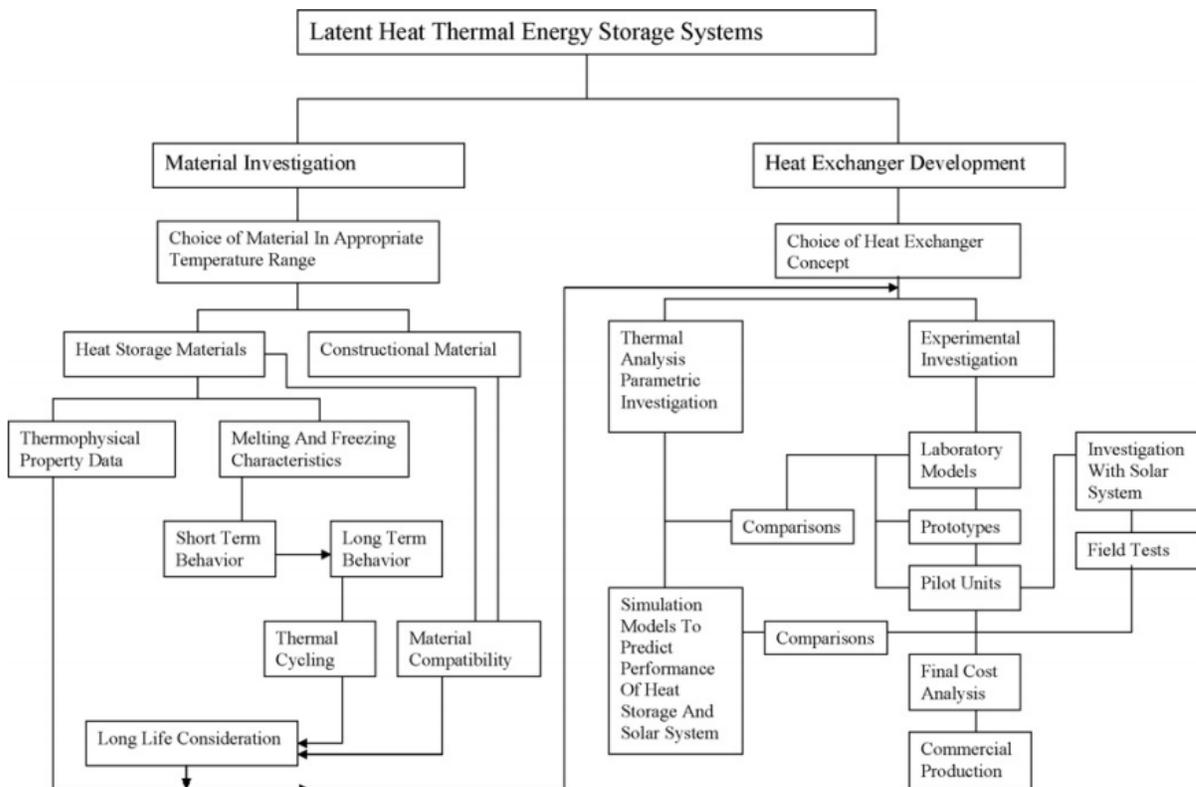


Figure 1. Stages involved in the development of a latent heat storage system [1]

physical properties and the most important, thermal conductivity in both fluid and especially solid phase. In terms of the features mentioned above with the exception of the thermal conductivity, the best candidates to be used as PCMs are organic compounds, especially paraffins. However, paraffins have a low value of the thermal conductivity, as most organic compounds have. Therefore, it is important to identify solutions meant to improve the heat transfer through the PCM.

Latent heat storage systems design is a complex process represented in stages in Figure 1 [1].

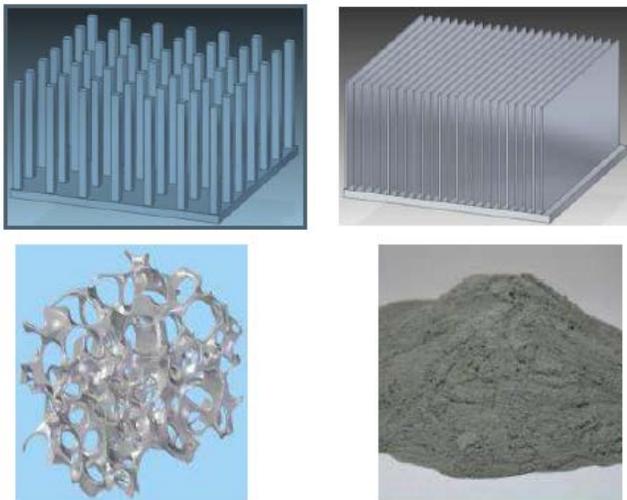


Figure 2. Thermal conductivity enhancers [11]

The main issue of PCMs is the low value of the thermal conductivity. In order to improve the heat transfer in the PCM mass various techniques exist, conventionally called thermal conductivity enhancers (TCEs) [11]. TCEs disperse evenly heat throughout the PCM while leaving a majority of the total volume for energy storage. A variety of TCEs have been investigated, including powders, particles, and fibers, as shown in Figure 2.

II. GRAPHITE – MAIN PROPERTIES AND USES

Plates and fins [11] are the simplest to manufacture and model, but offer inferior surface area and weight compared to both particles and foams. Some of the major engineering challenges when using particles and fibers include settling of the TCE over time and thermal coupling. Foams, on the other hand, can provide high specific surface area, high thermal conductivity, and are lightweight and structurally stable.

Similar to metal foams, graphitic foams possess high specific surface area—up to twice that of conventional heat exchangers [11]. Graphitic foams have certain advantages over traditional metal foams, including inertness to chemicals, low weight, and potential for high thermal conductivity [11]. Also, the physical and thermal properties of the foam are tailored to a specific application. Porosity, pore size, pores per unit volume, and anisotropy are all affected by altering processing conditions during foam production.

Graphitic carbon is generated mainly by two processes: (1) carbonization–graphitization of organic matter originating from living organisms, [2] and (2) precipitation from deep fluids saturated in carbon-bearing molecular and ionic species. Graphitic carbon exhibits a large range of structures (e.g. amorphous-like compounds, turbostratic structures, to crystalline graphite), and graphite and well-ordered graphitic carbon exhibit a huge structural anisotropy, with strong consequences for physical properties. For instance, electron delocalization in graphene layers yields a high in-plane electrical conductivity equivalent to that of metals. Perpendicular to layering, however, conductivity is so low that graphite is an insulator parallel to its c-axis. Other remarkable bulk properties of graphite and some synthetic graphitic carbon include a high thermal conductivity, a high sublimation point (approximately 3800 °C at atmospheric pressure), a low thermal expansion coefficient, and a relatively low density (ca. 2.1–2.3). Graphitic carbon may be used as raw material or be further processed for specific applications, such as in energy and electrical applications. The key property in this case is the high electrical conductivity of graphite, placing graphite at the forefront of modern technological applications in green energy utilizations. [3] For instance: (i) It is possible to intercalate various chemical species, such as alkalis, alkaline-earth metals, lanthanides, metallic alloys, and ionic compounds, between the graphene layers. This graphite intercalation is based on oxidation-reduction reactions between the graphene layers and the intercalated material, and it improves the electrical conductivity of graphite; some phases are even superconducting. Intercalated graphite is widely used in batteries. Graphite intercalated compounds synthesis is considered to be one way of developing the functionality of carbon materials; [3] (ii) It is also possible to expand graphite and generate exfoliated graphite: e.g., in overcoming Van Der Waals interactions by mechanical action or thermal expansion of an intercalated agent. This yields a low-density material used alone (e.g. in gaskets and seals) or mixed with other compounds (e.g. electrodes).

The recycling of graphite is limited (e.g. electrodes may be recycled), and only in few applications graphite is recovered due to low economic incentive and technical challenges. In addition, in some applications (e.g. brakes), graphite becomes dispersed in the environment, constituting a source of pollution. [4] However, it is possible to substitute natural graphite by its synthetic alternative, other compounds, or other forms of carbon. Crystalline graphite is also highly refractory and chemically inert, whereas the chemical reactivity of graphitic carbon increases with structural disorder and the abundance of chemical impurities.

Thermo-physical properties of graphite of interest in transient heat conduction are presented in Figure 3.

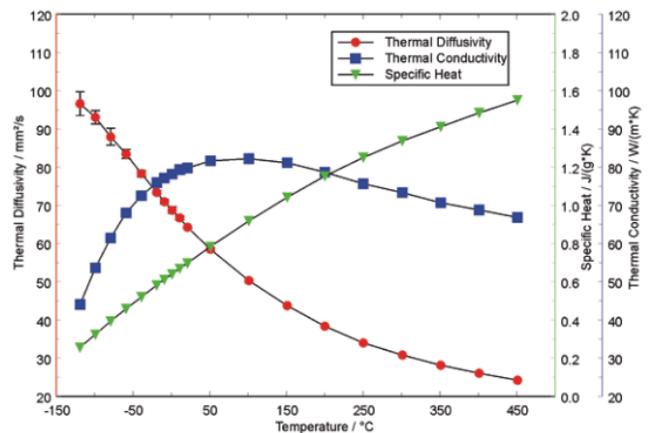


Figure 3. Main thermo-physical properties of graphite [5] Graphite foam was found to be the most efficient form in which graphite can be integrated with minimum cost into conventional PCMs. Graphite foam is a porous material with effective thermal conductivity defined as the ratio of bulk thermal conductivity to solid conductivity. When predicting the bulk thermal properties of graphitic foams, the rule of mixtures does not apply; that is to say the foam properties cannot be accurately predicted using volume-averaged calculations taking the foam to be a composite of graphite and air. This is due to the longer heat flow path around the foam pores, which is not taken into account in the rule of mixtures [10].

III. PCMS WITH GRAPHITE INSERTS. POSSIBILITIES OF INCORPORATING GRAPHITE UNDER VARIOUS FORMS IN PCMS

Guo et al [6] utilized highly-porous, highly conductive graphite foam in order to achieve incorporation into a paraffin with specific heat capacity 2890 J/kgK, thermal conductivity 0.21 W/mK (solid) and 0.12 W/mK (liquid), latent heat 173.4 kJ/kg and melting point approximately 320 K. The graphite foam used in these experiments is POCO-HTC™ open pore graphite foam, which has the average pore diameter of 400 μm, total porosity of 72.8%, density of 0.5 g/cm³, heat capacity of 0.7 kJ/kg·K and the average heat conductivity coefficient of 150 W/m·K. A numerical study was carried out on a thermal energy storage device shown in figure 4.

It consists of an inner tube, outer tube and an annulus space filled with paraffin wax/graphite foam composites. The outer tube was insulated. The volume averaged energy equation with phase change is used to model the heat transfer process inside the PCM/graphite composite with phase change. A transient simulation revealed a much better response of the graphite impregnated PCM, as shown in Figure 5

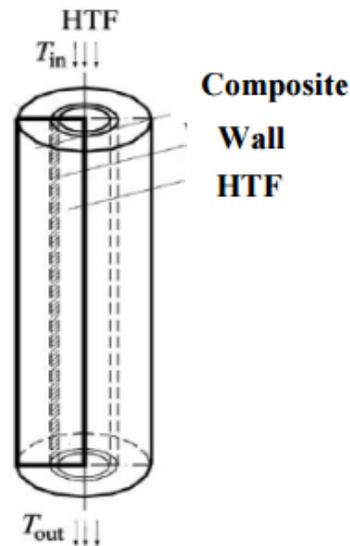


Figure 4. Schematics of the device [6]

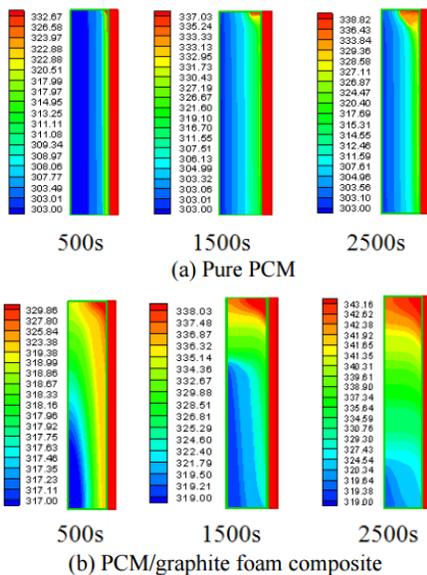


Figure 5. Comparison between thermal response of the pure PCM (a) and graphite inserts enhanced PCM (b) [6]

Cabeza et al. [7] built a solar pilot facility to test the PCM behavior in conditions closed to reality. The PCM heat storage system was designed to operate continuously coupled with the solar system, or can be coupled with an electrical heater. The PCM module geometry considered consisted of several cylinders at the top of the water tank. A number of experiments with two, four and six PCM modules were carried out in the real installation. A granular PCM-graphite compound of about 90 % (volume ratio) of sodium acetate trihydrate and 10 vol.% graphite was chosen as the PCM. Inclusion of a PCM module in water tanks for domestic hot-water supply was found to be a very promising technology with a dynamic system response much faster than that of a pure PCM heat storage system.

Zhang et al. [8] prepared LA-palmitic acid (PA)-SA/EP composite PCMs by vacuum impregnation method. The maximum mass ratio of LA-PA-SA retained in EP was found as 55 wt %. It was found that the thermal conductivity of LA-PA-SA/EP was increased by 95% by adding 2 wt % expanded graphite, and the thermal energy storage/release rates were also increased.

Sun et al. [9] prepared the form-stable PCMs by absorbing paraffin into EP method. Graphite as additive was added into the form-stable PCMs to improve thermal conductivity. The results showed that the thermal conductivity of the form-stable PCMs was increased as much as 192% by graphite with mass fraction of 5%.

IV. CONCLUSIONS

Graphite insertion in PCMs offer a significant increase of the heat conduction through the PCM, improving to a high degree the thermal performance of the PCM base thermal system. Graphite can be integrated into the PCMs as graphite foam or exfoliates. Graphite foam is more advantageous economically and offers better thermal performance. Exfoliates tend to migrate and form local agglomerations which is detrimental to the heat transfer. Foam is mechanically stable and preserves its thermal and mechanical properties with thermal cycling.

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