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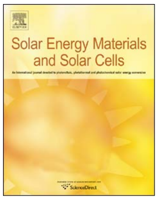

Synthesis and characterization of multifunctional energy composite: Solar absorber and latent heat storage material of high thermal conductivity

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ABSTRACT

Phase change materials (PCM) used in thermal energy storage systems present high storage capacity and require low temperature variation to allow effective heat charge or discharge density. However, these materials involve too low thermal conductivities ($< 1\ \mathrm{W\ m^{-1}\ K^{-1}}$) which can limit the heat transfer power between the heat transfer fluid and the phase change zone. In the first part of this study, high power level composites made of PCM (organic and also inorganic) and graphite have been elaborated in the thermal range from 50 to 350 °C in order to increase the effective thermal conductivity. In a second part, the assessment of their use as solar absorbers has been realized. Results show that these composites present high absorptance with respect to the whole solar radiation spectra. This allows new potentiality of integration of such materials in solar thermal processes offering a direct management of heat variation at the very first step of the process.

1. Introduction

Electricity and/or heat production using solar thermal technologies suffers from the intrinsic intermittence and energy dilution of the solar resource. Peak demand consumption and quick fluctuation management by heat storage can lead to the overall system optimization highly expected for their grid integration. Three main thermal storage principles can be considered: sensible heat, latent heat and thermochemical reaction [1,2]. This paper focuses on the latent heat storage approach and two mains applications are pointed out: on the first hand, at low temperature (below 100 °C), heat production using solar domestic hot water system (SDHW); on the other hand, at higher temperature (between 200 °C and 350 °C), electricity production involving concentrated solar power (CSP) plant.

SDHW systems are usually composed of solar collectors associated to a water tank using a heat transfer fluid (HTF) loop. For instance, for a family house, the typical installation is composed of a 4 m^2 collector and a 0.250 m^3 tank. Insertion of PCM inside the tank to increase its energy density and so reduce its volume has been already proposed several times in literature [3]. Our innovative approach, presented in a previous paper, [4] is to use the PCM directly inside the solar collector, in order to replace the traditional absorber made of copper coated with selective surface. This could give rise to several advantages such as the reduction or even the avoidance of the storage tank and the addition of new storage functionality to the absorber. However to realize such a system two major current limitations must be addressed: 1) the low conductivity of the raw PCM ($< 1\ \mathrm{W\ m^{-1}\ K^{-1}}$), 2) the storage material should have high absorptance. Bearing in mind those two critical issues, composites made of PCM and graphite have been investigated for this typical application.

This innovative approach has been extended to thermal energy storage for CSP plant. Up The state of the art ofthermal storage for thermodynamic solar processes is based on solid sensible heat (like concrete – [5] or post-industrial ceramic [6]), liquid sensible heat (like Gemasolar plant – [7]) or vapor sensible heat (like water vapor – PS10 Seville [8]) for medium temperature level. Several PCM prototypes have been assembled [9]. In all of those previous cases, the storage system is centralized and placed out of the solar collector field.

The novelty highlighted in the present paper is to consider a new genuine approach with a storage composite material directly embedded as a solar radiation absorber within the solar collector. This integration could enhance the system efficiency by reducing the number of heat transfer interfaces. It could furthermore damp solar radiation variations within the collector and consequently reduce strong variations in

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Table 1
Organic/Inorganic PCM main characteristics.

	Advantages	Disadvantages
Organic Paraffin (P), fatty acids (FA), sugar alcohol (SA)	Low toxicity No subcooling for P and FA Low corrosion	Inflammable for P Moderate storage capacity $T_{melting} < 200$ °C High subcooling for SA
Inorganic pure or hydrated salts, eutectics	High storage capacity Fireproof Large melting temperature range	Subcooling Segregation Corrosion Hygroscopic behavior

heat transfer fluid pressure and temperature with respect to the expected stability of fragile components like steam turbines.

The present paper is devoted to the material potential description at a laboratory scale. The elaboration routes for PCM/graphite composites will be presented first. Then, the characterization techniques for thermal conductivities and absorptance measurements will be introduced. Finally, results concerning low temperature composites (< 100 °C) as well as medium temperature (200–350 °C) will be exposed and discussed.

2. Composites elaboration

2.1. Investigated PCM

Non-eutectics PCMs are commonly classified in two categories: organic and inorganic. Mains characteristics of those materials are given in Table 1.

The selection of the most appropriate PCM must include various criteria as:

- Price as low as possible;
- Availability in industrial scale;
- Low toxicity, low corrosivity and high environmentally friendly;
- Phase change temperature in the appropriate range;
- Low or even no subcooling
- High storage capacity (volume and mass);
- Thermal properties stability versus large amount of thermal cycles.

The seven tested PCM are presented in Fig. 1 with their relevant storage properties namely mass and volume storage capacities. They present melting temperatures ranging from 50 to 350 °C which is the current limiting operating temperatures of solar applications from non-concentrated systems to parabolic trough collector.

The studied PCMs for SDHW application have been supplied by Rubitherm® (RT65 paraffin) and Alfa Aesar® Company (industrial grade stearic acid and sodium acetate tri-hydrated). For medium temperatures (200 °C < $T_{melting}$ < 350 °C) the selected PCM has been supplied by Lancaster for pure grade (KNO_3, $NaNO_3$, $Na/K/NO_3$ E) and by SGL for industrial quality ($Na/K/NO_3$ E and $ZnCl_2/KCl$ E).

Among PCMs presented in Fig. 1, sodium acetate tri-hydrated ($NaCH_3COO{\cdot}3H_2O$) is found to theoretically be the most interesting (for solar thermal application, $T_{melting}$ < 150 °C), in terms of specific enthalpy per mass and per volume (260 kJ kg^{-1} and 40 MJ m^{-3}). Nevertheless, the hydrated salts present, in general, unstable behaviors under increasing temperature. This is due to a loss of water molecules and subsequent formation of other hydrates or dehydrated salts. Therefore, they have to be used in hermetic containers. Similar observations were done on other hydrated salts like magnesium nitrate and aluminum sulphate. Hence, RT65 paraffin was selected to be associated with the graphite.

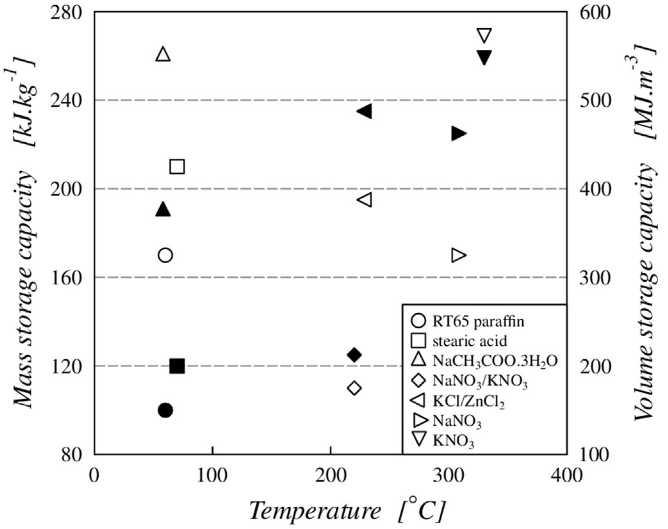

Fig. 1. Selected PCM weight (open symbol) and volumic (black symbol) storage capacity as a function of the fusion /solidification temperature.

At higher temperatures, KNO_3 offers the highest enthalpy with a mass storage capacity of 270 kJ kg^{-1} and a volume storage capacity 55 MJ m^{-3}. The corresponding graphite composites, as well as $NaNO_3$ and two others binary and ternary eutectics described below, have been realized.

2.2. Graphite

Graphite presents various forms available at industrial scales (graphite flakes, expanded graphite, ground expanded graphite, fibers, etc.) and laboratory scales (nanofibers, nanotubes and more). Among those, natural graphite flakes (NFG), expanded natural graphite (ENG) and ground expanded graphite powder (GFG) were selected and tested for PCM/Graphite composites elaboration and characterization. NFG, brand-named TIMREX SFG75 is provided by TIMCAL while ENG and GFG are supplied by SGL carbon. Scanning Electronic Microscope imaging of NFG and ENG are presented Fig. 2.

2.3. Elaboration

The variability of graphite shapes allows flexibility in terms of composite elaboration routes. Three different methods have been successfully tested: ENG matrix impregnation for organics PCMs, Timrex® SFG75 graphite flakes (NFG) and GFG dispersion and ambient temperature compression of PCM and ENG or GFG mixtures. Elaboration route methods are presented in details according to graphite and PCM characteristics.

2.3.1. ENG matrix impregnation for organics PCM

This elaboration route combines expanded natural graphite (ENG) and organics PCM. First ENG is poured in a cubic mould (allowing proper identification and subsequent characterization of the anisotropy) and then pressed to obtain a consolidated matrix. This matrix is then soaked into molten PCM for porosity infiltration by the PCM until maximum load is reached. This method has been found to be very relevant in case of organic PCM as 90% of the ENG matrix porosity is loaded by capillarity after several hours of immersion. On the other hand, this technique is rather inefficient in case of inorganic PCM (maximum 40% of porosity loaded). This technique is optimum when there is a high wetting behavior of the PCM over the graphic matrix. This is the case, at low temperature, with RT65 ($T_{melting}$=60 °C) and stearic acid ($T_{melting}$=66 °C). The corresponding composites have been elaborated by impregnation.