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## Potentialities of a low temperature solar heating system based on slurry phase change materials (PCS)

Gianluca Serale<sup>a</sup>, Ylenia Cascone<sup>a</sup>, Alfonso Capozzoli<sup>a</sup>, Enrico Fabrizio<sup>b</sup>, Marco Perino<sup>a,\*</sup><sup>a</sup>Politecnico di Torino, DENERG, Corso Duca degli Abruzzi, 24, 10129 - Torino(TO), Italy<sup>b</sup>University of Torino, DISAFA, Via Leonardo da Vinci, 44, 10095 - Grugliasco (TO), Italy

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### Abstract

Flat-plate solar thermal collectors are the most common devices to convert solar energy into heat. Water-based fluids are commonly adopted as heat carrier for this technology, although their efficiency is limited by some thermodynamic and heat storage constraints. To overcome some of these limitations, an innovative approach is the use of latent heat, which can be available by means of microencapsulated slurry PCMs (mixtures of microencapsulated Phase Change Materials, water and surfactants). The viscosity of these fluids is similar to that of water and they can be easily pumped. In the present work, some of the thermo-physical and rheological properties and material behaviour that interest flat-plate solar thermal collectors with slurry PCM as the heat carrier fluid are analysed. Concepts of solar thermal systems filled with a slurry phase change material are proposed and a prototypal system is presented. Possible advantages and drawbacks of this technology are also discussed.

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### 1. Introduction

Flat-plate solar thermal collectors are the most common devices to convert solar energy into heat. Recent studies reported an installed capacity of 234.6 GWh by the end of 2011, which correspond to a total of 335.1 million square meters of collector area in operation [1]. Conventional water-based solar thermal collectors have been widely

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\* Corresponding author. Tel.: +39-011-090-4423; fax: +39-011-090-4499.

E-mail address: [marco.perino@polito.it](mailto:marco.perino@polito.it).

investigated since the '40s [2] and, since then, several improvements have been achieved in their overall performance and efficiency. Nevertheless, since heating demand takes place when low or no solar energy is available, the exploitation of solar energy for space heating purposes through traditional solar collectors is often not profitable.

The heat transfer fluid (HTF) plays a very significant role in a solar thermal system. It absorbs energy in the collector and transfers it through the heat exchanger to the storage tank. The HTF properties – such as boiling and freezing points, viscosity and thermal capacity – need to be carefully considered in the selection of the working fluid for a solar heating system. Water is the most common HTF; however, to overcome its relatively high freezing point, a glycol additive is generally mixed with it to act as an antifreeze.

The adoption of traditional solar thermal systems based on water solutions implies a relatively high working temperature of the heat carrier fluid (50-60°C being a typical range). This temperature range is required to provide heat terminal units with a large enough enthalpy flux with reasonable flow rates and to adopt sufficiently small energy storage systems. Since a high temperature difference between the HTF and the environment causes considerable thermal energy losses in all the system components, an increase in the HTF temperature corresponds to a decrease in the instantaneous collector efficiency as well as in the global seasonal efficiency. Moreover, the higher the HTF temperature the lower the solar coverage, i.e. the time during which the solar thermal system can be exploited to produce heat. The relationships between HTF temperature, solar coverage and system efficiency was described by many authors [3, 4].

To overcome these limitations, several studies on the possibility of using HTFs other than water have been carried out [5]. Several research projects were conducted to study the effectiveness of solar thermal systems involving a two-phase heat transfer process. In this way, the isobaric process of phase change within the heat carrier fluid occurs at an almost constant temperature, and a great amount of heat is involved. Therefore, solar energy is exploited at lower thermal levels and heat losses for dissipation are reduced too. The use of refrigerant-filled solar collectors was investigated by many researchers and their application is not a complete novelty. Experiments on this concept date back to the '70s, when heat pumps integrated with solar collectors exploited the phase change of refrigerants which were used as HTF. In the first studies [6, 7], CFC, HCFC and HFC refrigerants were used, but they were not suitable for a long-term use due to their high Ozone Depletion Potential and Global Warming Potential. Recently, other natural fluids – such as propane or CO<sub>2</sub> – have successfully replaced those refrigerants [8]. Solar collector heat pumps filled with these new fluids have similar COPs and are less harmful to the environment.

All these past experiences, which took advantage of the latent heat of the carrier fluid, were based on the exploitation of the liquid-to-gas transition. Another possibility involves the exploitation of the solid-to-liquid transition. This is possible through the introduction in the solar system of phase-change materials (PCMs) with high latent heat of fusion. Most of the investigations in this direction focused on using these materials only to improve the efficiency of the storage tank and to reduce its size [9, 10]. Nevertheless, this strategy implies heat exchanges with finite temperature differences both between the HTF flowing inside the solar collector loop and the PCM storage, and between this storage and the carrier fluid flowing to the terminal units.

During the '80s Kasza et al. proposed to directly use PCMs inside water based suspensions, called slurries, as an enhanced HTF in the primary loop of solar collector systems [11]. They listed different properties to take into account in the choice of the heat carrier fluid and they demonstrated that this PCM based technology could provide several efficiency benefits. Nevertheless, there were some technological limitations due to the possible solidification of the slurry in the pipes during its phase transition.

Nowadays, thanks to the advancement in the PCM technologies, an alternative solution can be conceived. The circulation of the slurry in the pipes can be always guaranteed by using micro-encapsulated PCMs (mPCMs) suspended in water. In this way the two-phase fluid has constant rheological properties and the phase-change concerns only the core of the microcapsules. An mPCM slurry remains always liquid, even though with a high viscosity, and it can be pumped regardless of its state of aggregation. The potential of this technology was widely studied in the last few years [12, 13], although its applications as an HTF in the various loops of a solar system was never taken into account.

In the present work, some of the thermo-physical and rheological properties and material behaviour that interest flat-plate solar thermal collectors with slurry PCM as the heat carrier fluid are analysed. Concepts of solar thermal

systems filled with a slurry phase change material are proposed and a prototypal system is presented. Possible advantages and drawbacks of this technology are also discussed.

## 2. Proposal of a solar thermal system filled with a slurry phase change material (PCS)

### 2.1. PCM slurries (PCS)

Phase change materials (PCMs) have long been used for thermal energy storage due to the large amount of heat they absorb or release during their phase transition. They can be chosen to select the most suitable phase change temperature range for a specific application. PCMs can be organic materials (paraffin or non-paraffin) as well as inorganic materials. In recent years, PCMs have been developed into an always liquid form to increase the heat transfer rate by rising the surface to volume ratio. This binary system is called phase change slurry (PCS) [14]. It consists in a dispersion or a solution of a continuous phase – generally water – and a PCM – such as a paraffin – as the dispersed phase. The advantages of using PCSs in different thermal application were clear since the late '90s [15, 16].

The main advantage is that PCSs can be used both as thermal storage materials and heat transfer fluids. Since they can be pumped, the same medium can be used both to transport and store energy, hence reducing the heat transfer losses. Moreover, they have a high storage capacity during the phase change and heat transfer occurs at an approximately constant temperature [17]. To take advantage of these properties, the following requirements are needed: the phase change temperature range has to match the application, low pressure drops have to occur in the pumping system, the PCS has to be stable to both thermal and mechanical loads, capsules have not to leak and the pipes have not to clog [18].

Many types of slurry PCSs are available on the market [17]. For the solar thermal system application proposed in this paper, a micro-encapsulated PCS was chosen. In the chosen suspension, the PCM is encapsulated within a thin film in order to form a polymeric microcapsule which is dispersed in a water-glycol solution. Microencapsulation processes were mainly developed by pharmaceutical industries [19]. Generally, the particle size of microcapsules ranges between 2 and 2000  $\mu\text{m}$  of diameter. The shell thickness oscillates between 0.5 and 150  $\mu\text{m}$  and the core constitutes between 20% and 95% of the total mass [20].

In low temperature radiant panel systems, the optimal temperature for heat storage is about 35°C-40°C. In this way, the temperature difference between storage and HTF in room terminal units is the lowest. To match this application, a micro-encapsulated n-eicosane with a nominal melting temperature of 37°C was chosen [21]. The main thermo-physical properties of n-eicosane are described in Table 1.

Table 1. Thermo-physical properties of n-eicosane

Material	Average particle size ( $\mu\text{m}$ ) [17]	Nominal melting temperature ( $^{\circ}\text{C}$ ) [17]	Latent heat (kJ/kg)	Capsule composition [22] (%)	Thermal conductivity [14] (W/mK)	Density [14] ( $\text{kg}/\text{m}^3$ )
n-eicosane	17-20	37	190-200 [17]	85-90 wt. PCM	0.230 solid	856 solid
			247[14]	15-10 wt. Shell	0.151 liquid	780 liquid

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### 2.2. Design of a PCS solar thermal system

The application of PCMs and PCSs in solar thermal systems was studied and developed just in the storage tank. Generally, they were coupled with traditional HTFs (water or water-glycol) in the primary loop of the solar collector [23]. Nevertheless, this strategy implies exchanges with finite temperature differences between the HTF flowing inside the solar collector loop and the PCM storage as well as between the storage and the carrier fluid flowing to

the terminal units. These heat exchanges introduce irreversibilities and energy-exergy losses. To avoid these inefficiencies and reduce the overall temperature difference, a thermal solar system based only on PCS is herewith proposed. The PCS can be directly used as a heat carrier fluid in the various loops of the system.

Figures 1(a) and 1(b) show two possible system configurations that can be adopted. The option described in figure 1(a) is a two open-loops circuit filled with PCS. This option guarantees the maximum theoretical thermal efficiency due to the complete absence of finite temperature differences in the heat exchange between the primary and the secondary of the system. However, it is more challenging from a technological point of view than the option in figure 1(b).

In figure 1(b), an open primary loop circuit with PCS coupled with a closed secondary loop circuit with water is shown. This configuration is less efficient from the heat transfer point of view due to the temperature difference between storage tank and secondary HTF loop. However, the storage tank contains PCS as well as the previous solution and it guarantees an easier technological implementation. For these reasons, this last solution was adopted in the first instance by the authors as the most suitable for the scope of this work.

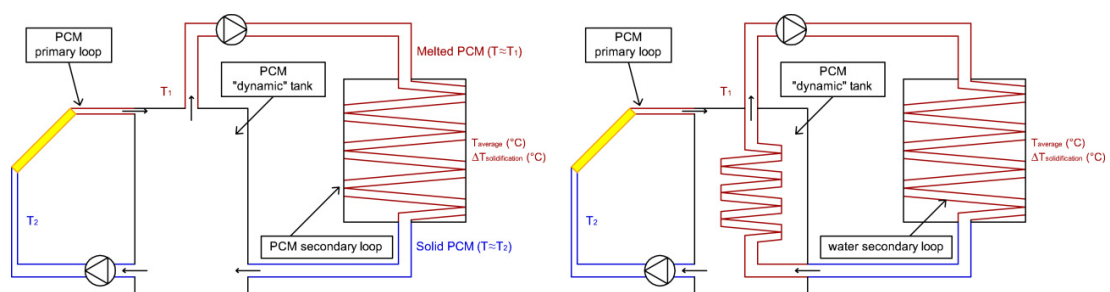


Fig. 1. (a) a two open-loops circuit; (b) an open-loop circuit with PCS and a closed-loop circuit with water

Once the n-icosane was chosen as micro-encapsulated PCM, the slurry properties could be controlled by choosing different concentration ratios of mPCM on water-glycol. The concentration of the mPCM components of the slurry influences both its thermophysical and rheological properties; the latter show a highly non-linear behaviour. The choice of the ratio of mPCM on solution has a very relevant impact on the efficiency of the system. It affects the relation between pumping work and heat transfer, which has a deep implication on energy savings in real applications [24]. A compromise between heat transfer characteristics and pressure drops of the fluid needs to be reached. This is a quite tricky trade-off, since improving a characteristic may worsen the other one. On one hand, a high concentration of mPCM increases the possibility of thermal latent storage of the material, on the other hand, it determines higher pressure drops due to the increased viscosity, which means higher energy demand for pumping. However, a higher thermal storage capacity also implies a lower flow rate, and hence a reduction in the electric energy demand from the pump [25].

Two research directions were followed. Firstly, a theoretical model capable of describing the behaviour of a flat plate solar collector filled with PCS was developed. Secondly, a system prototype was designed and realised.

### 2.3. Thermal model of a PCS filled flat plate solar thermal collector

On the basis of the well-known Hottler-Willer (HW) model for traditional flat plate solar collectors [26], a theoretical model describing the behaviour of the PCS filled solar collector was previously developed [27]. In this model, the panel is divided in parts depending on the kind of heat exchange – sensible or latent – occurring in the HTF (Fig. 2). The panel can be divided at most in three parts. The first part,  $\Delta y_1$ , represents the segment of panel between the inlet and the point where the HTF reaches the lower limit of the mPCM melting temperature range (sensible heat exploitation). The second part,  $\Delta y_2$ , corresponds to the section wherein the whole amount of mPCM completes the phase change, where hence the HTF temperature rises from the lower limit to the upper limit of the mPCM melting temperature range (latent heat exploitation). In the last segment,  $\Delta y_3$ , sensible heat exploitation

occurs again and the HTF reaches the outlet temperature. The length of any part changes according with any variation in the boundary conditions. By integrating the HW equations using melting temperature limits and enthalpy of fusion of n-eicosane mPCM as constant terms, the length of each segment can be determined.

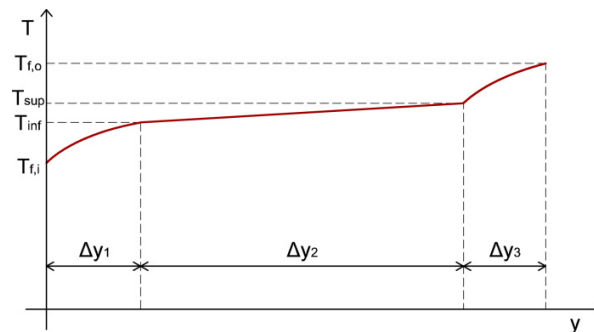


Fig. 2. Theoretical temperature distribution of the HTF through a slurry PCM filled solar panel

A set of simulations were run to compare the performance of a water based flat plate solar collector against the performance of a slurry PCM filled one. From the thermal point of view, results showed that the slurry PCM filled solar collector was more efficient than the traditional one [25, 27]. The mean seasonal efficiency increased of about 5% to 9% depending on the boundary conditions. Further benefits due to the storage tank were not studied for this particular type of system. However, a wide literature on thermal energy storage with PCMs is available [10, 11].

### 3. Proposal of a solar thermal system filled with a slurry phase change material (PCS)

Some technical problems related to this new kind of HTF need to be carefully considered. Possible issues are high pressure drops, clogging in the pipes, sedimentation in the storage tank and capsule rupture due to the pumping work.

#### 3.1. Capsule rupture or leaking

To ensure long-term operation, PCM microcapsules should be durable and should not be broken by the circulation pumps. Rupture of the microcapsules can cause several problems, such as clogging of the pipes and a change in the thermal properties of the slurries. Damage and rupture can be caused by mechanical stress due to the pump or agitation of the microcapsules [28]. Alvarado et al. [29] showed that an n-tetradecane mPCM with a diameter smaller than 10 mm could be durable and impact-resistant by using a cavity pump to do the durability test. Furthermore, Gschwander et al. [30] pumped different types of mPCM slurries for several weeks through different conventional system components (e.g. pumps, heat exchangers and expansion valves) in order to study their stability. Centrifugal pumps resulted to cause less damage or less destruction of the microcapsule shells.

#### 3.2. Pressure drops

Pressure drops are a function of some characteristics of the pipes (e.g. diameter, friction factor) and of the viscosity of the fluid. Since an increase in the pressure drops corresponds to an increase in the pump energy consumption, pressure drops need to be limited not to significantly reduce the benefits deriving from the improved thermal efficiency that can be achieved through the use of PCSs as HTF. For this reason, the rheological properties of the PCS played a fundamental role in the development of the system.

In the first stage of the development of the PCS based solar thermal system, the focus was only set on the material properties. Since the proposed technology aims at improving existing solar thermal systems, their components were not modified. The chosen diameters of the pipes were the largest among those commonly in use.

According to the results obtained from the tests with the prototype, specific components for the PCS solar thermal system will be designed in the future.

Suspensions – such as a PCS – are a class of complex fluids; they can be differentiated according to the physical and chemical nature of suspended particles and suspending fluid [31]. PCM slurries are considered to be Newtonian fluids [32] until the volume fraction of micro-particles is not very large (less than 20%). Furthermore, in this case pressure drops can be generally predicted by a single phase flow correlation [14]. When the volume fraction of mPCMs is higher than 20%, a non-Newtonian behaviour may appear, especially for low shear rates [33]. This happens because the fluid becomes a “dense” or “highly concentrated” suspension, which is a kind of suspension characterised by a different behaviour. By using additives such as surfactant agents, pressure drops can be effectively reduced [14] and the behaviour of the suspension can be assumed to be Newtonian [17]. For high concentrations, Vand [34] developed an empirical model capable of predicting the slurries apparent dynamic viscosity as a function of the micro-particle volumetric fraction and of a constant that depends on shape, size and type of the single particle. However, there have been numerous studies of suspension viscosity as a function of particle concentration and composition. With the existence of so many theoretical and empirical models it is difficult to find a unifying theme [38].

The rheological behaviour is influenced neither by the capsule material [20] nor by the PCM phase transition process [13]. The apparent viscosity of PCM slurries depends only on temperature, microcapsule size and PCM concentration [28]. Once the type of application and the material were chosen – solar thermal system and n-icosane, respectively – the temperature range and the microcapsule size were determined. Therefore, the concentration was the only parameter influencing the viscosity.

Delgado et al. studied the trend of pumping power as a function of the transported heat for a slurry PCM with 10% of micro-particle concentration [35]. In this configuration, the advantages were always higher than the disadvantages. Heinz et al. observed that, with a concentration up to 30%, the pressure drop was not considerably higher than with water; a 30% concentration resulted to be a good compromise between storage capacity and pressure drops [36]. Pressure drops of an n-icosane PCS flowing laminarily through rectangular copper minichannels were studied for 10% and 20% weight concentration [37]. Nevertheless, the relationship between viscosity and concentration is not linear and different types of micro-particles, flow rates or pipes geometry may have different rheological behaviours.

### 3.3. Storage tank

Besides what happens in the flat plate collector and through the pipes, some considerations on the behaviour of the material in the storage tank should be mentioned. In literature, many examples of PCSs used in heat storage tanks can be found [38]. Some of these tanks are specifically designed for thermal energy storage in residential solar energy systems [23, 31]. One of the main disadvantages of latent heat storage systems is the low thermal conductivity of many PCMs, which causes poor melting and solidification rates. To solve this problem, many solutions were proposed. Some authors improved the geometry of the storage tank and that of the heat exchanger [39, 40], others introduced highly conductive nano-particles [41] – such as graphite composites [42] or carbon nanotubes [43] – within the PCM to enhance the effective thermal conductivity of the material.

### 3.4. Creaming

During the preliminary tests on the PCS properties, some problems of creaming appeared when the fluid was not in motion. Creaming is the movement of the mPCM particles towards the superior part of the suspension as a result of gravity [17, 44]. Creaming is due to the density difference between the dispersed micro-particles (whose density is about  $856 \text{ kg/m}^3$  (solid) and  $780 \text{ kg/m}^3$  (liquid) [14]) and the continuous phase (water). As a result of creaming, in the superior part of the suspension a layer with a higher concentration of mPCM occurs. Even though the creaming phenomenon is defined as one of the most frequent problems in PCSs [17], not many studies about creaming are available in literature. The most important and recent study on this phenomenon was carried out by Delgado et al. [45], who proposed a method to determine the physical stability of the PCS by measuring samples with a rheometer in oscillatory mode. An unstabilisation process in PCM slurries can usually take hours or even days, hence it is

important to have a model which allows to predict the behaviour of the material over time. Generally, creaming can be solved by reducing the mPCM capsule size or by adding surfactants [17].

#### 4. Design solutions

As the problems highlighted in the literature may elide the advantages deriving from the adoption of PCSs in solar thermal systems, to understand the real functioning of the proposed technology a prototypal system was designed and realised. To overcome the possible drawbacks that can affect the system, specific design solutions were adopted.

As mentioned in [29] and [30], centrifugal pumps do not generally represent a problem of capsule rupture and PCM leakage out of the shell. However, for further certainty of no broken microcapsules due to the pump action, programmable peristaltic pumps were adopted. These pumps have the advantage of not touching the fluid flowing inside the pipe and of stressing the capsules less than other kinds of pumps. A Verderflex Scientific C R31 EI was adopted in the primary loop.

Pressure drops are a problem that occurs in every HTF. In the case of PCSs, pressure drops are proportional to the PCM concentration. Concentrations which optimise the ratio of transported heat on the pumping power can be found [35]. Moreover, an excessive concentration may cause pumping or clogging problems. For this reason, several pressure drop tests with different concentrations of n-eicosane were carried out before realising the prototypal system. These tests were performed using both a rheometer and a copper pipe circuit with piezometers. Copper pipes were chosen because they are typically used in flat-plate solar collectors. From these tests, the PCS viscosity resulted similar to that of water for PCM concentration lower than 20%. For concentrations up to 45%-50%, only a slight increase in the viscosity occurred. Clogging problems due to creaming were only observed when the fluid was not in motion. For higher concentrations the PCS could not be pumped.

As previously described, several examples of PCSs used in heat storage tanks can be found in literature. To adopt technologies which are commonly in use, a traditional tank and a spiral heat exchanger were chosen for the proposed system. Since the first tests will focus on the flat plate panel and on the circuit, specific measures concerning the tank may be adopted in the future. Nevertheless, when the PCS is not in motion – such as in the storage tank – the problem of creaming occurs. For this reason in the design process of the prototype, the HTF was chosen to be continuously maintained in motion also in the storage tank. This was made possible by the use of partitions in the storage tank and of a bypass circuit with a second peristaltic pump (Verderflex OEM M3000), which is switched on when the main pump of the primary loop is stopped. This process causes a major energy consumption and a more complex pumping system. Besides, natural convection within the tank usually causes a thermal stratification in the HTF. This phenomenon is generally used to improve the heat transfer with the secondary closed loop. By maintaining the PCS in motion, this stratification of HTF in the storage tank cannot be exploited. However, the adoption of a bypass circuit was chosen because it was easiest way to overcome the creaming phenomenon. Finding a chemical solution for the creaming problem was beyond the scope of this work and it can be a proposal for the future.

#### 5. Conclusions

‘Flat-plate solar thermal collectors are the most common devices to convert solar energy into heat. Water-based fluids are commonly adopted as heat carrier for this technology, although their efficiency is limited by some thermodynamic and heat storage constraints. To overcome some of these limitations, an innovative approach is based on the use of latent heat, which can be available by means of micro-encapsulated slurry PCMs (mixtures of micro-encapsulated PCMs, water and surfactants).

In the present work, conceptual proposals of solar thermal systems filled with PCSs were presented and a prototypal system based on n-eicosane PCS was developed. Some of the thermo-physical and rheological properties and material behaviour that interest flat-plate solar thermal collectors with slurry PCM as the heat carrier were analysed. To overcome the possible problems related to the use of PCSs as HTF – such as high pressure drops, clogging in the pipes, sedimentation in the storage tank and capsule rupture due to the pumping work – specific design solutions were adopted.

Future work will focus on monitoring the prototype performance and the retrieved data will be used to validate the theoretical model. Furthermore, the knowledge on the chosen PCS will be deepened. Improved solutions for solving the aforementioned drawbacks will also be investigated.

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