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Identification and characterization of promising phase change materials for solar cooling applications

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ABSTRACT

Solar cooling technology is an attractive way to use solar thermal energy to produce cooling for buildings. The employment of taphase change materials (PCMs) as heat storage medium, to increase the range of utilization of solar thermal energy, thus improving the overall system performance, is considered very attractive. Nevertheless, in order to allow the development of latent heat storage prototypes for such an application, it is mandatory to verify the thermo-physical performance as well as the long-term stability of the available materials. To this aim, in the present paper, the most attractive commercial PCM as well as neat chemical compounds operating in the temperature range between 80 °C and 100 °C, perfectly suitable for non-concentrating solar cooling systems, have been identified and completely characterized. In particular, several cycles have been performed on each material, to verify possible instabilities in their behavior. Most of the neat materials have confirmed to be promising for this application, thanks to their really high melting enthalpy, up to 255 J/g as showed for Aluminum Ammonium Sulfate Dodecahydrate. Nevertheless, all these materials are still not stable, showing high supercooling, allotropic phase transition, incongruent melting and even absence of re-crystallization, which makes necessary an intense work to bring them to a reliability level sufficient for real application. On the contrary, the commercial PCMs, even if mostly characterized by lower melting enthalpy, ranging between 120 and 150 J/g, confirmed their stability, which makes them ready for practical applications.

1. Introduction

Nowadays, the ever increasing demand for cooling of buildings is considered one of the major causes of peak electricity request occurring during summer seasons [1]. Indeed, most of the cooling needs are covered by the employment of electrically driven vapour compression chillers, thanks to their reliability, cost effectiveness and widespread diffusion. Nevertheless, during last years, an innovative technology, known as solar cooling, has gained more and more interest [2]. Such a technology is founded on the idea that, on seasonal basis, the cooling demand of buildings is in phase with the highest availability of solar irradiation. In such a context, the possibility to couple solar thermal collectors to a thermally driven chiller, to produce cool water for the building's request, seems quite promising [3]. Usually, a closed cycle solar cooling plant is based on three main components, namely, the solar collectors field, the high temperature thermal energy storage and the thermally driven chiller. Often, other components, such as a backup system, to either provide thermal energy to the chiller or cooling energy directly to the load, and a low temperature thermal energy storage, can be also part of the plant layout [3]. In the past, a lot of efforts have been paid to the identification of the optimal plant layout, in terms of surface of solar collectors, high temperature thermal energy storage size, backup system and thermally driven heat pump nominal power [4,5]. For solar cooling systems employing non-concentrating solar collector technologies (i.e. flat plane and evacuated tubes solar collectors), the high temperature heat storage relies on the sensible heat storage technique, mostly employing water as heat storage medium. In [6] other possible materials for sensible thermal energy storage, even for solar cooling applications, have been reported. Nevertheless, it is quite known that there are other opportunities to efficiently store heat. Among them, latent heat storage, based on the employment of phase change materials (PCMs) could be an interesting alternative [7]. Actually, in a general sense, they are characterized by higher heat storage density than water, which means smaller size of heat storage tank. Moreover, since they store and release heat in a narrow temperature range, they allow to feed the thermally driven chillers with an almost-constant temperature for long time, which can be even beneficial for the performance of the chiller itself. One can argue that, thanks to the high specific heat of water, application of PCMs in a temperature range below 100 °C is not as efficient as expected [8]. This

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is surely true if the focus is on storage for domestic hot water (DHW). In fact, for such an application, there is a large temperature difference between inlet tap water (e.g. 15 °C) and DHW storage (e.g. about 60 °C), which makes water the best choice. On the contrary, in a solar cooling plant, the temperature difference between inlet and outlet on the heat storage side is limited to the temperature difference across the regenerator of the thermally driven chiller, which, from experimental outcomes, is usually around 10 °C [9]. This narrow range makes latent heat storage really attractive for this application.

Looking through the literature, some papers dealing with PCM applications for heat storage in solar cooling systems are reported [10–14]. Actually, the majority of them are referred to solar cooling plants driven by concentrating solar thermal collectors, which means temperature higher than 150 °C. A wide review of these applications is reported in [9], where available materials as well as system integration and control are discussed. An interesting example of designing and construction of a heat storage for concentrating solar cooling application is reported in [11], where hydroquinone has been employed as latent heat storage medium. The encouraging experimental results obtained at lab scale allowed to scale up the heat storage up to a 5 t latent heat storage, for a real concentrating solar cooling plant in Sevilla. Concerning latent heat storage applications in non-concentrating solar cooling plants, only few works are reported, most of them dealing with theoretical analysis. In [12] a modelling activity has been carried out to analyze the achievable performance, both from energetic and economic point of view, of a solar cooling plant embedding a macro-encapsulated PCM into a water heat tank as high temperature heat storage. The simulation outcomes confirmed the possible increasing in overall performance employing the latent heat storage, even if the results are not particularly exciting. This is strongly related to the fact that the embedded PCM has a nominal melting temperature of 44 °C, which is far from the optimal melting point, ranging between 80 °C and 100 °C, needed to properly drive the chiller exploiting as much as possible the latent heat. An interesting application of PCM in solar cooling plant is the one reported by Helm et al. [13], in this case the latent heat of fusion is exploited on the heat rejection loop (i.e. temperature around 30 °C), instead of the high temperature storage. In such a way, the temperature level at which the heat is rejected is properly controlled, thus making the chiller more efficient.

From the carried out literature survey, it is evident that still not enough activities have been dedicated to the development of latent heat storage for solar cooling systems. In particular, analyzing the available materials in the range of interest (i.e. 80–100 °C), as reported in [15], it is evident that there is not a wide possible choice. This means that, in order to properly address the heat storage design, first of all, it is mandatory to analyze the effectiveness of the achievable material, both in terms of thermo-physical parameters as well as long-term cycling stability. In such a context, the present paper deals with the experimental evaluation of the most promising PCMs for high temperature heat storage in non-concentrating solar cooling plant. In particular, after having selected both commercial and non-commercial candidates, physic-chemical analysis as well as thermo-physical characterizations have been carried out on fresh and cycled materials, in order to identify the ones already sufficiently reliable for the foreseen application.

2. Materials and methods

Commercially available sorption chillers [16,17] usually need at least 70 °C as inlet driving temperature to achieve good efficiencies in operation. Taking into account a thermal gradient between thermal energy storage and sorption chiller of at least 10 °C, in order to optimize heat transfer efficiency, the identified melting temperature range to be analyzed for solar cooling application is between 80 °C and 100 °C.

With this aim, after a literature and market survey, we have selected organic and inorganic PCMs, commercial and neat chemical compounds (non-commercial PCMs), whose melting temperature is comprised within the above reported range. Table 1 shows the identified materials. All the non-commercial PCMs, with high purity ranging from 98% and 99%, were purchased from Sigma Aldrich® and were used as received. The commercial PCMs were manufactured by "PCM Products" and they are based on organic and inorganic compounds, as below:

- PlusIce A82: blend of linear and branched hydrocarbons;
- PlusIce S83: Magnesium Nitrate Hexahydrate;
- PlusIce S89: Magnesium Nitrate.

The producing company does not declare neither the purity of the chemical compound nor the presence and the nature of the additives

Table 1
PCMs selected for our application.

		Material	T_m [°C]	Melting heat [kJ/kg]	Density [g/cm^3]	Ref.
Neat Chemical compounds (Non-Commercial PCMs)	**Organic**	α-Naphthol (≥99%) Sigma-Aldrich®	96	163	N.A.	[18]
		Xylitol (≥99%) Sigma-Aldrich®	94	263.3	N.A.	[19]
		D − Sorbitol (≥98%) Sigma-Aldrich®	97	185	*N.A.*	[19]
		Acetamide (~99%) Sigma-Aldrich®	81	241	1.159	[18]
	Inorganic/hydrated salts	$KAl(SO_4)_2 \cdot 12H_2O$ (≥98%) Sigma-Aldrich® (CODE: APSD)	91	184	N.A.	[18,21]
		$(NH_4)Al(SO_4)_2 \cdot 12H_2O$ (≥99%) Sigma-Aldrich® (CODE:AASD)	95	269	1.640	[20,21]
Commercial PCMs	**Organic**	Plus-ICE A82 PCM prodcucts®	82	155	0.850	[22]
	Inorganic/hydrated salts	Plus-ICE S83 PCM prodcucts®	83	141	1.600	[22]
		Plus-ICE S89 PCM prodcucts®	89	151	1.550	[22]

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