Review paper

Potential for Mitigation of Solar Collector Overheating Through Application of Phase Change Materials – A Review

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ABSTRACT

Demand for domestic hot water and heating is rarely perfectly concurrent with solar irradiation, which means that collectors can overheat in periods of high incident radiation and low demand. Phase change materials have been used as energy storage in space heating applications to absorbs excess heat during low demand periods for use in peak demand periods. This paper reviews the current state of research on the possibility of application of such materials as energy storage for solar collectors, in order to avoid collector overheating. Finally, various materials were evaluated and ranked for this application based on required properties and price. An example model of such materials being applied in a typical family house domestic hot water solar system is also provided.

KEYWORDS

Phase change materials, Overheating, Temperature of stagnation, Flat plate solar collector.

INTRODUCTION

One of the major limiting factors in large scale application of solar thermal collectors is their price. In mass production conditions economies of scale minimize many production costs present in smaller production runs. This makes limitations of the production process itself and the price of raw materials the primary driving forces behind high production cost. Currently the selection of materials used in collector design is relatively limited due to strict and often conflicting demands of necessary material properties. This in turn also limits the production processes which can be used. In an average collector there are strict requirements for thermal, mechanical and optical properties of the material. A significant cause of this problem is collector overheating, i.e. a high temperature of stagnation.

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The temperature of stagnation is the highest temperature reached by the collector when exposed to maximum incident solar radiation and high ambient temperature at a time when no flow through the collector is present. This can happen due to flow problems in the system, but its most common cause in normal collector operation is that the set point temperature in the hot water tank is achieved and the pump is turned off in order to avoid overheating the water in the tank.

The temperature of stagnation of the most basic flat plate solar collector design is high and regularly exceeds 150 °C. This limits the selection of materials for collectors to materials with high thermal stability and appropriately high melting points. In industrial practice this has meant that metals have been the most common materials used to produce collector absorbers. The use of alternative and cheaper materials such as polymers has been very limited. The primary factor limiting the use of polymers is the fact that most polymers undergo glass transition at temperatures as low as 100 °C. That temperature is much lower than the temperatures a standard flat plate collector’s absorber reaches during stagnation.

In spite of these limitations there have been attempts to make a polymer flat plate solar collector. An example is the research by de la Peña and Aguilar [1]. This solution doesn’t reduce the high temperature of stagnation, but instead uses a special polymer that is stable at high temperatures. The price of this material is high, and the overall price of the collector is not reduced compared to collectors made with industry-standard materials.

Another option discussed is the use of channels for air-cooling behind the collector, as presented by Hengstberger et al. [2]. Kessentini et al. [3] used a polymeric transparent insulation material. Föste et al. [4] approached the problem from another angle, and use butane instead of water as a heat transfer medium. In addition to these, thermotropic and thermochromic materials have shown promise. Significant reduction of absorbed solar radiation has been noted by this method by Muehling et al. [5]. Similar results were obtained by Föste et al. [6] and Hussain et al. [7]. This reduction is still not sufficient to enable the use of commodity polymers in every part of the collector.

The methods listed above aim to reduce or increase heat transfer to or from the collector during stagnation. Another approach was considered in Hengstberger et al. [2], by examining the use of Phase Changing Materials (PCMs) as a form of overheating protection. This potential solution is positively reviewed and potential PCMs suitable for further study were suggested. Forzano et al. [8] and Dehgahn and Pfeiffer [9] discuss integration of PCMs as energy storage in buildings in a method that may be transferable for collector applications.

The possibility of application of PCMs as overheating protection in solar collectors is a topic which has not been extensively researched so far. This paper aims to provide an extensive overview of currently available materials. It also aims to provide an analysis of their potential applicability in this application. To show the potential of this technology, an example PCM protected system will be given for a typical family house solar domestic hot water system.

OVERVIEW OF PHASE CHANGE MATERIALS

PCM are materials which undergo phase transition at a technologically advantageous temperature and have a relatively high latent heat of fusion. While phase transition can occur in any material, only a limited number meet these specific requirements. There are usually additional requirements which include, but are not limited to: non-toxicity, low or high thermal resistance, small volume change after phase transition, inertness in contact with other materials, durability, and affordability. All of these requirements make PCM selection a complex task which requires an in-depth analysis.

Mao et al. [10] provided an overview of low-temperature PCMs and their latent heat properties. Palomba et al. [11] gave an overview of PCMs used in non-concentrating
solar applications and identified paraffinic materials and hydrated salts as the most promising solutions. Kahwaji et al. [12] provided a through overview of the properties of paraffins within the temperature range for building and domestic solar applications, giving important input values for future analysis. A similar analysis of materials was given by Tao et al. [13]. Raud et al. [14] provided a cost-effectiveness analysis of PCMs for solar thermal power. The required temperature range for solar application is under 100 °C, which includes all paraffins, but only a smaller number of other materials. Based on this data, it is possible to exclude materials with phase transition temperatures outside the range of applicability in domestic hot water solar systems. A partial overview of materials selected for analysis is given in Table 1 and is adapted from the work of Pereira de Cunha and Eames [15] and Sharma et al. [16].

Table 1. PCMs selected for evaluation (part of selection shown)

| Material                        | Type  | \( T_m \) [°C] | \( \Delta H \) [kJ/kg] | \( c_{pu} \) [kJ/kgK] | \( c_{pl} \) [kJ/kgK] | \( \rho_s \) [kg/m³] | Price [EUR/m³] |
|---------------------------------|-------|----------------|------------------------|------------------------|------------------------|------------------|----------------|
| Lauric acid                     | org.  | 44             | 212                    | 2.02                   | 2.15                   | 1,007            | 319.66         |
| Sodium sulph. decahydrate       | inorg.| 32             | 180                    | 1.93                   | 2.80                   | 1,485            | 55.59          |
| CaCl₂·(H₂O)₆, MgCl₂·(H₂O)₆     | eut.  | 25             | 127                    | 1.62                   | 2.27                   | 1,661            | 92.66          |
| Stearic acid/palmitic acid      | eut.  | 53             | 182                    | 1.72                   | 2.23                   | 971              | 406.52         |
| Paraffin 18                     | org.  | 28             | 244                    | 3.00                   | 2.00                   | 894              | 486.44         |
| Paraffin 22                     | org.  | 44             | 249                    | 3.00                   | 2.00                   | 908              | 509.60         |
| Paraffin 26                     | org.  | 56             | 256                    | 3.00                   | 2.00                   | 922              | 532.77         |
| Paraffin 30                     | org.  | 65             | 251                    | 3.00                   | 2.00                   | 936              | 555.93         |

The table above is not exhaustive. Recent research methods for modifying PCM properties have been suggested which may add new materials for consideration. Xiao et al. [17] suggested employing copper foam as the supporting material in hydrated salt PCMs to enhance their thermal conductivity, which is a limiting factor in solar applications. Jin et al. [18] studied composite hydrated salt PCMs and reported an improvement in the solar thermal conversion efficiency. Rao et al. [19] reported good thermal properties for the same type of material.

Another suggested approach to modifying PCM materials is the use of micro and nano particles. Qiu et al. [20] gave a broader review of micro and nano PCMs in thermal solar applications focusing on thermal conductivity. Sivasamy et al. [21] investigated Ag-nanoparticles dispersed myristic acid. Sari et al. [22] investigated silica fume/myristic acid composite doped with carbon nanotubes. They found that with a melting temperature of around 54 °C it is a promising PCM for solar applications. Further investigation of fabrication of nano PCMs was given by Zhang et al. [23]. Chen et al. [24] proposed the addition of a small amount of CuO nano-powders to paraffins to increase light absorption. Hybrid nanofluids in solar systems are reviewed further by Shah and Ali [25]. They conclude that their use has economic and ecological benefits, but also acknowledge that there are drawbacks like instability, increased friction loses and rheological issues which prevent wider commercialization. Kumar et al. [26, 27] found that adding small amounts of silicon dioxide (SiO₂) nanoparticles increased the thermal conductivity of paraffin PCMs. Chen et al. [28] successfully used a composite carbon monolith with an organic PCM n-octadecane to achieve a high system efficiency. Li et al. [29] showed similar increases in thermal conductivity with the addition of graphite flakes to the PCM material.

Other researchers suggested a different approach with the use of micro or nano-encapsulated PCMs. Bao et al. [30] showed that the thermal conductivity of microencapsulated PCM cement composites decreases with the increase of nanosilica content, but improves with the presence of carbon fibers by up to 17.8%. This finding has implications for facade mounted solar collectors. Liu et al. [31] and Jian et al. [32] provided comparable results for other microencapsulated PCMs. Ma et al. [33] reported higher thermal conductivity and specific heat for another microencapsulated PCM.
Ma and Zhang [34] studied a nano-encapsulated phase change slurry used in a volumetric absorption solar collector, and found promising results.

While eutectic materials usually have transition temperatures outside the useful range for domestic solar, Dheep and Sreekumar [35] found promising results with long term thermal reliability, good heat storage properties and less corrosive nature with metallic components when using phenly acetic acid as a PCM in solar air heaters. Mawire et al. [36] compared a eutectic colder (Sn63/Pb37) with high density polyethylene inside similar spherical aluminum capsules. They found that Sn63/Pb37 shows potential for medium temperature applications. A new eutectic PCM with a melting temperature of 75.56 °C was described by Purohit et al. [37]. It was then tested experimentally in a solar thermal system with good results. A solar thermal storage system using stearic acid/palmitic acid eutectic PCM had a higher charging efficiency compared to paraffin and puretemp68, as reported by Prakash et al. [38]. The behavior of a stable-form PCM created by impregnating delignified wood with capric-palmitic acid eutectic mixture was investigated by Ma et al. [39] and showed promising results. However, with a transition temperature as low as 23.4 °C this material has to be excluded from the applications considered in this paper. Rea et al. [40] considered an aluminum-silicon eutectic as a PCM, but the phase change temperature is too high for domestic solar applications. Calabrese et al. [41] researched the corrosion behavior of three metal alloys when exposed to a salt hydrate PCM. Additional research is still necessary to explore the behavior of polymer tanks with PCMs.

PCM emulsions are another approach to this issue. This promising technology for increasing energy storage capacity of solar systems has so far been limited because emulsions can become unstable and lose their properties. Agresti et al. [42] described a new way of stabilizing PCM emulsions and their solution provided a gain of up to 40% in thermal capacity and long-term emulsion stability, but it had issues with undercooling.

Another proposed way of increasing effectiveness of PCM materials is by increasing heat transfer in the storage tank by employing a novel fin design. Singh et al. [43] found that a reduction of 43% in melting time can be obtained by the use of a novel configuration in combination with graphene nanofilms. Zhou et al. [44] studied the use of PCMs as anti-freeze protection with good success. A composite aerogel-paraffin PCM was investigated by Min et al. [45]. This material was found to have a high thermal conductivity and therefore fast charging. Xiao et al. [46] described a novel light-to-thermal phase change hydrogel, which can be integrated in a solar collector. Alva et al. [47] suggested the use of branched polyurethane copolymers as PCMs. It has to be noted that its charging and discharging temperatures are not ideal for the use discussed here.

Addition of graphite or graphene to PCMs is also suggested in literature. The review by Allahbakhsh and Arjmand [48] outlined the recent progress in employing graphene-based nanostructures for mitigation of problems with low thermal conductivity and shape-instability in PCMs. Gu et al. [49] described the experimental process used to obtain a form stable PCM from palmitic acid, mullite and graphite. They achieved improvements in thermal conductivity over pure palmitic acid. Han et al. [50] demonstrated that a form stable PCM can be achieved using composite expended graphite. No change was reported in thermal properties over as many as 500 cycles. This research has provided experimental data aimed to enable the use of such materials in engineering design.

**METHODS OF INTEGRATION OF PCMs AND NUMERICAL ANALYSIS**

PCMs need to be integrated into a solar system to be an effective overheating protection. This section of the paper gives an overview of possible methods of integration of PCMs and their feasibility for domestic solar collector application.

Building integration is one possible method of solar collector installation. Zhou et al. [51] gave an overview of PCM integration into a building’s envelope. This may serve as a basis for research focusing in façade-mounted collector integration. A similar approach
was outlined by Saxena et al. [52]. They found a temperature reduction of 5-6 degrees in comparison with conventional solutions. Garnier et al. [53] discussed a novel building integrated solar water heater and showed good results with limited stratification. A similar example is given by Vanaga et al. [54]. Vasquez et al. [55] used a solar accumulator detached from the collector. Muhumuza et al. [56] described the use of small volumes of PCMs as a heat transfer fluid to create thermal diodes which increased collection efficiency. The optimization of the amount of PCMs in traditional building materials was studied by Rym's and Klugmann-Radziemska [57]. This approach could potentially be expanded to other materials, such as collector frames. Another example of integration of a PCM into a building’s structure in parallel to a solar system was shown by Dehghan and Pfeiffer [58]. In this case the two are not directly connected in a single system. A similar study was done by Zhou et al. [59] and Bouhal et al. [60]. An analysis of PCMs used in concentrating solar plants was given by Tehrani et al. [61]. Shaficiean et al. [62] considered the same problem in relation to heat pipe solar collectors. Asgharian and Baniasadi [63] reviewed the use of PCMs in general applications. They found that PCM integration decreases average photovoltaic panel temperature by 9.7%. In a part of their review, Fertahi et al. [64] presented results of different studies covering the problem of integrating PCMs in stratified storage tanks. Yuan et al. [65] explored the use of PCM to delay overheating of a PV cell during the day and increase its temperature overnight. The operational principle is the same as the one discussed in this paper, though with a different intended application. A similar study was performed by Ma et al. [66].

It is important to consider the optical system of a solar collector when discussing the issue of overheating. This section gives a brief overview of the optical properties of PCMs which can be applied in solar collectors. Zhu et al. [67] described a composite window which uses a highly selective coating of cesium tungsten bronze in combination with a paraffinic PCM. This combination protects the window from overheating. An overview of the behavior of the collector’s optical system when a PCM is integrated in the glazing was given by Liu et al. [68]. Abuska et al. [69] investigated the use of a honeycomb core for a flat plate solar air collector with a PCM-Rubitherm. They found that the heat conductivity was increased. This increase was particularly significant during the discharge period, but it also slightly reduced efficiency. Similar findings were reported by Egolf et al. [70] and again by Abuska et al. [71]. Wang et al. [72] suggested integration of PCM with the buildings and active management on a day-ahead scheduling basis. This could also be applied in principle to mitigate overheating.

PCMs can also be integrated within the tank of the solar system. A number of papers covering this scenario are presented here. Mousa et al. [73] studied the behavior of a water tank with integrated PCM pipes, both theoretically and experimentally. Zhou et al. [74] investigated a solar system with a PCM in the storage tank and found an improvement in the solar fraction of the system. A numerical comparative approach towards the same problem was provided by Bouhal et al. [75]. Mahdi et al. [76] used numerical simulations to study the behavior of paraffin wax in a shell and tube latent heat thermal storage unit and found that the addition of fins enhanced the melting process by an average of 50%. A similar analysis of a finned absorber plate was given in by Josyula et al. [77]. Reyes et al. [78] described the use of a combination of two different paraffins with different melting temperatures to enhance the discharge efficiency of a solar thermal system. They found that a combination of two materials is beneficial if the lower melting temperature material is placed first.

Experimental verification is expensive and time consuming, so numerical simulations can provide a cost-effective method for testing new PCMs and methods of their application. The following section presents an overview of latest research and work in this field.

Al-Musawi et al. [79] developed a numerical model to investigate the use of a PCM as coolant in a photovoltaic thermal system. They found an increase of 8% in electrical and
25% in thermal efficiency in the case where a PCM is used. PCM integration in a photovoltaic thermal system was also experimentally tested by Choubineh et al. [80]. A similar model was developed by Rabie et al. [81] for a concentrator photovoltaic system. Motte et al. [82] presented a mathematical model of a PCM thermal process in a solar collector system. They focused primarily on heat loss reduction and overall performance improvement. The behavior of PCM in a solar chimney system was simulated numerically by Xaman et al. [83]. A similar model was developed by Fadaei et al. [84]. This is conceptually similar to a PCM integrated in a ventilated collector, and as such may be of interest for further research. A theoretical model for a solar desalinator with a PCM was given by Abu-Arabi et al. [85]. It showed good agreement with experimental results. Swami et al. [86] used a similar approach for solar dryer with PCM. Yadav et al. [87] provided a CFD simulation of the drying process in a system with a PCM. Amirifard et al. [88] suggested the use of PCMs for solar ponds. They found a 6.1% increase in charging time. Plytaria et al. [89] discussed the use of PCMs in solar cooling. They reported that the use of PCMs provided an up to 30% reduction in auxiliary energy. Wei et al. [90] presented a novel PCM based thermal energy storage system. The thermal performance of this system was evaluated with a detailed analytic thermodynamic model. The results showed that such a system is feasible. Mao et al. [91] developed a similar model in MATLAB. An experimentally validated model of an integral solar collector which has a PCM storage section integrated into a flat-plate collector was developed by Bilardo et al. [92]. This model uses an electrical analogy scheme to model the behavior of the collector. Zhao et al. [93] provided a detailed overview of the practical application of PCM integrated solar heating in Tibet.

Hirmiz et al. [94] proposed a reduced analytical methodology for sizing PCM storage tanks based on a comparison of numerical and analytical methods. Gulfam et al. [95] provided an overview of the selection process for a paraffinic PCM. Numerical parametric analysis was conducted by Kazemian et al. [96]. It was found that an increase in the melting temperature of PCM employed in a photovoltaic thermal system increased the surface temperature and decreased the percentage of PCM melted. A review was given by Jimenez-Xaman et al. [97] on the current state of research in PCMs for solar chimneys. It had a particular focus on computational fluid dynamics and global energy balance models. Based on this, a new model was formulated by Vargas-Lopez et al. [98]. Reyes et al. [99] showed that by using a fuzzy logic control system the period of energy retention of the PCM could be extended. In principle, the same should be true for the discharge from a PCM.

Elbahjaoui and El Qarnia [100] developed a model based on the finite volume method for a flat-plate collector with latent heat storage units composed of rectangular slabs. This model was later used by Elbahjaoui and El Qarnia [101] to perform an optimization study for a solar system in Marrakesh. A similar analysis was given by Allouhi et al. [102]. Sarbu and Dorca [103] provided a review of PCM materials followed by a two-dimensional heat transfer simulation model using a control volume technique. Forzano et al. [104] gave a model for energy savings per m$^3$ of PCM integrated into a building’s envelope. This is similar in its approach to the evaluation presented in this paper. A model for encapsulated PCMs was given by Raul et al. [105]. Augspurger et al. [106] provided a model for solar salts.

**EVALUATION OF PHASE CHANGE MATERIALS**

To determine the usefulness of individual PCMs it is necessary to compare them to a standard solution. In this paper that solution is taken to be a larger water tank. The first step in this evaluation process is to calculate the effective heat capacity ($c_{ef}$) [Wh/kg] for all considered materials. This is done using equation:
c_{\text{ef}} = \left[(T_m - T_{\text{low}})c_{p,s} + (T_{\text{high}} - T_m)c_{p,l} + \Delta H_m\right] \times 0.27778 \quad (1)

It includes both sensible and latent components. $T_m$ is the transition temperature of the PCM. The variables $c_{p,s}$ and $c_{p,l}$ are the heat capacities of the solid and liquid states of the PCM. $\Delta H_m$ is the latent heat of fusion. These values are given for individual PCM in literature as stated in the previous section. The value of 0.27778 is used to convert the kJ/kg heat capacities found in literature into the desired Wh/kg unit. Before calculation it is necessary to check that the temperature of fusion falls between $T_{\text{low}}$ and $T_{\text{high}}$. If not, then the appropriate term is removed from the equation, and in the other term $T_m$ is replaced by $T_{\text{high}}$ or $T_{\text{low}}$, respectively. $\Delta H_m$ also needs to be disregarded in the case where $T_{\text{high}}$ is lower than $T_m$.

For this analysis $T_{\text{low}}$, the temperature the PCM tank reaches after overnight cooling is taken to be 20 °C. $T_{\text{high}}$ is the highest allowed temperature in the solar system and therefore the tank. In this case it is set at 70 °C. This is well below the glass transition temperature of most commodity plastics which is between 90 and 120 °C. While it is true that heat transfer to and from PCMs is limited by their high thermal resistance, i.e. low thermal conductivity, the focus of this paper is on PCMs and tank design is beyond its scope. It should be noted that specific solutions were discussed by Faegh and Shafii [107], Khan et al. [108], Silva et al. [109], Liu et al. [110] and Kapsalis and Karamanis [111]. Guidelines outlined in these reviews are considered in this evaluation, but are not included in the calculation process.

Using eq. (1) the baseline value for $c_{\text{ef}}$ for water ($c_{\text{ef},w}$) can be calculated as 58.1 Wh/kg. The density of water is taken from the literature for $T_{\text{high}}$. The values obtained for other materials are then compared with water using equation:

$$r_{\text{ef}} = \frac{c_{\text{ef},\text{PCM}} \times \rho_s}{c_{\text{ef},w} \times \rho_w} \times 100 \quad (2)$$

The values of heat capacity and density are taken for each PCM that is considered, based on eq. (1) and data from literature. Based on $r_{\text{ef}}$ [%] another selection can be made. All PCMs which have a $r_{\text{ef}}$ smaller than 100% can be discarded, since using water is more volumetrically favorable than using such materials. As water is significantly cheaper than all considered PCMs, there is little reason to use PCMs instead of water if there is no decrease in tank volume.

To determine the economic viability of the remaining PCMs, the required capacity of the PCM tank needs to be determined based on the installed area of collectors of a domestic hot water solar system. The simulation model includes a flat plate collector array. To be applicable for polymer solar collectors the outlet temperature of water in the collector array ($T_w$) was set to 70 °C. This temperature is high enough to allow the water in the tank to be heated to a temperature above 60 °C and low enough to be below the glass transition temperature of most commodity plastics. The efficiency of the solar collector was calculated using equation, taken from Rodriguez-Hidalgo et al. [112]:

$$\eta_{\text{NC}} = 0.85 - 4.07 \left(\frac{T_w - T_a}{G_T}\right) - 0.007 \ G_T \left(\frac{T_w - T_a}{G_T}\right)^2 \quad (3)$$

Collector inclination was set at an angle which ensures perpendicular incidence of solar radiation at noon and an intensity and temporal distribution for the summer solstice at a latitude of 45° North. This determines the incident angle ($\theta_{\text{inc}}$) on the collector. The ambient temperature was set to 35 °C to simulate high temperatures in the summer. These inputs are shown in Table 2.
Table 2. Maximum incident solar radiation per hour

| Time [h] | 6   | 7   | 8   | 9   | 10  | 11  | 12  | 13  | 14  | 15  | 16  | 17  | 18  |
|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| θinc [°] | −90 | −75 | −60 | −45 | −30 | −15 | 0   | 15  | 30  | 45  | 60  | 75  | 90  |
| Qdiff [Wh/m²] | 43  | 55  | 126 | 140 | 159 | 162 | 153 | 179 | 178 | 101 | 89  | 56  | 27  |
| Qbeam [Wh/m²] | 239 | 395 | 481 | 600 | 684 | 747 | 777 | 729 | 665 | 640 | 518 | 394 | 255 |

Values in the table above were obtained from the Photovoltaic Geographical Information System (PVGIS) of the European Institute for Energy and Transport. The values are given for a location with longitude 16°E and latitude 45°N, during the summer solstice. \( Q_{\text{diff}} \) is the diffuse component of incident solar radiation. \( Q_{\text{beam}} \) is the direct (beam) component of incident solar radiation. Reflected incident radiation from surrounding surfaces has to be disregarded to generalize the case considered, since reflected radiation entirely depends on the local conditions on site. The total incident radiation on the collector surface is given by the following equation:

\[
G_T = Q_{\text{beam}} \times \cos(\theta_{\text{inc}}) + Q_{\text{diff}}
\] (4)

This is the maximum hourly value that can be transferred into the PCM tank by a collector array with ideal efficiency. From this the minimum (theoretical) volume of the PCM tank that needs to be included in the system to prevent collector overheating can be calculated, considering a collector with real efficiency obtained from eq. (3). This is given by equation:

\[
V_{\text{min}} = \frac{\sum G_T \times \eta_{\text{NC}}}{c_{\text{ef}} \times \rho_s}
\] (5)

Minimum tank capacity required and price of the required PCM for each case are given in Table 3. The prices for PCMs are wholesale prices of the material, and do not include transport and installation costs, as that is beyond the scope of this analysis. Both the price and the volume are given per m² of flat plate collector surface. In real world applications they need to be multiplied by the actual installed area of the collectors. Values presented per m² of collector surface are more versatile as they enable easy calculation for different commercial collector setups.

Table 3. Evaluation of PCMs (part of selection shown)

| Material            | Type   | \( T_m \) [°C] | \( \Delta H \) [kJ/kg] | \( c_{\text{ef}} \) [Wh/kg] | \( \eta_{\text{ef}} \) [%] | \( V_{\text{min}} \) [m³/m²] | Price [EUR/m²] |
|---------------------|--------|----------------|------------------------|-----------------------------|---------------------------|------------------------|---------------|
| Lauric acid         | org.   | 44             | 212                    | 87.9                        | 151.4                     | 0.039                  | 12.62         |
| Sodium sulph. decyhydrate | inorg. | 32             | 180                    | 86.0                        | 148.1                     | 0.027                  | 1.52          |
| CaCl₂(H₂O)₃ MgCl₂(H₂O)₆ | eut.   | 25             | 127                    | 65.9                        | 113.5                     | 0.032                  | 2.96          |
| Stearic acid/palmitic acid | eut.   | 53             | 182                    | 76.9                        | 132.4                     | 0.047                  | 19.03         |
| Stearic acid – acetamide | eut.   | 65             | 213                    | 85.0                        | 146.4                     | 0.042                  | 23.75         |
| Paraffin 18         | org.   | 28             | 244                    | 97.8                        | 168.4                     | 0.040                  | 19.44         |
| Paraffin 22         | org.   | 44             | 249                    | 103.6                       | 178.5                     | 0.037                  | 18.92         |
| Paraffin 26         | org.   | 56             | 256                    | 109.0                       | 187.7                     | 0.035                  | 18.52         |
| Paraffin 30         | org.   | 65             | 251                    | 110.1                       | 189.7                     | 0.034                  | 18.84         |

DISCUSSION

Prices given in Table 3 provide a minimum cost of the necessary PCM, as the method outlined in the previous section does not take into account heat transfer efficiency or rate in the PCM tank. In practice an increase in PCM volume would be necessary depending on the exact configuration of the tank and its heat transfer system. However, since most listed materials can be used in a number of configurations then a comprehensive comparison would only be possible if all such configurations were compared. This is not feasible because of the wide scope and because data is not available for a wide variety of
configurations. Therefore, most configurations would need to be either experimentally or numerically tested.

Further consideration needs to be given to health concerns for any solution with PCMs. Domestic hot water applications require a medium that is non-toxic to humans as there is a risk of contamination of hot water. This water may be ingested by humans in case of tank or heat exchanger failure. Paraffins are the safest PCM option in this respect as they are safe for human consumption. While some inorganic and eutectic PCMs have significantly lower cost per m² of collector the added cost of additional heat exchangers needed to separate them entirely from the domestic hot water circuit, and the potential danger in case of human ingestion may render them inapplicable.

Compared with water, PCMs are not as sensitive to low temperatures and are at no risk of damage if the PCM is cooled to lower temperatures during winter months since the phase change behavior is already accounted for in tank design. Such tanks are therefore suitable for external installation. This is also favorable for overnight heat dissipation. If the tank can be placed outside it can cool using outside air without affecting the heat balance of the building. The cooling will also be at a much higher rate than would be possible in a boiler room setup.

Finally, the applicability of PCM tanks as passive method of overheating protection needs to be further examined. This is due to the fact that they need to be in reserve during normal operation. Furthermore, they need a more complex regulation system to ensure that flow through their heat exchanger only occurs during collector stagnation. To achieve this, a separate pump or an automatic valve would need to be used. Both of these components are susceptible to various modes of failure. Failure of these components could then cause the collector to be left without overheating protection. Therefore, such a solution can’t be considered truly passive. In order to achieve a fully passive solution the PCM would need to be integrated in the collector, as suggested in Hengstberger et al. [2].

CONCLUSIONS

From the above analysis it can be concluded that PCMs have potential as overheating protection in solar collectors. Many of the materials reviewed offer advantages in terms of volumetric savings compared to using larger water tanks. The downside of such a system is cost as PCMs are significantly more expensive than water. Yet, the possibility of integration of PCMs directly into collectors or in tanks which can be left outside during the whole year, may justify their use regardless of cost.

Of the materials analyzed, two salt hydrates (sodium sulphate decahydrate and sodium thiosulfate pentahydrate) and two eutectic PCMs [CaCl₂ (H₂O)₆ MgCl₂ (H₂O)₆ and Mg(NO₃)₂ (H₂O)₆ MgCl₂ (H₂O)₆] proved the most cost-effective. These two salt hydrates also have the highest \( r_{ed} \) out of the materials that were analyzed. While paraffins take all top ten spots in terms of \( c_{ef} \), their relatively low density means that they are not able to achieve as high a value of \( r_{ed} \) as these other materials. It should be noted, however, that paraffins still do achieve relatively high values of \( r_{ed} \) and Paraffin 30 ranks among the top ten materials considered here. Paraffins are very interesting materials as they offer significant advantages in terms of safety, given that they are safe for human ingestion.

Further research is recommended towards more practical applications of this technology and the design of a practical system which would employ PCMs as overheating protection in solar collectors. Future research should expand this model to take into account the heat transfer in the PCM itself, as that can be a bottleneck for the operation of the system and may influence material choice in the end.

NOMENCLATURE

\[ c \quad \text{specific heat capacity} \quad [\text{kJ/kgK}] \]
\( G_T \)  
insolation  
\[ \text{[Wh/m}^2 \text{]} \]

\( r \)  
ratio of volumetric heat capacities of Phase Change Material and water  
\[ \% \]

\( Q \)  
incident radiation per hour per unit of collector area  
\[ \text{[Wh/m}^2 \text{]} \]

\( T \)  
temperature  
\[ \text{[°C]} \]

\( V_{\text{min}} \)  
minimal required volume of Phase Change Material  
\[ \text{[m}^3\text{PCM/m}^2\text{coll]} \]

**Greek letters**

\( \rho \)  
density  
\[ \text{[kg/m}^3 \text{]} \]

\( \eta_{\text{NC}} \)  
efficiency of a flat plate solar collector  
\[ \% \]

\( \theta_{\text{inc}} \)  
angle of incidence of solar radiation  
\[ \text{[°]} \]

\( \Delta H_m \)  
latent heat of fusion  
\[ \text{[kJ/kg]} \]

**Subscripts and superscripts**

\( a \)  
ambient

\( \text{beam} \)  
beam component of solar radiation

\( \text{diff} \)  
diffuse component of solar radiation

\( \text{eff} \)  
effective

\( \text{high} \)  
maximum temperature in the tank

\( \text{low} \)  
temperature after overnight cooling

\( m \)  
phase transition

\( p.l \)  
heat capacity in liquid state of Phase Change Material

\( p.s \)  
heat capacity in solid state of Phase Change Material

\( \text{PCM} \)  
phase change material

\( s \)  
density in solid state of Phase Change Material

\( w \)  
average for water at collector inlet and outlet

**Abbreviations**

eut.  
Eutectic

inorg.  
Inorganic

org.  
Organic

PCM  
Phase Change Material

sulph.  
Sulphur

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