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HEAT STORAGE BY TWO-GRADE PHASE CHANGE MATERIAL

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Abstract

A two-grade heat storage system (60 °C – 30 °C and 30 °C – 20 °C) based on calcium chloride hexahydrate and calcium chloride tetrahydrate was developed. The storage capacity changes during the cycles are given, and a possible use of a solar energy storage system for domestic hot water is discussed.

Keywords: solar energy, heat storage, phase change material, calcium chloride hexahydrate.

1. Energy Storage by Phase Change Materials

Phase change materials (PCM) based on melting and freezing have several advantageous properties. The specific heat storage (energy/volume) of these materials is much greater than that of water, brick or stone. The energy storage occurs mainly at the melting point, so these systems can be considered as isothermal heat storage systems.

The appeal of phase change materials lies in the fact that their use may bridge the time lag between availability and use of energy, thus making the use of solar energy more economical, and by storing electrical energy as thermal energy in periods outside the peaks, the load of electrical power stations may be made more uniform.

The work done with phase change materials during the past decade consisted mainly of fundamental research and pilot plant experiments. Several models have been developed for analyzing the thermal characteristics of latent heat thermal energy storage systems [1]–[4]. Pilot plant experiments have been focused on solar heat pump systems [5, 6], and concrete wall and floor systems for building energy storage [7, 8].

The repeated melting and crystallization during the heat storage process may result in a decrease of the heat storage capacity. Several accelerated thermal cycle tests of latent heat-storage materials have been suggested to predict the thermal characteristics in case of longer use [9].

The well-known PCMs are as follows: $CaCl_2 \cdot 6H_2O$, $Na_2SO_4 \cdot 10H_2O$, $CH_3COONa \cdot 3H_2O$, paraffins, stearic acid [10].

Sometimes the isothermal storage level might be disadvantageous. If the energy to be stored is available at a much higher temperature level than the melting point of the heat storage material, the storage occurs at a lower temperature level than that of the source.

A worse case may occur if the melting point of the PCM is higher than the temperature level of the energy source. Then there is no heat storage and a large amount of heat may be lost.

These cases may occur during solar energy storage when the temperature of the energy transporting medium from the solar collector is higher than the melting point of the PCM applied (the storage is realized at a not sufficiently high temperature) or the temperature of the transporting medium is lower than the melting temperature of the PCM (there is no storage).

There are three possibilities to solve this problem.

1. Application of a material with high specific heat. The average specific heat of solid materials is $3\ \mathrm{kJ} \cdot \mathrm{dm}^{-3}\mathrm{K}^{-1}$, the specific heat of water is $4.18\ \mathrm{kJ} \cdot \mathrm{dm}^{-3}\mathrm{K}^{-1}$, therefore a large volume must be involved in the storage process.
2. Application of two phase change materials, one with a lower melting point and another with a higher melting point (the storage volume can be reduced, but two separate storage tanks are necessary).
3. Application of a crystal hydrate which crystallizes in two different hydrate forms and the two forms have different melting points [11, 12].

Calcium chloride may be a promising material to accomplish the third way mentioned above. Calcium chloride forms different crystal hydrates ($CaCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 4H_2O$, $CaCl_2 \cdot 2H_2O$) and they have different melting points 29.9 °C, 43.3 °C, 130 °C.

To widen the temperature range of storage by a PCM the following composition was applied: 211.4 mol $CaCl_2$/1000 mol H_2O. This composition corresponds to point P_1 in the phase diagram of $CaCl_2 - H_2O$ (*Fig. 1*).

To explain the storage process let the starting point be P_1 (charged position at 43.3 °C). During the process of exhausting the storage system starts to cool following the liquidus curve $P_1 \rightarrow P_2$. The energy dissipation is accompanied by a continuous temperature decrease and by the crystallization of $\alpha - CaCl_2 \cdot 4H_2O$.

The process continues down to 29.9 °C when another material, $CaCl_2 \cdot 6H_2O$ crystallizes and the process remains isothermal. In lack of seeding crystals, the crystallization of $\alpha - CaCl_2 \cdot 4H_2O$ continues in the form of a metastable phase (dashed line). This process is harmful from the point of view of the heat storage system and can be prevented by the addition of a seeding crystal, strontium hydroxide octahydrate.

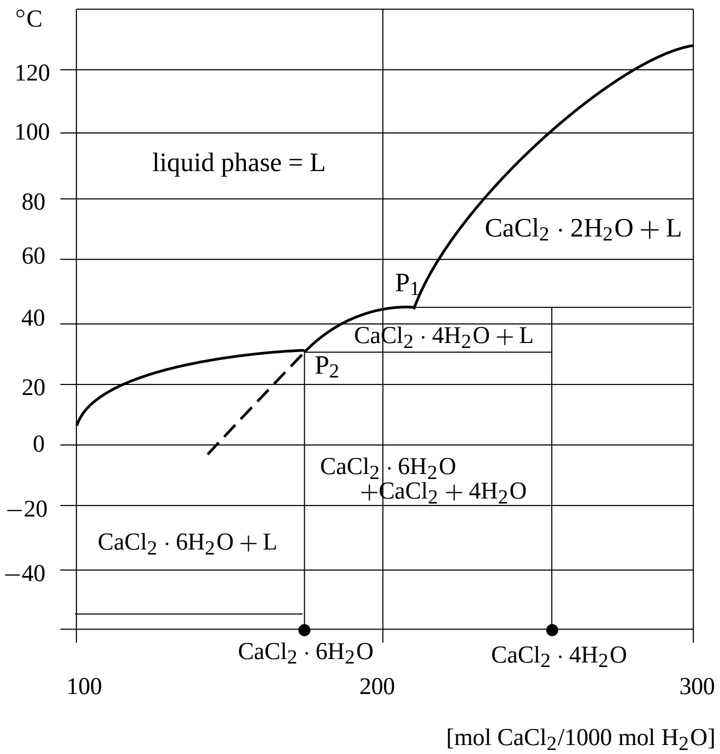

Fig. 1. Section of the phase diagram of the $CaCl_2 - H_2O$ system

During the energy storage period the starting point is P_2, where $CaCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 4H_2O$ are present. $CaCl_2 \cdot 6H_2O$ melts totally at 29.9 °C (semicongruent melting). Increasing the temperature, the liquid dissolves more and more $CaCl_2 \cdot 4H_2O$ (endothermal process). The rate of dissolution is generally not high enough to reach the equilibrium, therefore when the temperature exceeds 43.3 °C, $CaCl_2 \cdot 4H_2O$ melts. The melting process is peritectic, and a small amount of solid $CaCl_2 \cdot 2H_2O$ will be formed during the melting. The precipitated and settled material should be dissolved in the liquid phase, but the rate is very low again. So, increasing the number of heat storage cycles, this phase separation may cause a decrease in the heat storage capacity.

2. Experimental

A transparent PVC tube, 1200 mm long, diameter 90 mm was filled with 7.2 dm^3 57 mass% $CaCl_2$ solution (technical grade). 5 g of $Sr(OH)_2 \cdot 8H_2O$ was applied as seeding crystal. Inside the tube an electrically heated plate (110 W) 1110 × 80 mm was vertically inserted. The heatflow density was measured on the outer surface of the tube and the temperature was measured in the middle of the tube. During the heating – cooling cycles natural air convection was allowed. The two ends of the tube were insulated. The heat storage tube was subjected to heating (8 hours) and cooling (16 hours) cycles at room temperature (20 ± 3 °C). The heatflow density was recorded for some cycles.

Longer cycle times measured in air instead of water provide more reliable results from the point of view of the examination of the decrease in heat capacity (degradation of phase change material). Short cycle times shorten the time of the supercooled state, so a smaller amount of metastable phase of $\alpha - CaCl_2 \cdot 4H_2O$ can be formed.

A characteristic heatflow from the tube surface versus time curve is represented in *Fig.* 2. The first shoulder of the curve observed during the heating period (1–8 hour) is due to the isothermal melting of $CaCl_2 \cdot 6H_2O$. After the shoulder the dissolution and melting of $CaCl_2 \cdot 4H_2O$ occur. In the cooling period a small shoulder represents the crystallization of $CaCl_2 \cdot 4H_2O$. The heatflow minimum shows that the crystallization of $CaCl_2 \cdot 6H_2O$ does not start at the melting point of $CaCl_2 \cdot 6H_2O$ (29.9 °C).

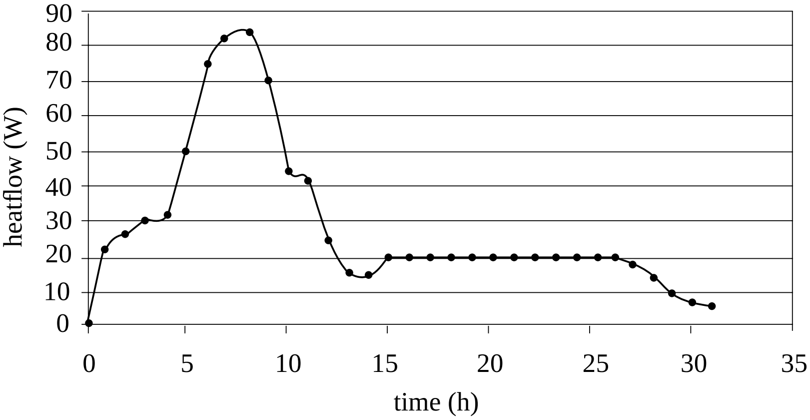

Fig. 2. Heatflow of the heat storage tube in the 260th cycle

After 1 – 2 °C supercooling the seeding crystals initiate the crystallization and the heatflow rises and remains constant for a longer time.

To measure the heat capacity the curve was integrated from 85 W heatflow (60 ± 3 °C) to the heatflow minimum (29 ± 2 °C) (storage capacity of the first grade) and between the heatflow minimum (29 ± 2°C) and 3 W heatflow (storage capacity of the second grade) (22 ± 2°C).

3. Properties of the Two-Grade Storage System

The system (211.4 mol $CaCl_2$/1000 mol water/$Sr(OH)_2 \cdot 8H_2O$ seeding crystals) can be considered as a two-grade heat storage system. The high level storage can be accomplished in the range of 60 – 30 °C (I. grade, phase change of $CaCl_2 \cdot 4H_2O$) and the low level can be achieved between 30 – 20 °C (II. grade, phase change of $CaCl_2 \cdot 6H_2O$). The temperature range was chosen arbitrarily and could be justified by practical considerations.

Theoretically the low level storage is isothermal, because the heat of phase change is used at the crystallization and melting temperature (29.9 °C) of calcium chloride hexahydrate. Because of the peritectic character of the solid/liquid phase change of calcium chloride tetrahydrate, the storage at the higher level is not isothermal. Therefore, the high-level storage system can be considered in the range of 60 – 30 °C as a heat storage system with high specific heat.

The storage units containing a PCM often change their storage capacity as a function of cycle number and the way of operation. These changes may be reversible or irreversible. The change of the storage capacity of the first grade (60 – 30 °C) and the second grade (30 – 20 °C) during the cycles can be seen in *Fig. 3*.

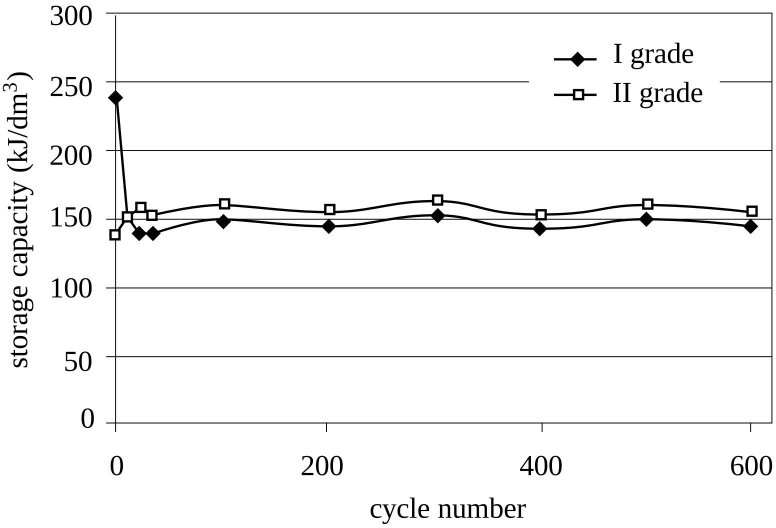

Fig. 3. Heat storage capacity of the first and second grade versus the cycle number

The storage capacity of the first grade decreases rapidly while the capacity of the second one slowly increases. Increasing the cycle number the storage capacities remain nearly constant. The decrease is due to the peritectic melting of $CaCl_2 \cdot 4H_2O$ (segregation of $CaCl_2 \cdot 2H_2O$) and the slow dissolution of the solid material. Due to the precipitation of $CaCl_2 \cdot 2H_2O$ more water is available for the formation of $CaCl_2 \cdot 6H_2O$, thus the amount of this material and the capacity increase. Reaching an equilibrium between precipitation and dissolution, the storage capacity remains constant.

The storage capacity of the grades depends on the way of operation. After hundred cycles between 20 – 60 °C the temperature of the phase change material during the next heating – cooling cycles never dropped below 30 °C. These cycles resulted in a slight increase in the storage capacity of the first grade and approached 250 kJ/dm^3 (*Fig. 4*). The increase in storage capacity is due to the slow dissolution of $CaCl_2 \cdot 2H_2O$ and $CaCl_2 \cdot 4H_2O$ segregated during the previous cycles in the temperature range 60 – 20 °C.

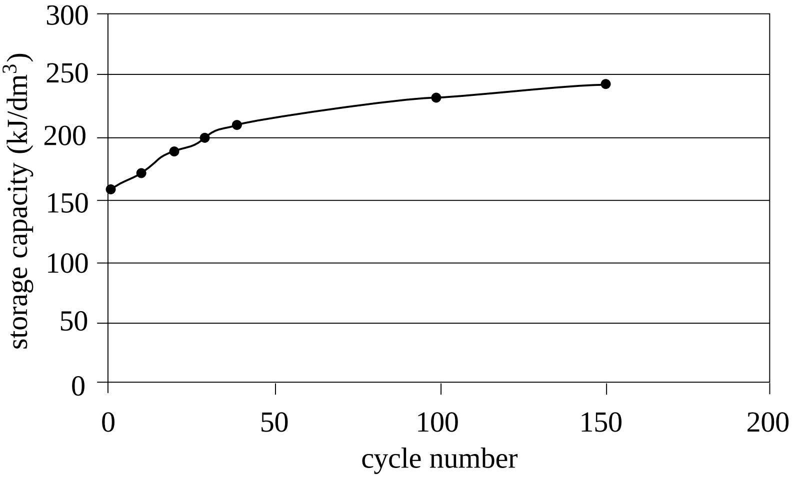

Fig. 4. Heat storage capacity of the first grade (minimum temperature during the cycles $t_I > 30$ °C)

There is another possible way of operation of the storage system if the temperature of the PCM during the storage cycles never exceeds 38 °C. In this case the storage capacity of the second grade continuously decreases and stabilizes at about 90 kJ/dm^3 after the 60th cycle (*Fig. 5*). This is due to the formation $\alpha - CaCl_2 \cdot 4H_2O$ in each supercooling period. This way of operation is not preferable for this system for a longer time. The decrease is not irreversible because some storage cycle regenerates the storage capacity if the temperature maximum in the PCM exceeds 50 °C.

4. Solar Radiation in Hungary

The climate of Hungary is continental. The total global solar radiation is represented in *Fig. 6*. The average energy collected by a flat solar collector for domestic hot water can be seen in *Fig. 7*.

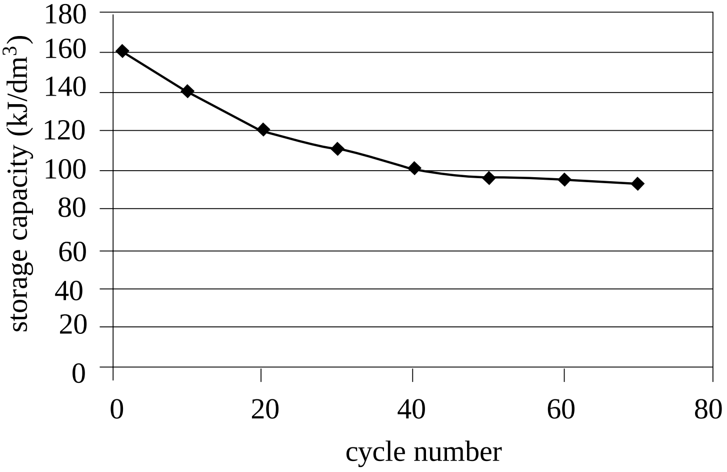

Fig. 5. Heat storage capacity of the second grade (maximum temperature during the cycles $t_{II} < 38$ °C)

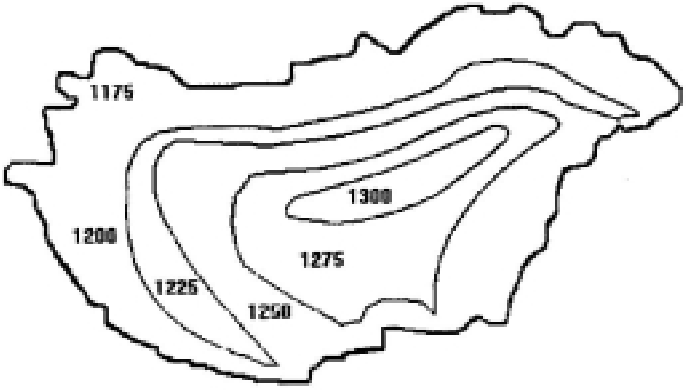

Fig. 6. The annual total solar radiation in Hungary (kWhm^{-2}year^{-1}

The average utilizable solar energy during the summer half year (15. Apr. – 15. Oct.) is 2.8 kWh $\cdot$ m^{-2}day^{-1} and during the winter half year (15. Oct. – 15. Apr.) 1.1 kWh $\cdot$ m^{-2}day^{-1}. The heat consumption of a domestic hot water supply system can be seen in *Fig. 8*.

The available solar energy and the heat consumption of domestic hot water suggest that the efforts to trap solar energy is not a fiction in Hungary.

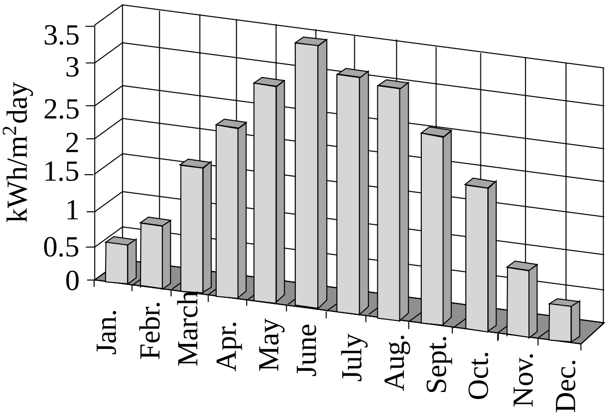

Fig. 7. The average utilizable solar radiation for domestic hot water (Hungary)

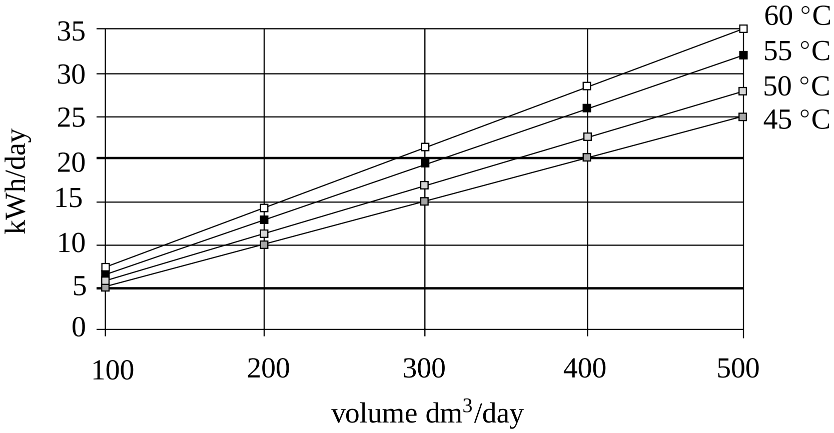

Fig. 8. Heat consumption of domestic hot water supply

5. Double Grade PCM for Domestic Hot Water

The problems of heat storage in solar water heating systems are to be dealt with from two different points of view: on the one hand, the available solar gain, on the other hand, the time schedule of hot water consumption should be considered.

The ratio of the maximum and minimum of the average daily solar gain of different months is 6:1, under Hungarian climatic conditions. It is obvious that at lower solar gain a lower energy carrier temperature can be achieved. If the phase-change temperature of the PCM used corresponds to these conditions, a phase change will occur on all days when the solar gain exceeds a certain value.

If a PCM of a low phase change temperature is selected, the process of phase change will take place even at a low solar gain, thus the number of days, when the latent heat storage can be used, will be high during the year. However, the stored heat is less valuable, due to the low temperature level. Selecting a higher phase change temperature, the process of phase change will take place only at a higher solar gain. The number of days with higher solar gain is less, thus the period in which latent heat storage can be used, is short. On the other hand, the stored heat is much more valuable, due to the high temperature level. A double grade PCM combines the advantages of both versions.

From the point of view of hot water consumption the following points should be considered: the maximum of the hot water temperature cannot exceed the temperature of the energy carrier medium, moreover, it is less by $4-6$ K, depending on the heat exchanger between the hot water and the energy carrier, thus the volume of hot water in the storage tank and the temperature of the energy carrier defines the maximum of the storage capacity. The system cannot accumulate more energy, even if the solar gain would help a further heat accumulation.

Having a phase change material with a melting point close to the maximum of the available temperature, the excess of solar gain can be accumulated without the increase of temperature. The capacity of the system will be limited by the latent heat and the mass of the PCM.

Besides the increase of the heat storage capacity, this type of PCM improves the conditions of heat exchange during the heating up period. The heat exchange is more efficient, if the temperature difference between the stored hot water and the energy carrier is bigger. The presence of the double grade PCM in the storage system slows the increase of the hot water temperature, improving in such a way the efficiency of the heat exchange.

This is not favourable if the temperature of the hot water is lower than 36 °C, however, at such a low temperature an auxiliary heating must be switched on anyway, whether or not a PCM is applied. A possible scheme of a storage system is represented in *Fig. 9*.

The PCM is to be located in the upper part of the storage tank. The energy carrier – domestic hot water heat exchanger is opened if $\text{Tec} - \text{Tl} \geq 3-4$ °C. The energy carrier – PCM heat exchanger is on, if $\text{Tec} - \text{Tl} < 3-4$ °C and $\text{Tec} > \text{Tpcm}$.

In lack of consumption, the heat transfer between the PCM and the tank water occurs by natural convection. A forced flow increases the heat transfer during consumption. Due to the limited heat transfer coefficient between the PCM and the hot water ($U \sim 4-5\ \mathrm{W \cdot m^{-2} K^{-1}}$), the heat exchanger between the PCM and hot water cannot be considered as an ‘instant’ one, heating up the water as it flows through when consumption takes place, even if it has a large surface. The surface to volume ratio of PCM containers can be increased if the PCM is encapsulated in small units.

The low heating up process of the PCM is advantageous, when domestic hot water is heated by a heat exchanger in the lower part of the storage tank – the heat will be absorbed by the PCM slowly, water of higher temperature will be available in this period for consumption. Later, when the water temperature is high enough

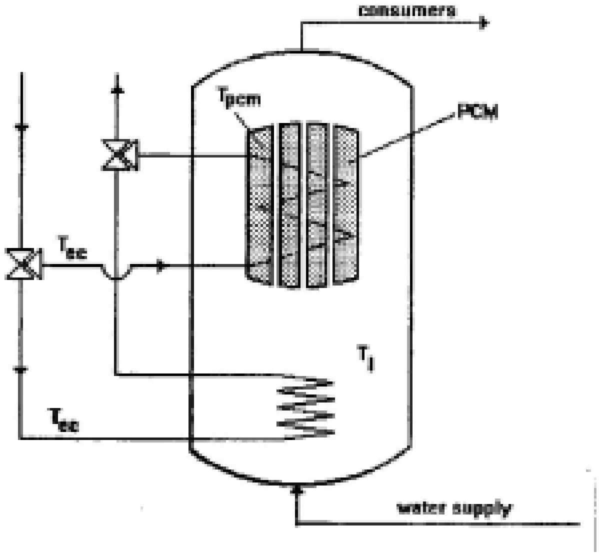

Fig. 9. Scheme of a storage tank (Tec: temperature of energy carrier, Tl: temperature of the water, Tpcm: temperature of the phase change material)

and the sensible capacity of the storage system is full, the PCM itself can be heated by the energy carrier.

The PCM can be encapsulated in small units, the energy carrier can flow through a coil, the domestic hot water between the units, and the units and the coil. The PCM containing storage system may reduce the tank volume and serve as a preheater for the gas boiler. The thermal behaviour of this system is planned to be measured in the near future.

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