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Prototype thermochemical heat storage with open reactor system

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HIGHLIGHTS

▸ A selection study on salt hydrates for thermochemical heat storage is carried out.
▸ A lab scale open sorption thermochemical heat storage system is built.
▸ The lab prototype thermochemical storage is tested with 17 l of $MgCl_2 \cdot 6H_2O$.
▸ The lab prototype was able to provide 50 W heating power at 60 °C, with an instantaneous COP of 12.
▸ Improvement of heat recovery and pressure drop will increase the performance.

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ABSTRACT

Thermochemical (TC) heat storage is an interesting technology for future seasonal storage of solar heat in the built environment. This technology enables high thermal energy storage densities and low energy storage losses. A small-scale laboratory prototype TC storage system has been realized at ECN, applying an open sorption system concept. The packed bed contains 17 dm^3 of sorption material and is capable of generating 150 W of thermal power. An effective energy storage density of approximately 0.5 GJ/m^3 was obtained.

1. Introduction

In summer, the solar heat available exceeds the residential heat demand, while in winter the heat demand exceeds the solar supply. For the future conversion of passive houses into energy neutral houses, a solution is to store the excess solar energy in summer, and use it to meet the heat demand in winter by means of seasonal heat storage. However, conventional storage technology based on water tanks requires large volumes of typically >40 m^3 per residence. Such volumes are too large to be placed inside an average family house. An alternative option is to store heat by means of chemical processes using a reversible reaction: $A(s) + B(g) \Longleftrightarrow AB(s) + \text{heat}$. Such thermochemical heat storage has an energy storage density up to 10 times higher than water (depending on the thermochemical material used), with the additional benefit that, after charging, the heat can be stored for a long time without losses. With thermochemical materials (TCM), the entire heating demand of a low-energy house during winter could be met using a storage volume of 4–8 m^3, that is charged during summer by solar collectors. These materials can be dried in summer with heat from a solar thermal collector system. During winter, water vapor is fed to the dried material, resulting a reaction in which the heat is released again. This heat can be used for space heating and tap water heating.

Thermochemical heat storage can be of different types: based on physisorption in adsorbing materials (e.g. zeolites), based on absorption in hygroscopic solutions (e.g. a NaOH solution) and based on absorption in salts (e.g. salt hydrates). Presently, heat storage with zeolites receives much attention [1,2]. These materials have a good cyclic stability and an energy storage density that is substantially higher than water, but that is modest when compared to other thermochemical materials. Furthermore, the use of zeolite for seasonal heat storage is rather expensive. Hygroscopic solutions [3] are interesting because of their low cost and good transport characteristics, allowing a system design with a dedicated reactor separate from the storage vessels. Compared to absorption in zeolites or solid salt hydrates, they have a relatively

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low temperature rise. Also, the harmful character of suitable salt solutions is a point of attention for application in the built environment. Salt hydrates, finally, are promising because of their potentially high energy storage density and low cost, while the main disadvantage is their lower stability and relatively slow kinetics. In addition, some salt hydrates are corrosive. Since low cost and high energy density are seen by the authors as mandatory for seasonal heat storage [4], the research presented here focuses on low-cost salt hydrates.

2. TC storage system concept

The TC heat storage research at ECN focuses on open sorption systems as shown in Fig. 1. In such systems, water vapor is exchanged with the ambient. The storage is charged during summer with solar heat from the vacuum tube array. A fan is used to drive the heated air through a packed bed filled with the storage material, thereby charging (drying) the material, and the water vapor released by the salt is discharged to the ambient. During winter, when the heat is needed, moist and cold ambient air is flown through the system and exits as hot and dry air, due to the energy released in the reaction between the dried salt and the water vapor. This air can be used for space heating and tapwater heating. In winter, the amount of moisture in the air is limited. Therefore, to obtain sufficient performance, it may be required to increase the moisture content of the air by additional evaporation of water using heat from a low temperature heat source such as a borehole (not shown in the figure).

3. TC material selection

Many characteristics are important for the active material in a thermochemical heat storage, such as energy storage density, temperature range, cyclability and reaction kinetics. Because of the large amount of thermochemical material required for seasonal heat storage applications, as well as the strict safety regulations in the built environment, safety and cost of the materials are also very important aspects.

A literature study was carried out for thermochemical materials based on a number of selection criteria. The most important of these were the energy storage density and the charge/discharge temperature. This temperature was selected to be between 50 °C (which was considered to be the minimum temperature for tap water heating) and 150 °C (which was considered to be the maximum temperature that could be supplied by a solar collector system while still having a sufficient collector efficiency). The focus of the literature study was on salt hydrates, because of their potential for low cost, high energy density and safety. For the temperatures for charging and discharging, the equilibrium temperature was taken for the salt-water reaction at 12 mbar water vapor pressure (being the vapor pressure at 10 °C, which is a typical borehole temperature in the Dutch climate).

A number of salt hydrates was identified from the literature as potentially interesting. Four promising materials identified in the selection were $MgSO_4{\cdot}7H_2O$, $Al_2(SO_4)_3{\cdot}18H_2O$, $MgCl_2{\cdot}6H_2O$ and $CaCl_2{\cdot}6H_2O$. As an example, for magnesium chloride, literature values are shown in Fig. 2, based on data from Kipouros and Sadoway [5]. The figure shows a graph of the equilibrium pressure for the different dehydration steps in magnesium chloride as a function of temperature. For a vapor pressure of 12 mbar (corresponding to evaporation at 10 °C), the corresponding equilibrium temperatures are shown in Table 1.

To check the literature values and to obtain information on the reaction kinetics, the selected materials were tested under dynamic conditions. Several materials were tested, among which $MgSO_4{\cdot}7H_2O$, $Al_2(SO_4)_3{\cdot}18H_2O$, $MgCl_2{\cdot}6H_2O$ and $CaCl_2{\cdot}6H_2O$. First, the materials were tested by TGA measurements, as described previously by Zondag et al. [6]. As an example, the dehydration of $MgCl_2{\cdot}6H_2O$ is shown in Fig. 3. Clearly, the $MgCl_2{\cdot}6H_2O$ shows significant drying when heated to 150 °C.

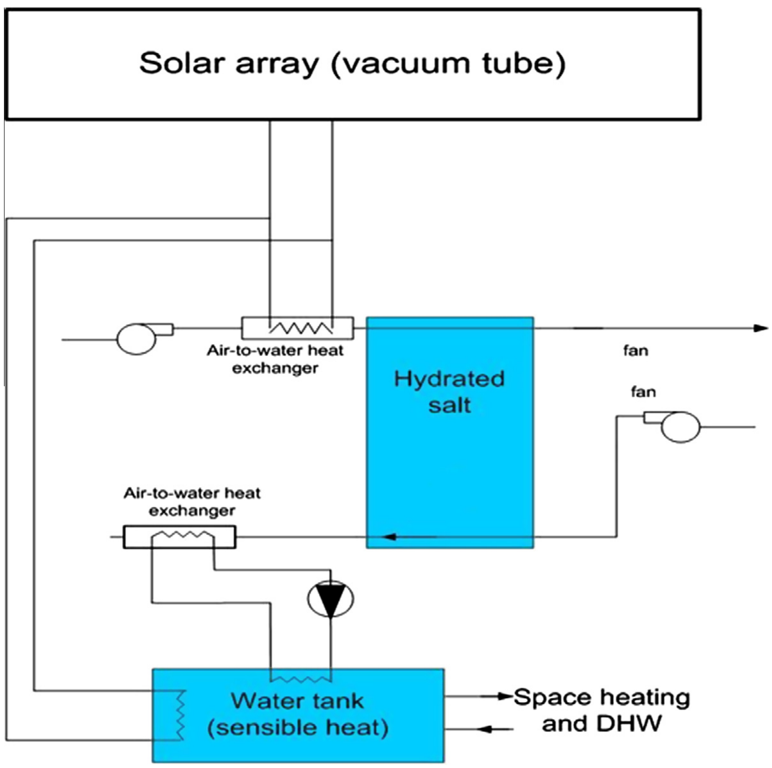

Fig. 1. Open sorption TC heat storage system.

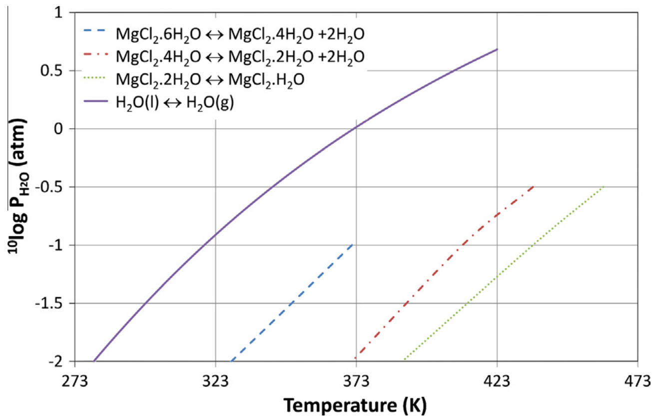

Fig. 2. Pressure–temperature diagram of the equilibrium curves for the hydrates of $MgCl_2$ (data from Kipouros [5]).

Table 1
Equilibrium temperatures of different hydrated forms of $MgCl_2$ at 12 mbar vapor pressure [5].

Reaction	Equilibrium temperature
$MgCl_2 \cdot 6H_2O \Longleftrightarrow MgCl_2 \cdot 4H_2O + 2H_2O$	57 °C
$MgCl_2 \cdot 4H_2O \Longleftrightarrow MgCl_2 \cdot 2H_2O + 2H_2O$	96 °C
$MgCl_2 \cdot 2H_2O \Longleftrightarrow MgCl_2 \cdot H_2O + H_2O$	117 °C

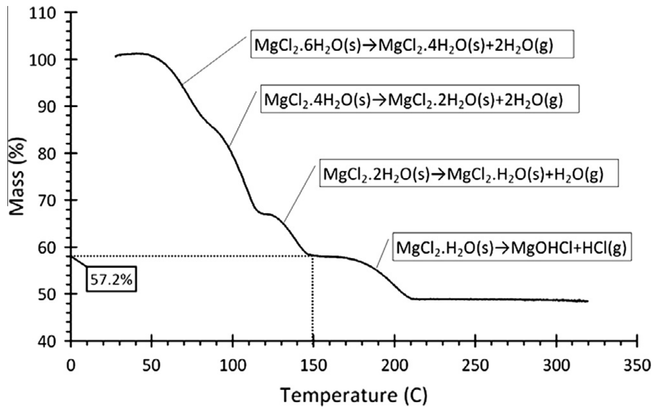

Fig. 3. Mass of $MgCl_2 \times 6H_2O$ versus temperature, showing the water loss during the dehydration process (heating rate 1 °C/min).

Next, the materials $MgSO_4{\cdot}7H_2O$, $Al_2(SO_4)_3{\cdot}18H_2O$ and $CaCl_2{\cdot}6H_2O$ were dried at 150 °C, while $MgCl_2{\cdot}6H_2O$ was dried at 130 °C, because of side reactions at higher temperatures (see Fig. 3). Subsequently, these materials were placed in an evacuated setup and were hydrated with vapor supplied by an evaporator [6,7]. In Fig. 4, the results of these hydration measurements are shown. The temperature rise in the materials is measured on uptake of water. Two conditions are shown:

- Reactor at 25 °C, evaporator at 25 °C (25R-25E). This is a test under lab conditions. In both $CaCl_2$ and $MgCl_2{\cdot}2H_2O$, the temperature rose from 25 °C to 87 °C (a temperature rise of 62 °C). The two tested sulfates showed a much lower temperature rise.
- Reactor at 50 °C, evaporator at 10 °C (50R-10E). This corresponds to realistic conditions as would occur in an actual system, in which water vapor is generated by a borehole at 10 °C. For $MgCl_2{\cdot}2H_2O$, a temperature rise from 50 °C to 68 °C was found, while for $CaCl_2$, a lower rise from 50 °C to 60 °C was measured. Again, the performance of the sulfates was lower.

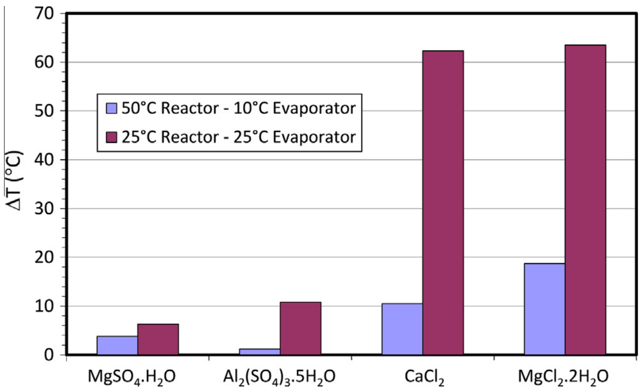

Fig. 4. Temperature rise in evacuated setup on hydration.

Based on these results, $MgCl_2{\cdot}6H_2O$ was chosen as the active material to be used in the reactor, using the reaction:

$$MgCl_2 \cdot 6H_2O(s) + \text{heat} \Longleftrightarrow MgCl_2 \cdot 2H_2O(s) + 4H_2O(g)$$

With this reaction, a high energy storage density of ~2 GJ/m^3 can be realized on crystal level. For a packed bed with 50% porosity, this results in ~1 GJ/m^3. In addition, the discharge temperature is sufficiently high to be used for tap water heating at 60 °C, and the charge temperature is sufficiently low to be able to regenerate the storage material by means of solar thermal collectors at 130 °C.

4. Experimental setup

A reactor system was built, containing a reactor with a packed bed capacity of 17 l. The setup consists of a full system, so apart from the reactor also the other system components appearing in Fig. 1 are present, such as a heat source (resembling the solar collectors), a heat sink (resembling the residential load), the heat exchangers and the fan. An open system has been built (see Fig. 1), in which the water vapor is taken from the ambient air.

A schematic representation of the built system is shown in Fig. 5, while photographs of the built prototype are shown in Fig. 6. The system can both charge and discharge the packed bed. In the design, going from dehydration to hydration, the flow direction is reversed, as indicated by the arrows in Fig. 5.

The reactor system was designed to produce a power of 50 W to the load. The power that can be generated is directly proportional to the moisture flow entering the packed bed. An air flow of approximately 500 l/min was used. A condenser was connected to the air inlet for hydration, to remove any excess water from the incoming lab air, and reduce the vapor pressure in the incoming air to 12 mbar. Otherwise, a high vapor pressure in the lab air would lead to a performance that would be higher than could be expected under realistic winter conditions.

A thermostat bath that could both heat and cool was used for the heat source and the heat sink, providing the function of solar collector in the charging setup and the function of thermal load in the discharge setup.

An important component in the system is the air-to-air heat exchanger. Heat in the outgoing air is used to preheat the incoming air. The performance of this component is essential for the overall thermal efficiency of the charging and discharging of the TC storage system.

5. Results and discussion

Hydration and dehydration experiments have been carried out successfully in the prototype storage system. During dehydration,

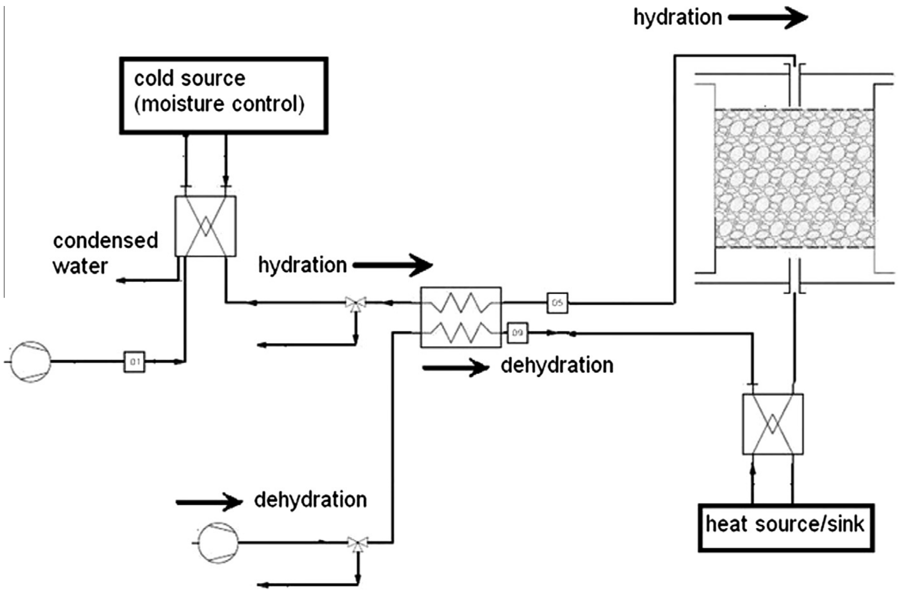

Fig. 5. Schematic representation of TC reactor storage system setup.

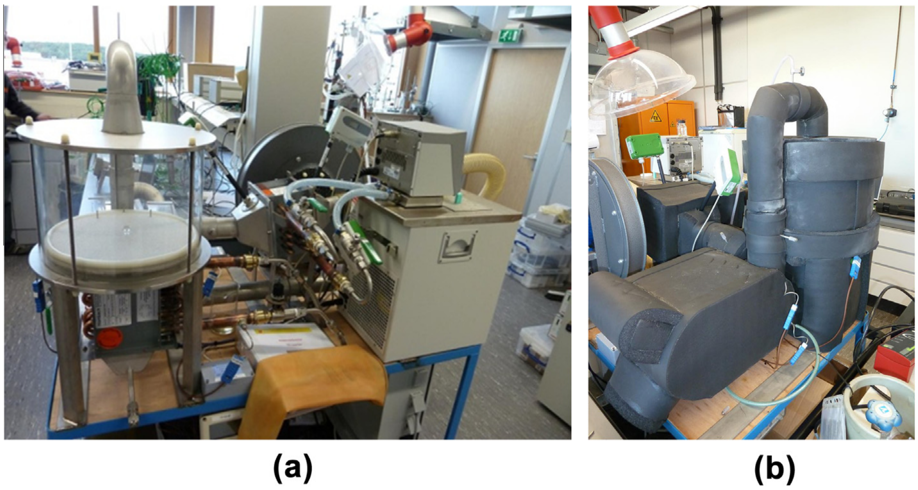

Fig. 6. Photographs of prototype thermochemical storage system, (a) before and (b) after insulation.

the storage was charged using 130 °C heat. The dehydration temperature front was seen to proceed through the storage reactor from the inlet to the exit, and the active material was seen to dehydrate. Note the steps in the temperature curves measured in the packed bed, as shown in Fig. 7. These are related to the dehydration steps in the $MgCl_2{\cdot}6H_2O$. In addition, Fig. 8 shows the vapor pressure at the outlet of the TC storage system. Clearly, during the first 1800 min (=30 h), additional water vapor is generated in the reactor system by dehydration of the packed bed, as is clear from the increase in vapor pressure between inlet and outlet.

The storage was cooled down to ambient temperature after the dehydration, while the heat remained stored in chemical form. On subsequent hydration, laboratory air was flown through the system. The lab air was first passing the condenser (set to 10 °C), to generate 12 mbar saturated air. Next, the air was preheated in the air-to-air heat exchanger (ATA) by the outgoing air and then entered the storage. The air temperatures in the system during hydration are shown in Fig. 9. The figure shows a temperature rise in the storage of 14 °C in the bed, that heats up the incoming air from 50 °C to 64 °C. The heated air then passes the heat exchanger

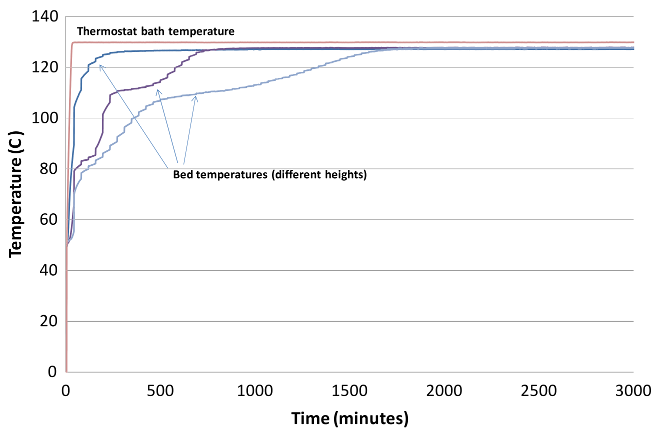

Fig. 7. Temperatures in the packed bed during charging (dehydration) of the TC heat storage at 130 °C.

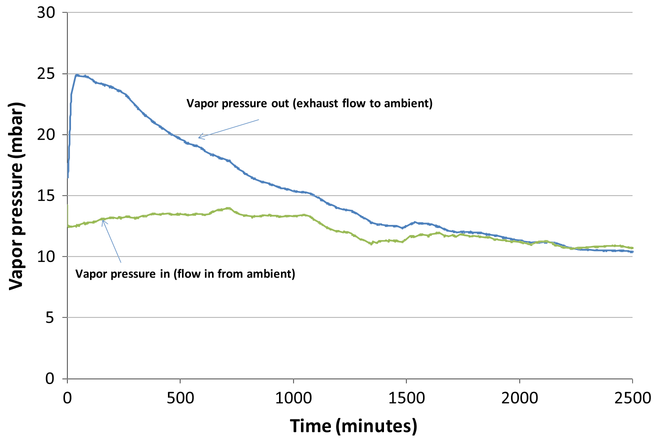

Fig. 8. Water vapor pressure at the entrance and the exit of the TC reactor system during charging (dehydration) at 130 °C.

to the load, that was set to 60 °C, and finally leaves the system through the air-to-air heat exchanger, in which it gives its remaining heat to the incoming airflow. With an airflow of 510 l per minute, the air was transferring a thermal peak power of 50 W to the thermostat bath functioning as the load, as shown in Fig. 10. Thermal power was delivered over a period of 1500 min (=25 h). This is consistent with the time interval in which in Fig. 9 the air temperature at the exit from the bed is higher than the temperature of the thermostat bath (=60 °C).

Fig. 10 shows that the packed bed generates a thermal power of about 150 W, in order to heat the air from 50 °C to 64 °C. However, only 50 W is transferred to the load, while about 100 W is lost to the exit airflow. This is due to insufficient heat recovery between the incoming and outgoing air flows. Fig. 9 shows a large temperature drop of almost 9 °C over the hot side of the air-to-air heat exchanger, which in an ideal case would be zero, indicating that the efficiency of the heat recovery needs to be improved. If all heat could be recovered, the full 150 W generated in the packed bed could be transferred to the load. Note that any improvement in the heat recovery has a strong effect on the performance of the TC storage system, both in power and in discharge time. An effective storage density of approximately 0.5 GJ/m^3 is found. It is expected that this value can be improved further.

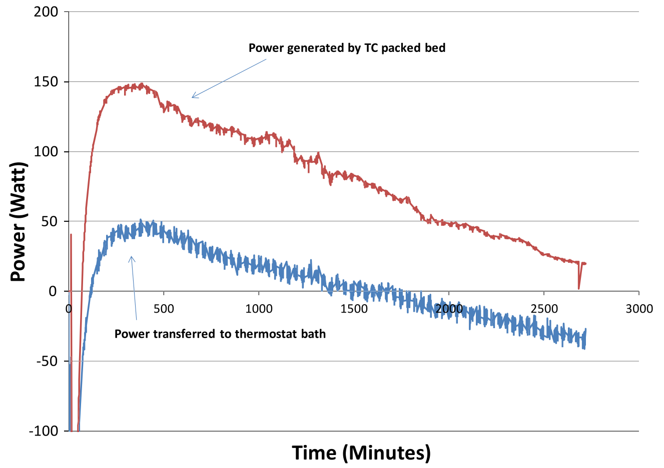

Fig. 10. Power transferred from the TC reactor to the thermostat bath (bath is kept at 60 °C).

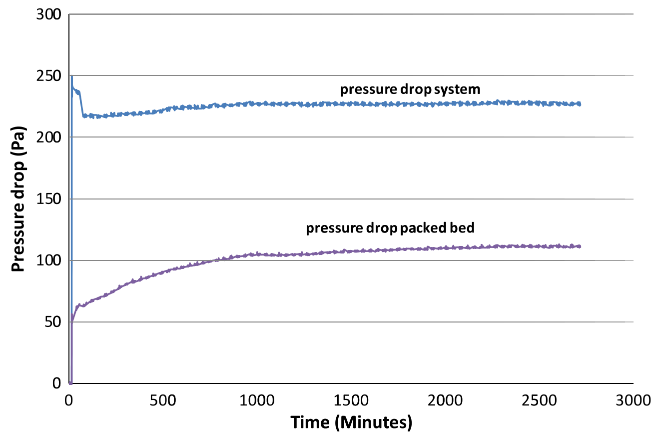

Fig. 11. Pressure drop in the TC storage system during hydration.

Finally, the pressure drop in the system is important, since this determines the electrical fan power required for the system. This pressure drop was not optimized yet in the design of the present system. As shown in Fig. 11, a pressure drop of about 100 Pa was

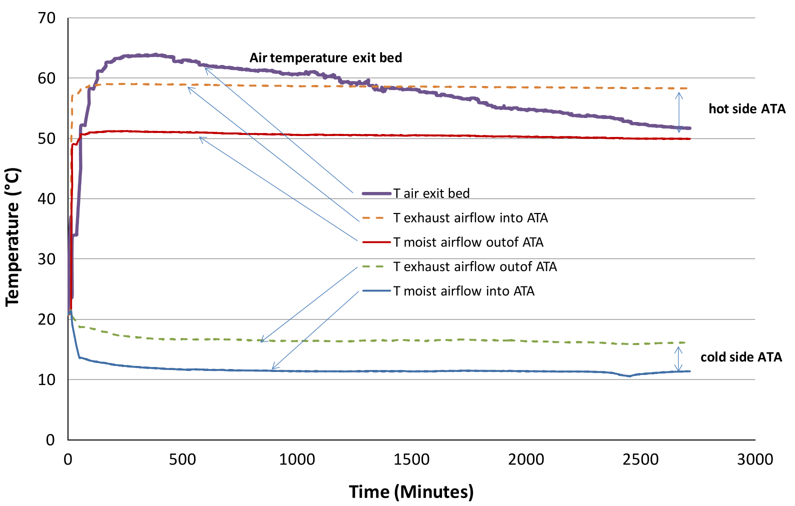

Fig. 9. Temperatures in the TC reactor system during hydration at 12 mbar. Indicated are the temperature of the air heated by the TC reactor and the temperatures in the air-to-air heat exchanger ATA (hot and cold side).

measured over the packed bed for the flow used in the experiments (510 l/h), and a pressure drop of about 220 Pa over the entire system (including not only the packed bed, but also the heat exchangers and tubing). Note that the pressure drop over the bed increases during the hydration, which can be related to the swelling of the magnesium chloride on uptake of water vapor.

The required fan power can be calculated from the flow rate and the pressure drop. An instantaneous electrical COP of the system can be calculated based on:

$$\mathrm{COP}_{el} = \frac{P_{\mathrm{heating}}}{P_{\mathrm{fan}}}$$

Assuming a fan efficiency of 50%, a required fan power of about 4 W is calculated during the hydration. With a useful thermal power of 50 W, this would result in an instantaneous electrical COP of 12. If the heat recovery can be improved towards the full thermal power of 150 W generated by the bed, while the pressure drop can be reduced, an instantaneous electrical COP of 30 seems within reach. However, the overall COP of a future installed system will be substantially lower than this instantaneous COP, because the calculation above does not take into account the power required for the dehydration, and also the electricity use of other components in the system is ignored. Assuming that the fan power during dehydration is the same as during hydration, and the electricity use of other components is relatively small, an overall system COP could be in the range of 10–15, which is comparable to values found in the literature for other optimized open sorption systems [8,9].

6. Conclusions

$MgCl_2{\cdot}6H_2O$ has interesting properties for application as a thermochemical heat storage material since it is capable of delivering heat at a temperature level sufficiently high for both tap water heating and space heating, while high energy densities in the order of 1 GJ/m^3 can be realized. In addition, the TC material is very cheap and non-toxic.

A laboratory prototype TC storage system has been realized at ECN, applying an open sorption system concept. The packed bed can store 17 liters of sorption material and is capable of generating 150 W of thermal power, from an airflow of 510 l/min with a vapor pressure of 12 mbar. The bed can produce heat over 40 h, indicating under the present conditions an effective energy density of approximately 0.5 GJ/m^3. However, due to heat losses in the system, the power transferred to the load is presently only 50 W. This is due to insufficient heat recovery, which will be improved in the next stage of the research. Furthermore, from the pressure drop measured in the bed, an instantaneous electrical COP of 12 is now found, but it is expected that this will rise to about 30 on optimization of heat recovery and pressure drop in the system.

Acknowledgements

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