Prototype thermochemical heat storage with open reactor system

H.A. Zondag
B.W.J. Kikkert
S.F. Smeding
R. de Boer
M. Bakker

November 2012
ECN-M--12-073

INNO-ST-09

Prototype thermochemical heat storage with open reactor system

Herbert Zondag[1,2], Benjamin Kikkert[1], Simon Smeding[1], Robert de Boer[1], Marco Bakker[1]

[1] Energy research Centre of the Netherlands ECN, P.O.Box 1, 1755ZG Petten, the Netherlands, Phone: +41-224-564941, e-mail: zondag@ecn.nl
[2] Dept. of Mechanical Engineering, Eindhoven University of Technology, the Netherlands, e-mail: h.a.zondag@tue.nl

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) ⇔ AB(s) + heat. Such thermochemical heat storage has a 5 to 10 times higher energy storage density than water, 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 to 8 m^3, that is charged during summer by solar collectors.

Salt hydrates are a very promising type of TCM. These salts can be dehydrated in summer with heat from a solar thermal collector system. During winter, water vapour is fed to the dried salt, resulting a reaction in which the heat is released again. This heat can be used for space heating and tap water heating. In this paper, the performance of a lab scale prototype TCM heat storage is presented, with a storage volume of 15 liter.

2. TC storage system concept

The TC heat storage research at ECN focuses on open sorption systems as shown in Figure 1. In such systems, water vapour 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 vapour 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. 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 by using heat from a low temperature heat source such as a borehole (not shown in the figure).

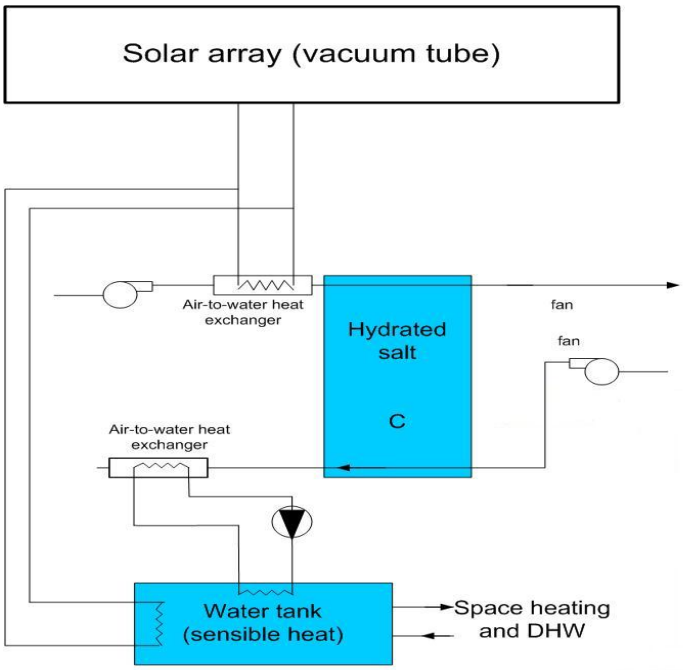

Figure 1: Open sorption TC heat storage system

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 equilibrium temperature in combination with the vapour pressure at 10°C (a typical borehole temperature in the Dutch climate). The equilibrium 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).
A large range of materials was identified from the literature as potentially interesting. As an example, magnesium chloride was found to have the right equilibrium temperatures, as can be seen in Figure 2. This figure shows a plot from Kipouros (1987) of the equilibrium temperature for magnesium chloride hydrates as a function of water vapour pressure. The figure indicates for a vapour pressure of 12 mbar (corresponding to evaporation at 10°C), the following reactions:

reaction	**Equilibrium temperature**
$MgCl_2x6H_2O \Leftrightarrow MgCl_2x4H_2O + 2H_2O$	61°C
$MgCl_2x4H_2O \Leftrightarrow MgCl_2x2H_2O + 2H_2O$	96°C
$MgCl_2x2H_2O \Leftrightarrow MgCl_2xH_2O + H_2O$	117°C

The literature overview resulted in a list of materials. However, the equilibrium temperature in itself does not give any information on the reaction kinetics. Therefore, the selected materials were tested under dynamic conditions.

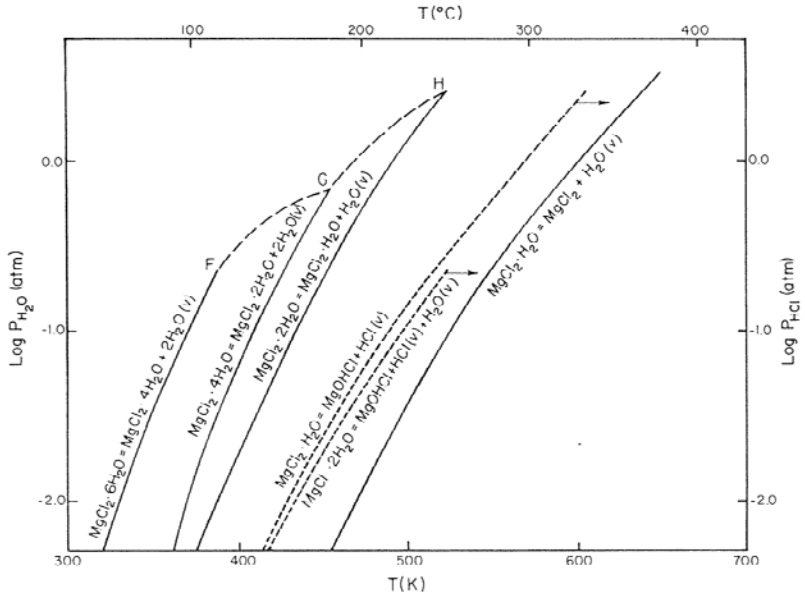

Figure 2: Pressure-temperature diagram of the equilibrium curves for the hydrates of MgCl2 (figure from Kipouros, 1987).

Several materials were tested, among which $MgSO_4.7H_2O$, $Al_2(SO_4)_3.18H_2O$, $MgCl_2.6H_2O$ and $CaCl_2.6H_2O$. First, the materials were tested by TGA measurements, as described previously by Zondag (2011). As an example, the dehydration of $MgCl_2.6H_2O$ is shown in Figure 3. Clearly, the $MgCl_2.6H_2O$ shows significant drying when heated to 150°C.

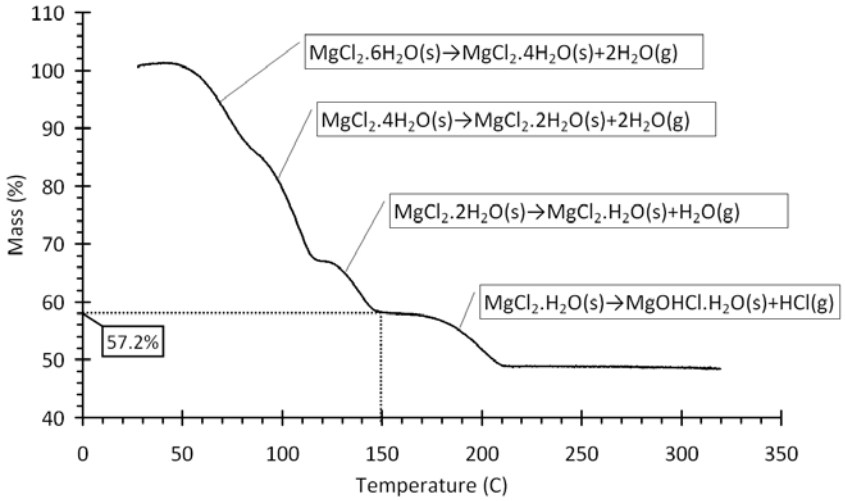

Figure 3: Mass of MgCl2x6H2O versus temperature, showing the water loss during the dehydration process (heating rate 1°C/min).

Next, the materials $MgSO_4.7H_2O$, $Al_2(SO_4)_3.18H_2O$ and $CaCl_2.6H_2O$ were dried at 150°C, while $MgCl_2.6H_2O$ was dried at 130°C, because of side reactions at higher temperatures (see Figure 3). Subsequently, these materials were placed in an evacuated setup and were hydrated with vapour supplied by an evaporator (Essen, 2009; Zondag, 2011). In Figure 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 $MgCl_2x2H_2O$, 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 vapour is generated by a borehole at 10°C. For $MgCl_2x2H_2O$, 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.

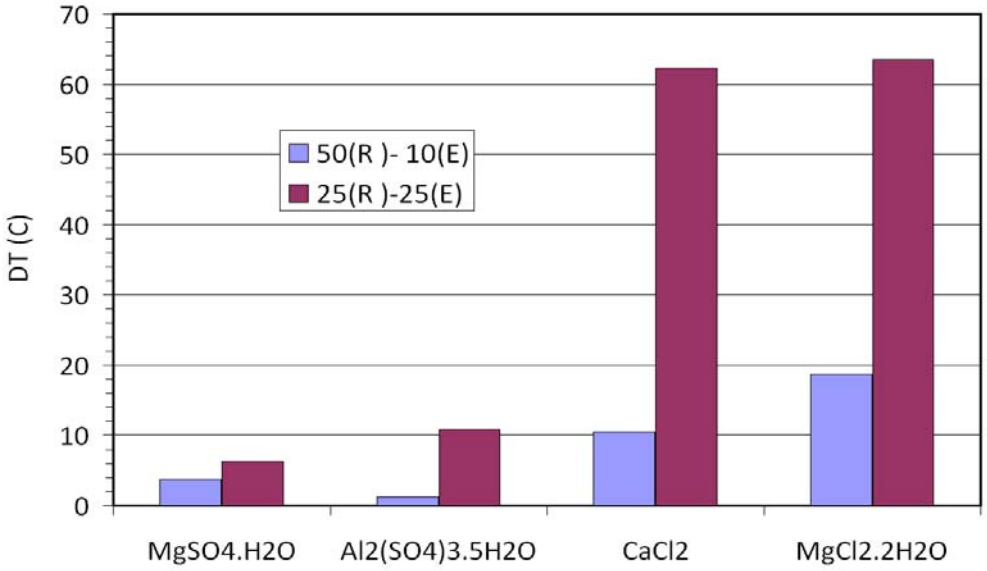

Figure 4: Temperature rise in evacuated setup on hydration at 12 mbar.

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

$$MgCl_2 \cdot 6H_2O(s) + heat \Leftrightarrow MgCl_2 \cdot 2H_2O(s) + 4H_2O(g)$$

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 15 liters. The setup consists of a full system, so apart from the reactor also the other system components appearing in Figure 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 Figure 1), in which the water vapour is taken from the ambient air.

A schematic representation of the system is shown in Figure 5, while photographs of the built prototype are shown in Figure 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 Figure 5.

The reactor system was designed to produce a power of 50 Watt to the load. The power that can be generated is directly proportional to the moisture flow entering the packed bed. An air flow of 600 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 vapour pressure in the incoming air to 12 mbar. Otherwise, a high vapour 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.

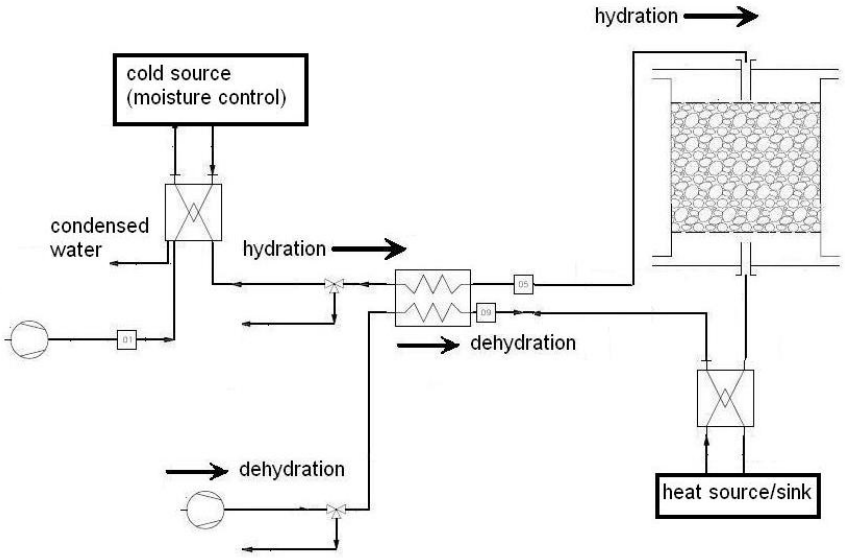

Figure 5: Schematic representation of TC reactor storage system setup.

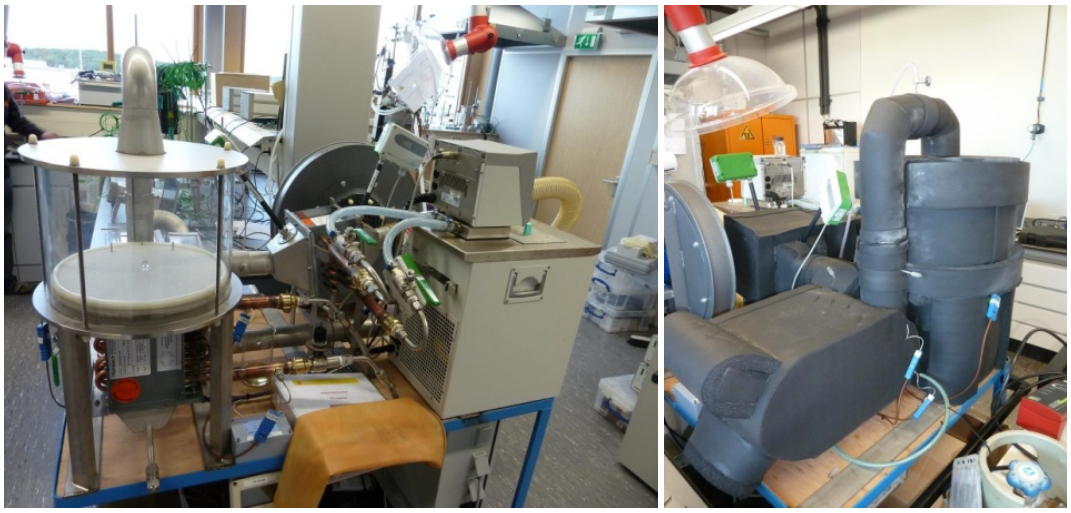

Figure 6: Photographs of prototype thermochemical storage system, (a) before and (b) after insulation.

5. Results and discussion

Hydration and dehydration experiments have been carried out successfully in the prototype storage system. During dehydration, 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 Figure 7. These are related to the dehydration steps in the $MgCl_2x6H_2O$. In addition, Figure 8 shows the vapour pressure at the outlet of the TC storage system. Clearly, during the first 1800 minutes (=30 hours), additional water vapour is generated

in the reactor system by dehydration of the packed bed, as is clear from the increase in vapour pressure between inlet and outlet.

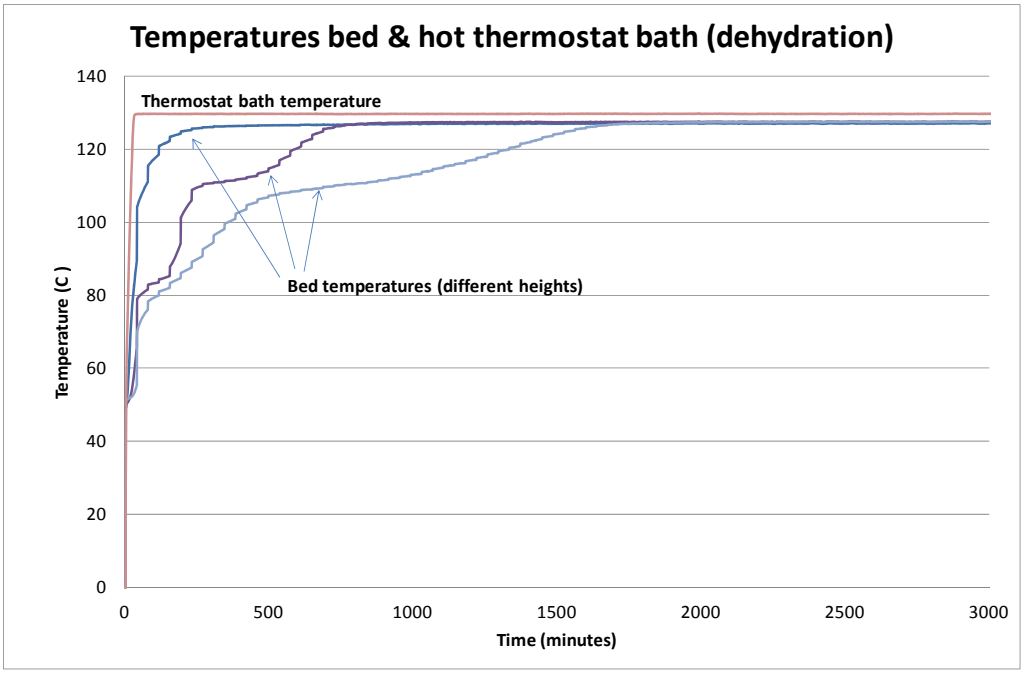

Figure 7: Temperatures in the packed bed during charging of the TC heat storage at 130°C.

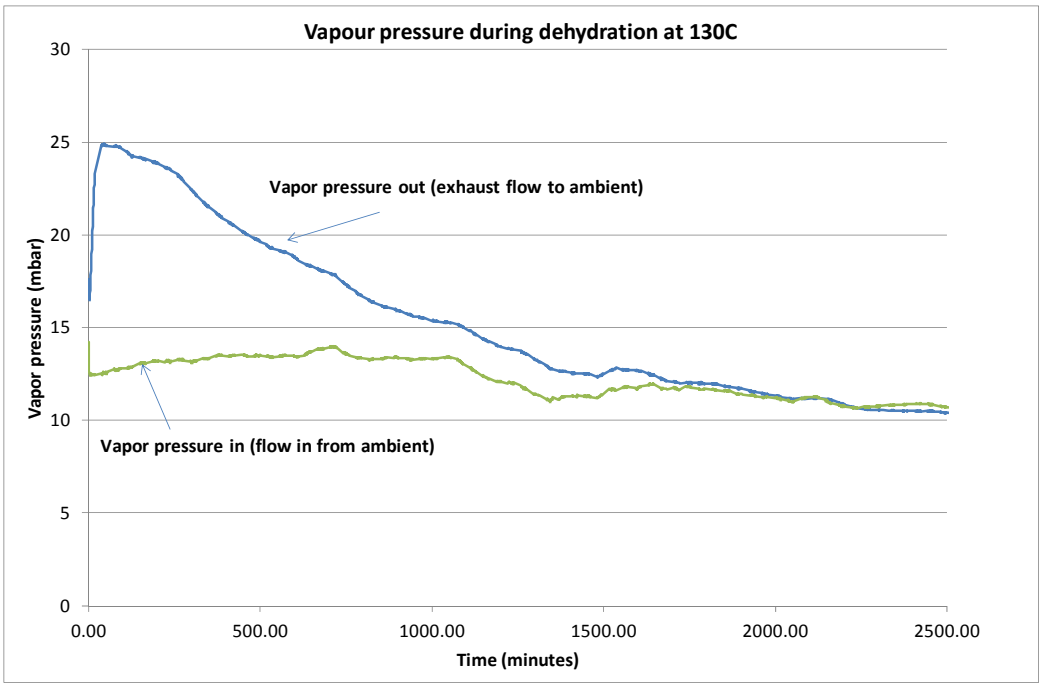

Figure 8: Vapour pressure at the entrance and the exit of the TC reactor system.

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 Figure 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 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 600 liter per minute, the air was transferring a thermal peak power of 50 Watt to the thermostat bath functioning as the load, as shown in Figure 10. Thermal power was delivered over a period of 1500 minutes (=25 hours). This is consistent with the time interval in which in Figure 9 the air temperature at the exit from the bed is higher than the temperature of the thermostat bath (= 60°C).

Figure 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. Only 50 Watt is transferred to the load, while about 100 Watt is lost to the exit airflow. This is due to insufficient heat recovery between the incoming and outgoing air flows. Figure 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 Watt 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. Integration of the power yields an effective storage density of more than 0.5 GJ/m^3. It is expected that this value can be improved further.

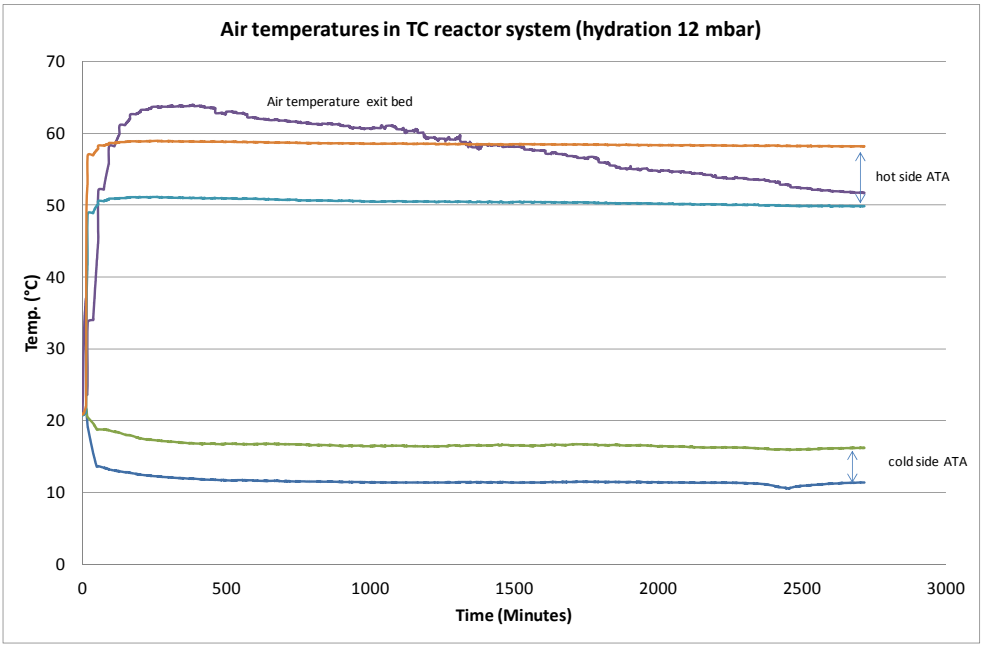

Figure 9: Temperatures in the TC reactor system during hydration. Indicated are the temperature of the air heated by the TC reactor and the temperatures in the air-to-air heat exchanger ATA (hot and cold side).

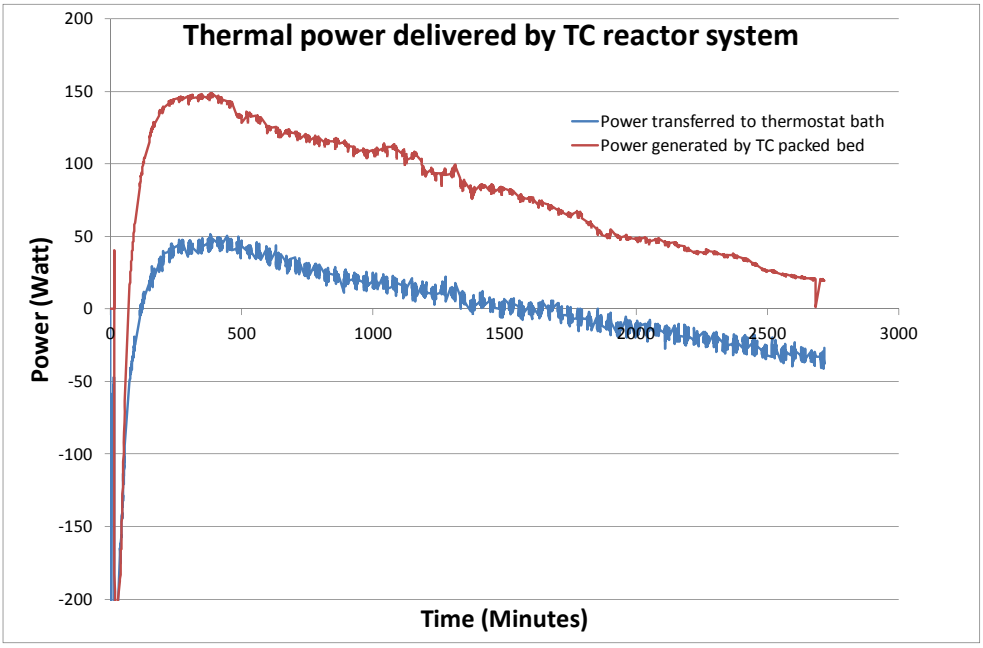

Figure 10: Power transferred from the TC reactor to the thermostat bath (which is kept at 60°C).

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 optimised yet in the design of the present system. A pressure drop of about 100 Pa was measured over the packed bed for the flow used in the experiments (600 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 vapour.

The required fan power can be calculated from the flow rate and the pressure drop. Assuming a fan efficiency of 50%, a required fan power of about 4.5 W is calculated. With a useful thermal power of 50W, this would result in a COP (= ratio between useful generated thermal power and consumed electrical power) of 10 for the hydration only. However, assuming that the heat recovery can be improved towards the full thermal power of 150 Watt generated by the bed, while the pressure drop can be reduced, an electrical COP of 30 seems within reach.

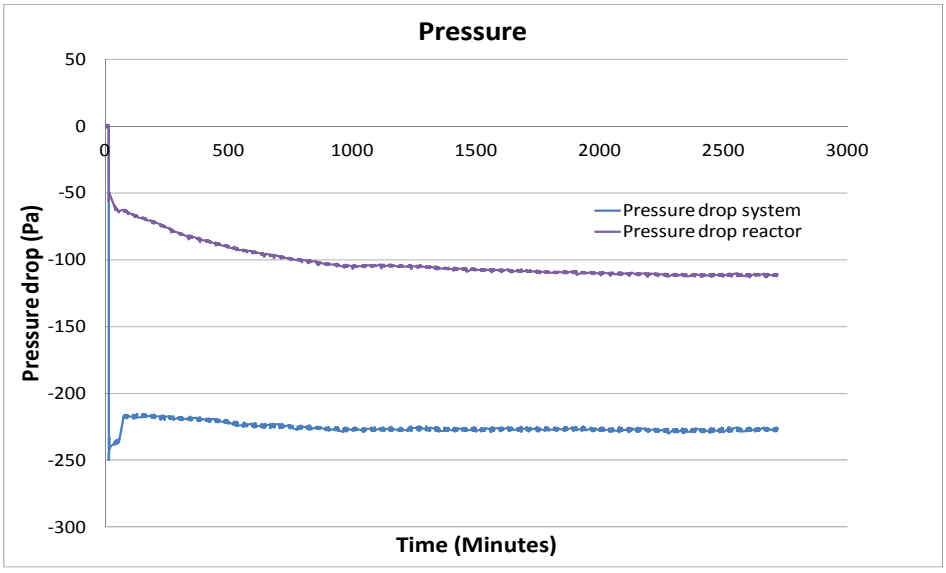

Figure 11: Pressure drop in the TC storage system during hydration.

6. Conclusions

$MgCl_2.6H_2O$ is a suitable material for thermochemical heat storage. The material 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 on open sorption system concept. The packed bed can store 15 liters of sorption material and is capable of generating 150 Watt of thermal power, from an airflow of 600 l/min with a vapour pressure of 12 mbar. The bed can produce heat over 40 hours, indicating under the present conditions an effective energy density of more than 0.5 GJ/m^3. However, due to heat losses in the system, the power transferred to the load is presently only 50 Watt. 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, it is concluded that during hydration an electrical COP of 10 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.

7. References

- Essen, V.M. van, Bleijendaal, L.P.J., Cot Gores, J., Zondag, H.A., Schuitema, R., Helden, W.G.J. van (2009), Characterization of salt hydrates for compact seasonal thermochemical storage, Effstock Conference 2009, Stockholm, Sweden.
- Kipouros, G.J., Sadoway, D.R. (1987), The Chemistry and Electrochemistry of Magnesium Production, Advances in Molten Salt Chemistry, Vol. 6, Edited by G. Mamantov, C.B. Mamantov and J. Braunstein, Elsevier, Amsterdam, pp. 127-209.
- Zondag, H.A., Kikkert, B.W.J., Smeding, S. and Bakker, M. (2011), Thermochemical seasonal solar heat storage with $MgCl_2.6H_2O$: first upscaling of the reactor, IC-SES Conference, Belfast.

8. Acknowledgements

This work was partially funded by the EU under the 7thframework programme as part of the E-hub project, project reference 260165.

ECN
Westerduinweg 3
1755 LE Petten
The Netherlands

P.O. Box 1
1755 LG Petten
The Netherlands

T +31 88 515 4949
F +31 88 515 8338
info@ ecn.nl
www.ecn.nl