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Seasonal Sorption Heat Storage – Research On Thermochemical Materials And Storage Performance

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SEASONAL SORPTION HEAT STORAGE – RESEARCH ON THERMOCHEMICAL MATERIALS AND STORAGE PERFORMANCE

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ABSTRACT

Advantages of thermochemical heat storage over conventional heat storage are a higher energy density and loss-free storage of the heat after charging, since the heat is stored in chemical form. At ECN, a thermochemical heat storage is developed for seasonal heat storage applications. This paper shows results of materials testing, experiments with a lab scale reactor and first modeling results. The required output temperature of 60°C was realised.

INTRODUCTION

In the Netherlands, the main part of the residential energy demand consists of space heating and tap water heating. During the summer period, the available solar energy is sufficient to cover the tap water heating demand for houses equipped with solar thermal collectors. However, during winter, the heating demand exceeds the solar supply (Figure 1). Solar energy can be harvested in summer to fulfill the heat demand in winter by means of a seasonal heat storage system. However, for a passive house of 110 m² with a winter heat demand estimated at 6 GJ, seasonal heat storage in a traditional water tank would require a tank volume above 40 m³ which is way too large to be integrated in individual houses. Therefore, more compact heat storage technologies have to be found. ECN is developing a compact heat storage system based on the reversible reaction of water vapor with a ThermoChemical Material (TCM). TCMs have a high energy density (1 GJ/m³ in packed bed) which result for the abovementioned 6 GJ heat demand in a storage of about 6 m³. This is suitable for integration in individual houses. Interesting TCM materials for seasonal heat storage are salt hydrates, which are available in large quantity at low cost, are environmentally friendly and can take up and release heat under the conditions of seasonal heat storage. During summer, the salt is dehydrated by means of solar heat from vacuum tube collectors. During winter, the salt is hydrated again, releasing the heat.

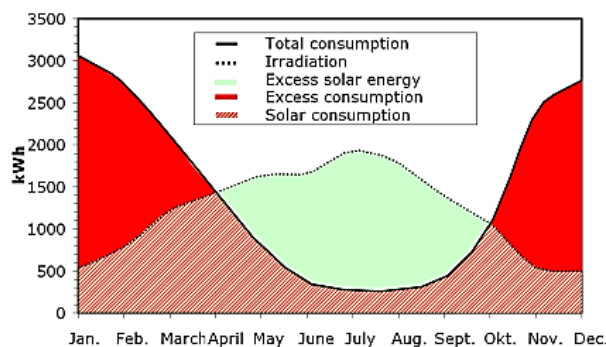


Figure 1: Household energy consumption and solar irradiation over a year in the Netherlands.

TC MATERIALS DEVELOPMENT

In an screening of TCMs carried out at ECN, MgCl₂·6H₂O showed a promising performance. The dehydration of MgCl₂·6H₂O under 12 mbar of water vapour is shown in Figure 2. The figure shows clearly two dehydration steps:

1. MgCl₂·6H₂O ⇒ MgCl₂·4H₂O + 2H₂O T_{onset} = 70°C
2. MgCl₂·4H₂O ⇒ MgCl₂·2H₂O + 2H₂O T_{onset} = 105°C

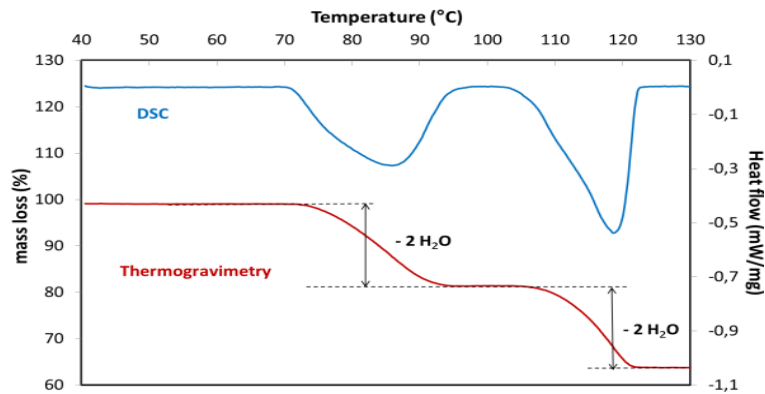


Figure 2: Dehydration of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (heating rate 0.5 K/min)

Figure 3 shows X-ray diffraction results for $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ at increasing temperature. The figure shows that the sample remains crystalline during the entire dehydration procedure. Again, the same two dehydration steps are observed. Note that at 140°C, also MgOHCl is shown, which is a result from the side reaction $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}(\text{s}) \Rightarrow \text{MgOHCl}(\text{s}) + \text{HCl}(\text{g})$. This reaction is undesirable because it reduces the amount of active material and produces HCl gas that is corrosive to the system. Therefore, during dehydration, the temperature should be kept below 130°C.

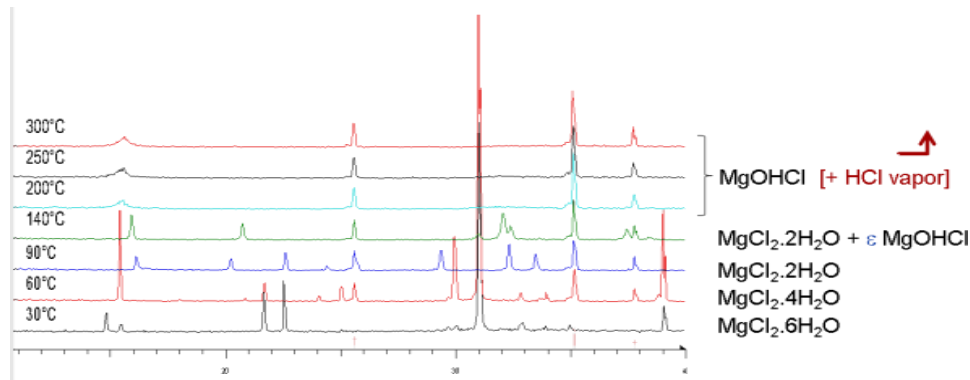


Figure 3: X-ray diffraction of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ at different temperatures

In addition to the dehydration reaction, it is also important that the reverse hydration reaction is sufficiently fast and at sufficiently high temperature. Results for a dehydration-hydration cycle are shown in Figure 4. A significant hysteresis is found even at the low heating rates used in this study, indicating that the hydration is less fast than for instance in zeolites. However, this is still sufficient to provide tap water and space heating from a seasonal storage. From the DSC result, an energy density was found of 1.4 GJ/m^3 on crystal level for the reaction of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ to $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$, corresponding to 0.7 GJ/m^3 for a packed bed with 50% porosity.

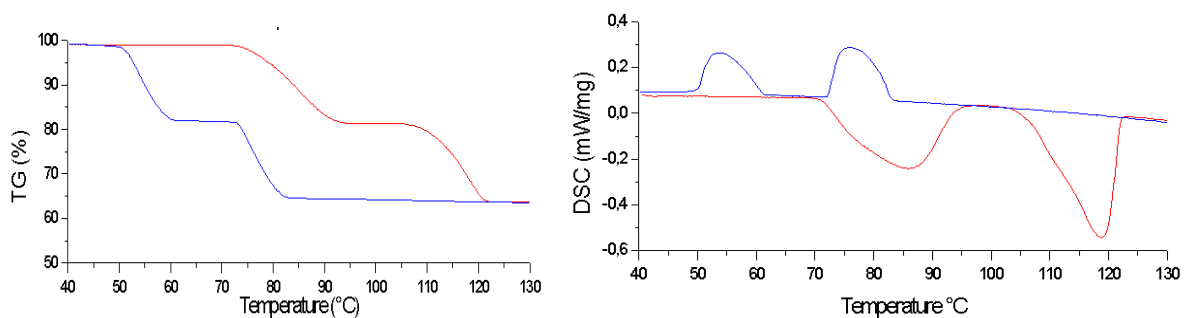


Figure 4: Dehydration-hydration cycle. Left: mass change. Right: power uptake and release. Red line: dehydration (Heating rate: 0.5 K/min), blue line: hydration (Cooling rate: 0.2 K/min.)

Finally, the stability of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ at low temperatures during hydration is also critical. The salt is hygroscopic to such an extent that it tends to overhydrate and go into solution under ambient

conditions (Ferchaud, 2012). However, if the material is hydrated at 12 mbar vapour pressure with temperatures above 30°C, the $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is stable. This condition is automatically fulfilled in the reactor design developed at ECN, as will be shown in the next paragraph.

TC REACTOR DESIGN AND TESTING

The heat storage design focuses on a packed bed through which air is flown (Figure 5). During summer, the salt hydrate materials can be dehydrated by means of air heated by solar thermal evacuated tube collectors. During winter, the dehydrated salt is hydrated with moist air from the ambient. To improve the reactor performance, the vapor pressure of the incoming air is increased to 12 mbar by means of the evaporation of water with 10°C heat taken from a borehole.

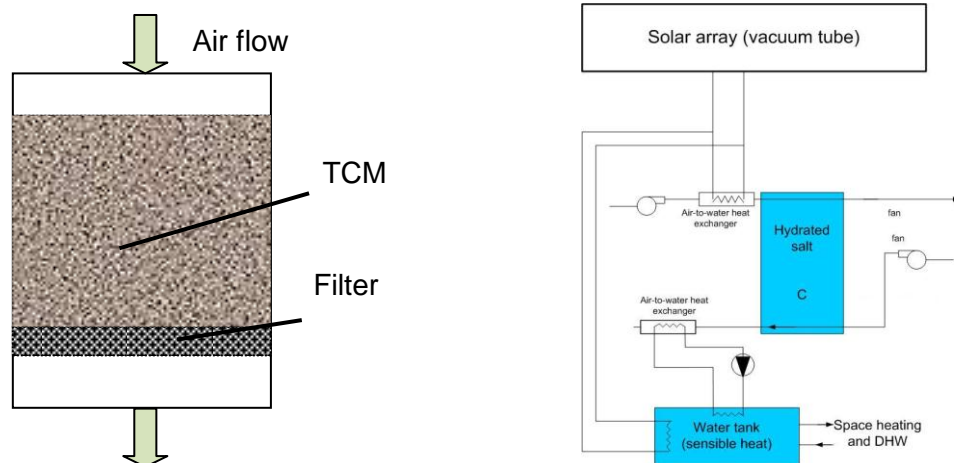


Figure 5 : (a) Design of the 6m³ packed bed reactor optimized for seasonal heat storage, (b) system sketch

The storage design is very important for the performance. A prototype lab scale thermochemical open sorption heat storage system with a storage capacity of 20 liters was built and tested at ECN (Zondag, 2011). As TCM material, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was used. The prototype setup is shown in Figure 6.

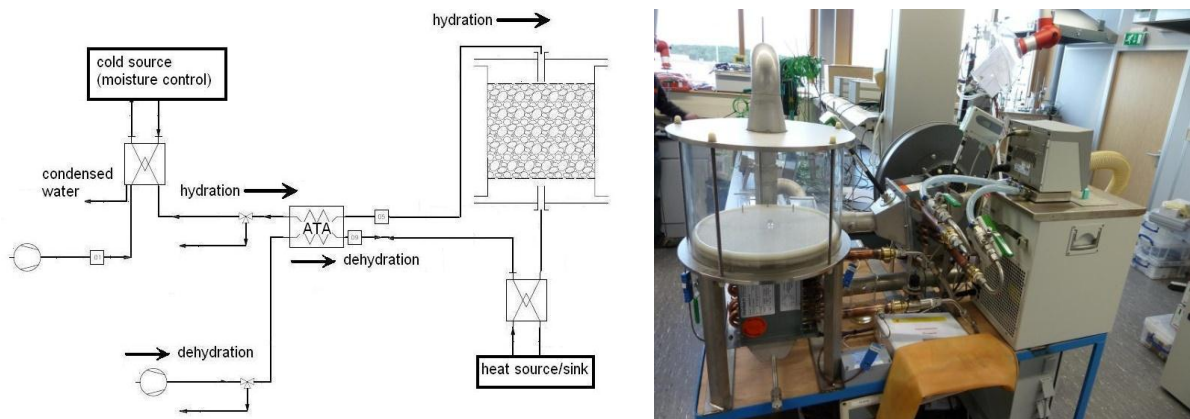


Figure 6: Lab prototype open sorption TC storage system (a) system design, (b) lab prototype.

The temperatures in the lab prototype during the dehydration phase are shown in Figure 7. The bed temperature profiles clearly show the effect of the dehydration of the $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Note that the plateau temperatures are similar to the temperatures previously shown in Figure 4.

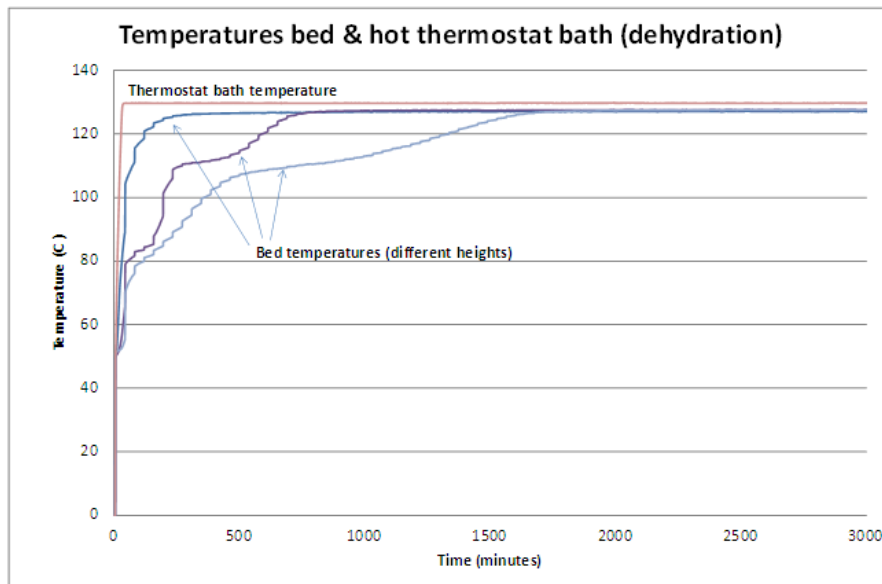


Figure 7: Charging of Lab-scale storage (dehydration of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$).

Figure 8 shows the discharging of the storage, on flowing through moist air with 12 mbar vapour pressure. A temperature rise of about 15°C is reached in the bed, heating the air from 50°C to 65°C . The hot air is flown through a heat exchanger connected to a thermostat bath, providing 50 W of heating power to the 60°C thermostat bath. This indicates the suitability of the present system with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ for tap water heating. On hydration, the prototype ThermoChemical storage was found to be able to deliver heat at 60°C for about 20 hours.

The incoming moist air was preheated to 50°C by the outgoing dried air via the air-to-air heat exchanger (ATA) shown in Figure 6. In this way, high output temperatures can be obtained, and at the same time, the increased inflow temperature prevents overhydration of the $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, as explained before. Unfortunately, in the present setup, the heat recovery in the air-to-air heat exchanger was insufficient, resulting in significant heat loss via the outgoing air flow. This will be improved in later designs.

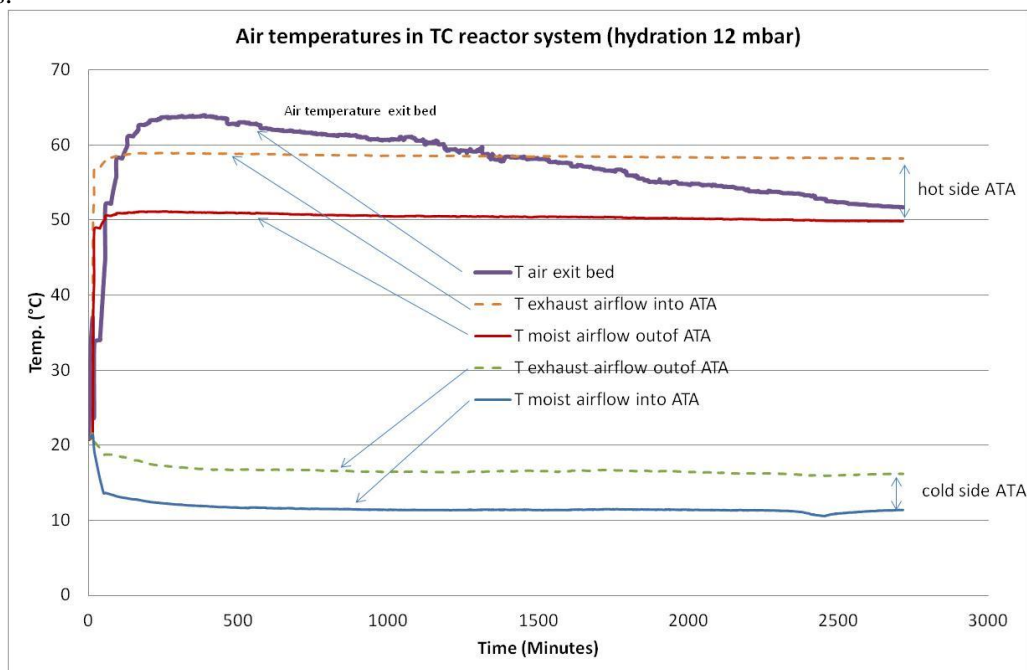


Figure 8: Discharging of Lab-scale storage (hydration of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$).

TC STORAGE MODELING

A reactor model was built for an open sorption packed bed reactor filled with salt hydrate, using the commercial software Comsol Multiphysics. The model makes use of the mass balance, momentum balance (modified Navier-Stokes) and energy balance equations, as well as the Clausius-Clapeyron equation to describe the thermochemical equilibria of the salt hydrate. The model was only used to describe the dehydration phase; hydration simulations will be carried out later. The chemical reaction rate for dehydration is modeled with the equation:

$$r_w = -C_a \exp\left(-\frac{E_a}{RT_s}\right) \left(\frac{P_f - P_{eq}}{P_{eq}}\right)$$

The geometry of the model is shown in Figure 9.

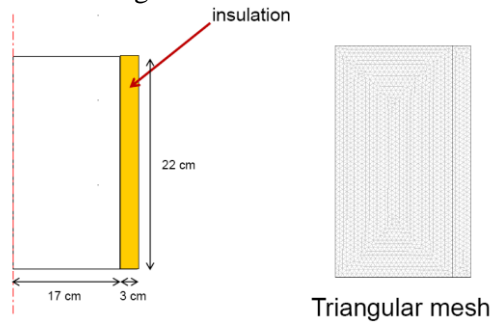


Figure 9: Model geometry of packed bed

The model was validated with the experiments. The results are shown in Figure 10, for the case in which a 600 liter/min flow of 12 mbar moist air is flown through the reactor. Qualitatively, the match is very good. Quantitatively, the model responds somewhat faster than was found in the experiments. The difference may be due to the choice for the kinetics parameters or to some inaccuracy with respect to the exact sensor location in the bed. This will be improved at a later stage. Figure 11 shows the progressing of the temperature front through the bed on dehydration. Initially, a sharp front exists. However, since most of the heating energy is stored in the dehydration reaction in the bed, a temperature distribution is quickly formed in the bed corresponding to the reaction temperatures of the desorption process, as shown in the rightmost graph in Figure 11. The aim of the model is to optimize the reactor design and process conditions by means of a parameter study, to minimize heat losses and auxiliary fan energy. This will be carried out after the optimization of the model kinetics and the hydration modeling are finalized.

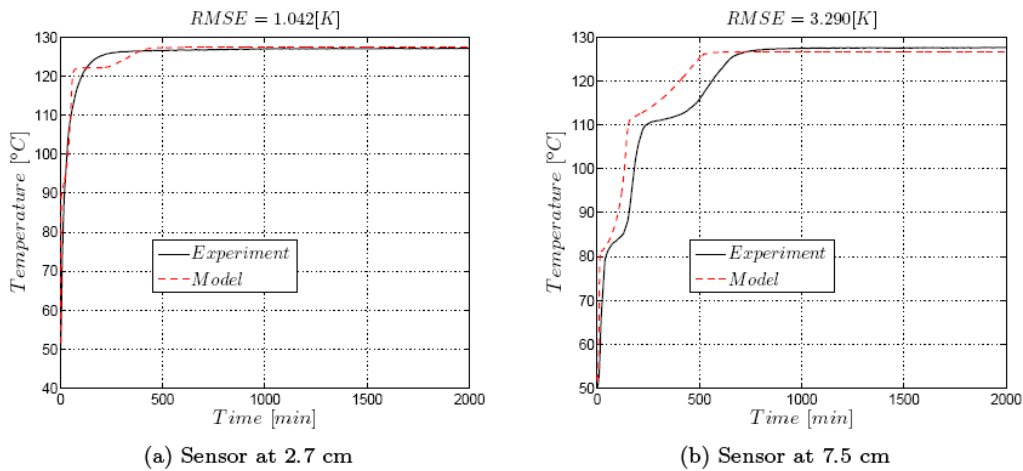


Figure 10: Comparison of bed temperatures in experiment and numerical model.

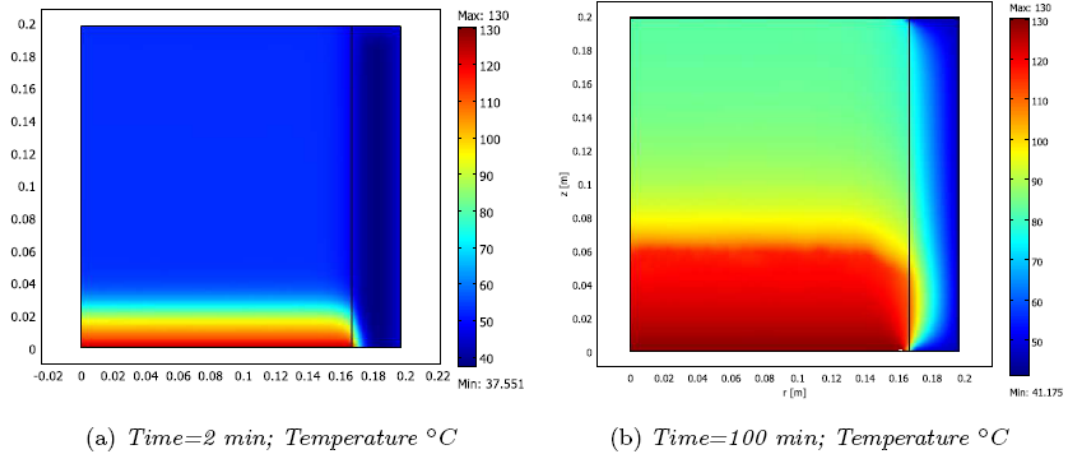


Figure 11: Progressing of temperature front through the bed during dehydration.

CONCLUSIONS

$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ can be dehydrated at temperatures below 130°C . By the subsequent hydration, sufficiently high temperatures can be generated to provide tap water heating at 60°C . A lab prototype was shown to be able to provide these temperatures under realistic winter conditions, indicating the suitability of this technology for seasonal heat storage.

A model was built to model the conditions in the packed bed during dehydration. The model shows a good qualitative agreement with the experiments. After further optimization of the model and implementation of the hydration reactions, the model will be used to optimize the reactor design.

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