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Introduction

The heat demand in the summer can be completely fulfilled using solar heat, but in the winter the heat demand is exceeding the solar supply. A solution is to store the excess of solar energy in the summer, and to use it to fulfill the heat demand in the winter.

Water is traditionally used for storing heat (e.g. solar boiler), but seasonal heat storage requires large water tanks ($>40\text{m}^3$) that are too large to be placed inside a family building. An alternative option is to store heat by means of chemical processes using the reversible reaction: $A+B \rightleftharpoons C+\text{heat}$. With thermochemical heat storage, energy storage densities can be reached that are ten times higher than for heat storage in water. Additionally, after the thermochemical material has been charged, the heat can be stored for a very long time without losses. Interesting materials are cheap, non-toxic, non-corrosive, have sufficient energy storage density and have reaction temperatures in the proper range. A large materials inventory by ECN identified a number of interesting materials, including magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) as one of the most promising materials for seasonal heat storage (Zondag, 2007).

Material characterization

In order to verify the performance of the magnesium chloride hydrate, the sample mass was measured as a function of temperature using TGA equipment, as shown in Figure 1. When heating the material at a rate of $1^\circ\text{C}/\text{min}$, these measurements showed that the dehydration of the hexahydrate started at about 50°C and the formation of monohydrate started at about 120°C . These results indicate that the dehydration of the material occurs in a temperature range that is within reach of solar thermal collectors. From the molar masses of the magnesiumchloride hexahydrate and the the desorbed water molecules, the dehydration of hexahydrate to monohydrate can be calculated to reduce the sample mass to 55.7%, which is in reasonable agreement with the 57.2% found in the measurement.

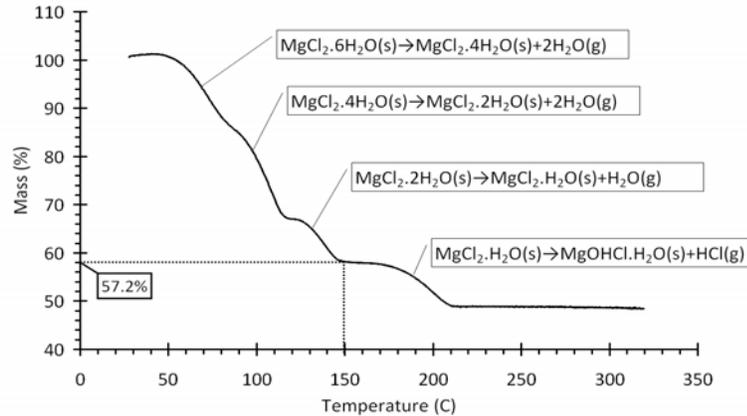


Figure 1: TGA measurement of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Heating rate $1^\circ\text{C}/\text{min}$ in dry nitrogen atmosphere, sample mass 10 mg.

Next, hydration measurements were carried out in an evacuated setup, as shown in Figure 2. During hydration with moisture from an evaporator at 25°C (corresponding to a vapor pressure of 32 mbar), the temperature in the sorption bed rose from 25°C to 85°C . With an evaporator temperature of 10°C (vapor pressure 12 mbar) and an initial reactor temperature of 50°C , the temperature in the sorption bed rose from 50°C to 70°C .

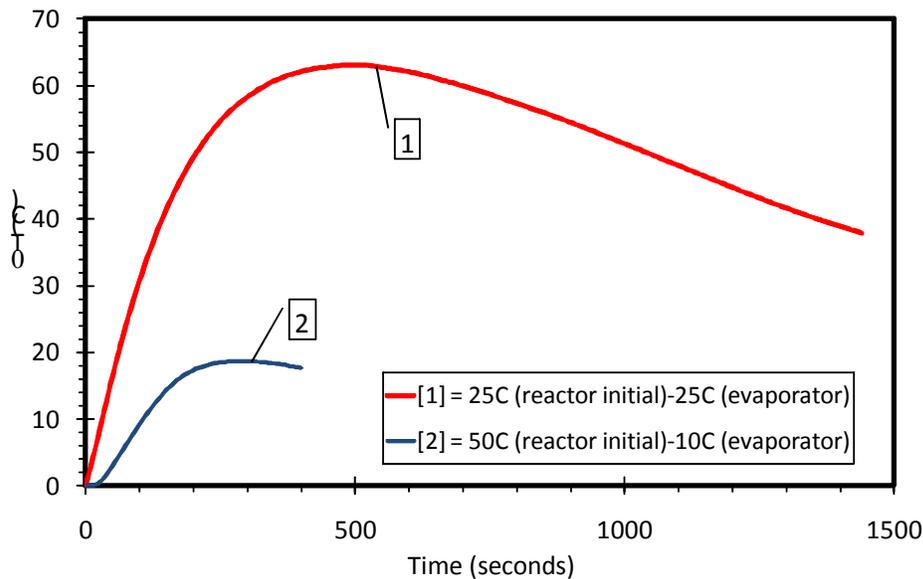


Figure 2: Temperature rise in sorption bed, measured in evacuated setup.

Since these temperatures are sufficiently high to be able to use the material for tap water heating, these results are very promising. However, two undesirable features of the material were found:

1. During dehydration at temperatures above 135°C , the formation of HCl was found. The formation of this gas not only degrades the TC storage material, but also is strongly corrosive. Therefore, such high temperatures should be avoided on dehydration by a proper control of the solar thermal collector system.

2. After long-term hydration of the magnesium chloride, the material nearest to the evaporator was found to overhydrate, transforming to a gel-like structure. This can be avoided by using a suitable carrier material.

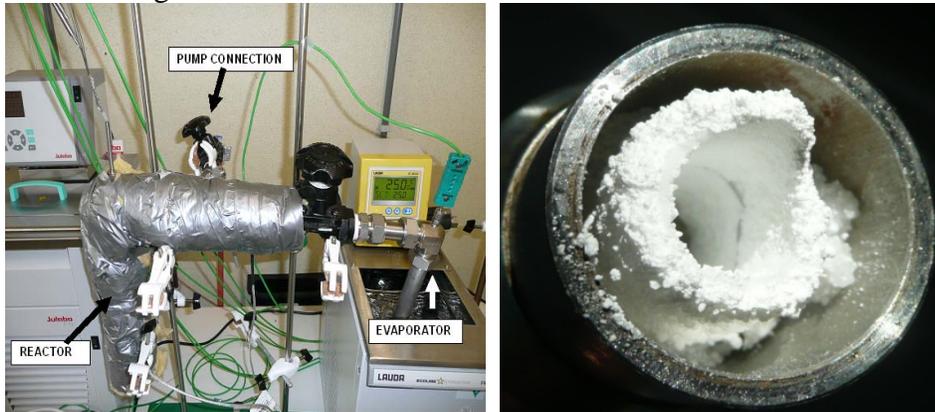


Figure 3: (a) Evacuated setup, (b) Overhydration of the magnesium chloride in the evacuated setup.

Open sorption reactor measurements pure salt

For seasonal storage, the choice was made to focus on an open sorption reactor. This choice was based on a techno-economical study carried out at ECN (Zondag, 2010), that indicated that such a reactor type was most promising in terms of economics and reliability. A first open sorption reactor with a capacity to store 300 grams of TC material was built from PMMA, as shown in Figure 4. Due to the low temperature resistance of PMMA, this test reactor could only be used for hydration measurements.

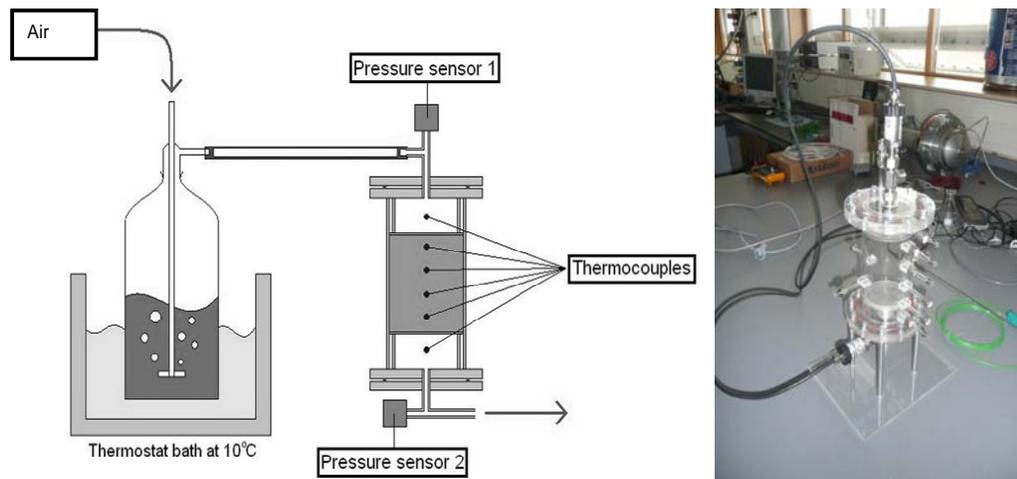


Figure 4: (a) Test setup with open sorption reactor, (b) Open sorption test reactor. In the first tests, the material was hydrated with a 20 slpm humid air flow. Again overhydration was found. This overhydration transformed the top of the bed into a solid layer, resulting in an increasing pressure drop over the bed. Also, some expansion of the bed was observed.



Figure 5: (a, b) Formation of a hard impregnable layer due to overhydration in open sorption reactor.

Due to the problems associated with overhydration, it was decided to stop the measurements with the pure salt.

Open sorption reactor measurements salt with carrier

To avoid the problems related to overhydration, the magnesium chloride hydrated was impregnated into a carrier material, as shown in Figure 6a. On measuring the pressure drop over the bed, it was found that the pressure drop was substantially lower than for the pure salt, as shown in Figure 6b. In addition, the first measurements seem to indicate that the pressure drop stabilizes at a constant value and the increase in pressure drop associated with overhydration does not appear, indicating that the carrier material functioned as expected. However, more extensive measurements are required to confirm this.

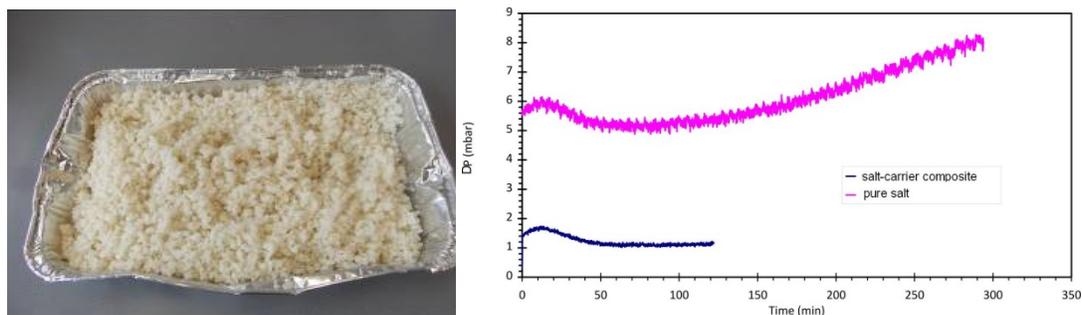


Figure 6: (a) Composite of Magnesium chloride hydrate with carrier, (b) pressure drop over reactor using composite material, compared to using pure salt.

A sample of 245 gram $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ composite was dried at 130°C and subsequently hydrated with a humid nitrogen flow of 20 slpm and 12 mbar vapor pressure. The temperature in the bed during hydration is shown in Figure 7. A temperature rise of 20°C is observed in the bed. This temperature rise is substantially lower than the one in Figure 2, due to the fact that the temperature rise that can be reached in an open reactor is lower than in a closed reactor, because of the thermal capacity of the airflow. At the entrance of the reactor, a fast rise in temperature can be seen, related to the hydration of the material, followed by a slow decline as the hydrated material is cooled down by the incoming cold and humid airflow. The heat of hydration is carried with the airflow and heats the downstream part of the bed. Therefore, the temperature of the downstream part of the bed already rises before the hydration of this part has started. This results in a

high temperature front moving quickly through the bed at the onset of the hydration, followed by a much slower low temperature front indicating the local completion of the hydration reaction.

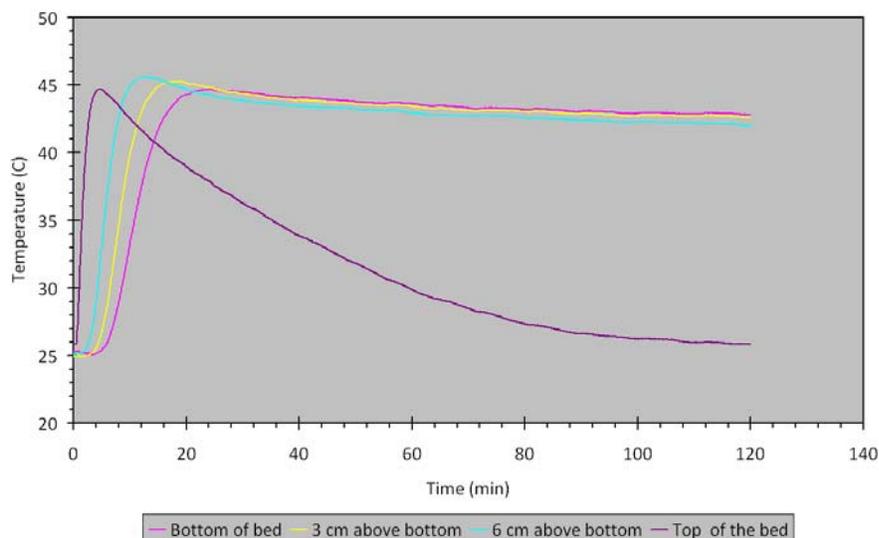


Figure 7: Experimental vertical temperature profiles during the hydration of the $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ composite at room temperature and $P_{\text{H}_2\text{O}}=12$ mbar (RH=100% at 10°C).

Figure 8 shows the temperature of the nitrogen flow and the entrance and the exit of the reactor. Again a temperature lift of 20°C is obtained. The figure shows that the exit air temperature is slightly lower than the bed temperature as indicated in Figure 7. The entrance nitrogen flow shows a decline, due to the fact that the evaporation in the bubble flask reduces the bubble flask temperature to below the ambient temperature. Ignoring the thermal mass of the reactor and the bed, assuming full dehydration of the air and an enthalpy release in the material of 65 kJ/mol of water (an estimate for the total hydration enthalpy per mole of water), a theoretical temperature rise of 26°C could be obtained by the airflow. However, part of this heat is diverted to the heating of the bed and the reactor, thereby reducing the maximum outflow temperature. Therefore, the present result of 20°C temperature rise seems is roughly as expected.

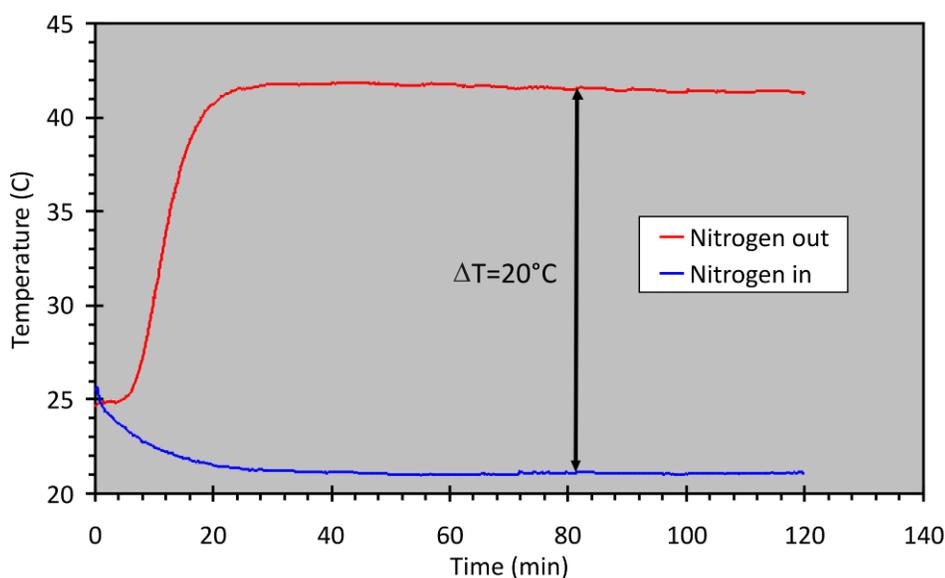


Figure 8: Temperature of the nitrogen flow at the entrance and the exit of the reactor.

First results in an upscaled reactor

For seasonal heat storage, a large volume of salt and correspondingly a large reactor is required. A quick-and-dirty attempt was made to upscale the system shown in the previous paragraph to a ten times larger system. A new reactor was built that can contain 3.6 kg of material. In order to compare the performance of the new reactor to the older reactor, again hydration experiments were carried out with a moistened nitrogen flow of 20 slpm, with a vapour pressure of 12 mbar.

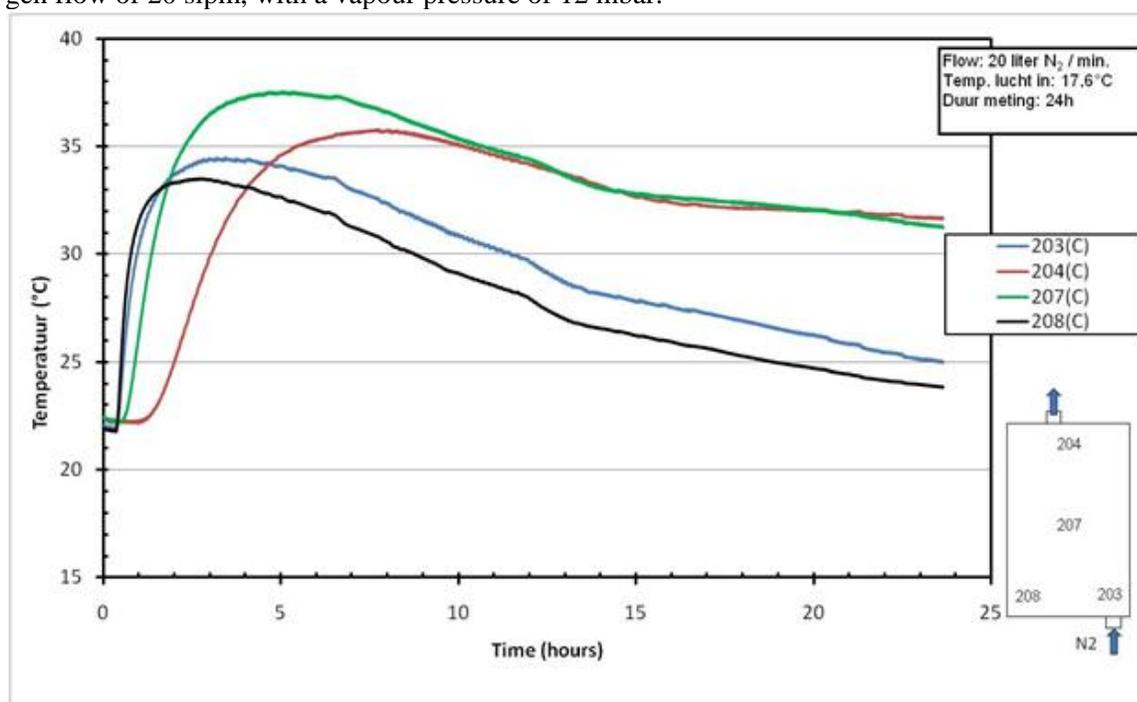


Figure 9: Temperature measurements in new reactor.

The results are shown in Figure 9. This figure shows the temperatures at different locations in the bed. The figure shows a maximum temperature rise in the material of 15°C. The lower temperature near the wall is due to heat loss to the ambient, which is significant because the reactor was not thermally insulated. The good correspondence between the thermocouples 203 and 208 indicates a homogeneous hydration of the material in the reactor. Note that after 24 hours of hydration, the reactor bed still shows a significant temperature rise. While the thermocouples at the entrance have returned to ambient temperature, the thermocouple halfway the bed shows a temperature similar to the thermocouple near the exit of the bed, indicating that the hydrated zone has not reached the middle of the bed yet. A rough indication of the energy output over the first 23 hours is obtained by integrating the power in the nitrogen flow over time, which gives 0.14 MJ/kg. However, since the hydrated zone had not even reached halfway the bed, the total energy that can be extracted from the bed will be substantially higher than this.

Conclusions

The dehydration of MgCl₂·6H₂O and subsequent hydration at 12 mbar vapor pressure (corresponding to evaporation at a typical borehole temperature of 10°C) gives a good temperature rise of 20°C. This is a promising result for the future use of this material for seasonal domestic heat storage for space heating and tap water heating.

It was found that upscaling of the reactor was possible, and a reasonable performance was obtained even with a low cost simple reactor design. Furthermore, on hydration of 3.5 kg of the magnesium chloride composite, it was found that after delivering a heated airflow for 24 hours the bed still was not fully hydrated, indicating the large storage capacity of the material.

References

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