THERMOCHEMICAL SEASONAL SOLAR HEAT STORAGE WITH $MgCl_2.6H_2O$: FIRST UPSCALING OF THE REACTOR

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INTRODUCTION

In the summer, the available of solar heat exceeds the total heat demand of a building, but in the winter the heat demand is exceeding the solar supply. For the future conversion of a passive house into an energy neutral house, a solution is to store the excess of solar energy in summer, and to use it to meet the heat demand in winter. Water is traditionally used for storing heat (e.g. solar boiler), but seasonal heat storage requires large water tanks (>40m^3) that are too large to be placed inside an average family house. An alternative option is to store heat by means of chemical processes using the reversible reaction: $A + B \Leftrightarrow C$ + 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, 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. Because of the large amount of thermochemical material required for such storages, as well as the strict safety regulations in the built environment, safety and cost of the materials are important aspects. Because of safety criteria, the focus in the present research is on water as the sorbate. Because of low cost and high storage density, the focus is on salt hydrates, rather than silicagel or zeolites. In this paper, R&D on system aspects, materials selection and characterization, as well as on reactor concepts is presented.

SYSTEM DESCRIPTIONS

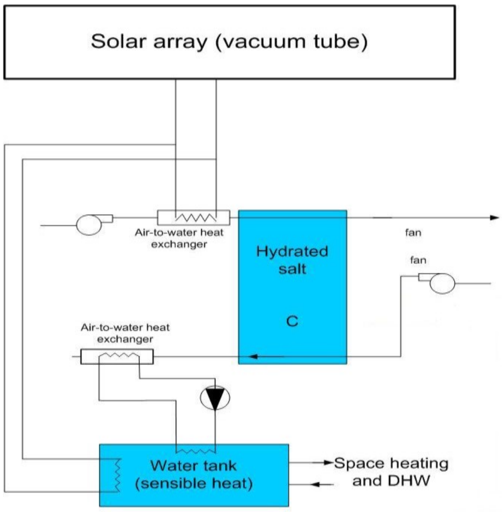

Figure 1: System layout open sorption system

If salt hydrates are applied in a seasonal storage system, during summer the salt hydrate is dried, resulting in a (partially) dehydrated hygroscopic salt. During winter, water vapour is fed to the dried salt, resulting in the release of hydration heat, that can be used for space heating and tap water heating. A typical layout for an open thermochemical heat storage system is shown in Figure 1. In this open system, 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. 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.

MATERIAL SELECTION

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). In addition, also cost and safety were important criteria. The literature overview resulted in a list of materials, of which several were tested, among which $MgSO4.7H_2O$, $Al_2(SO_4)_3.18H_2O$, $MgCl_2.6H_2O$ and $CaCl_2.6H_2O$. First, all salts were tested by means of thermogravimetric analysis (TGA). The results are shown in Figure 2. This analysis confirms that all salts can be dehydrated between 50 and 150°C.

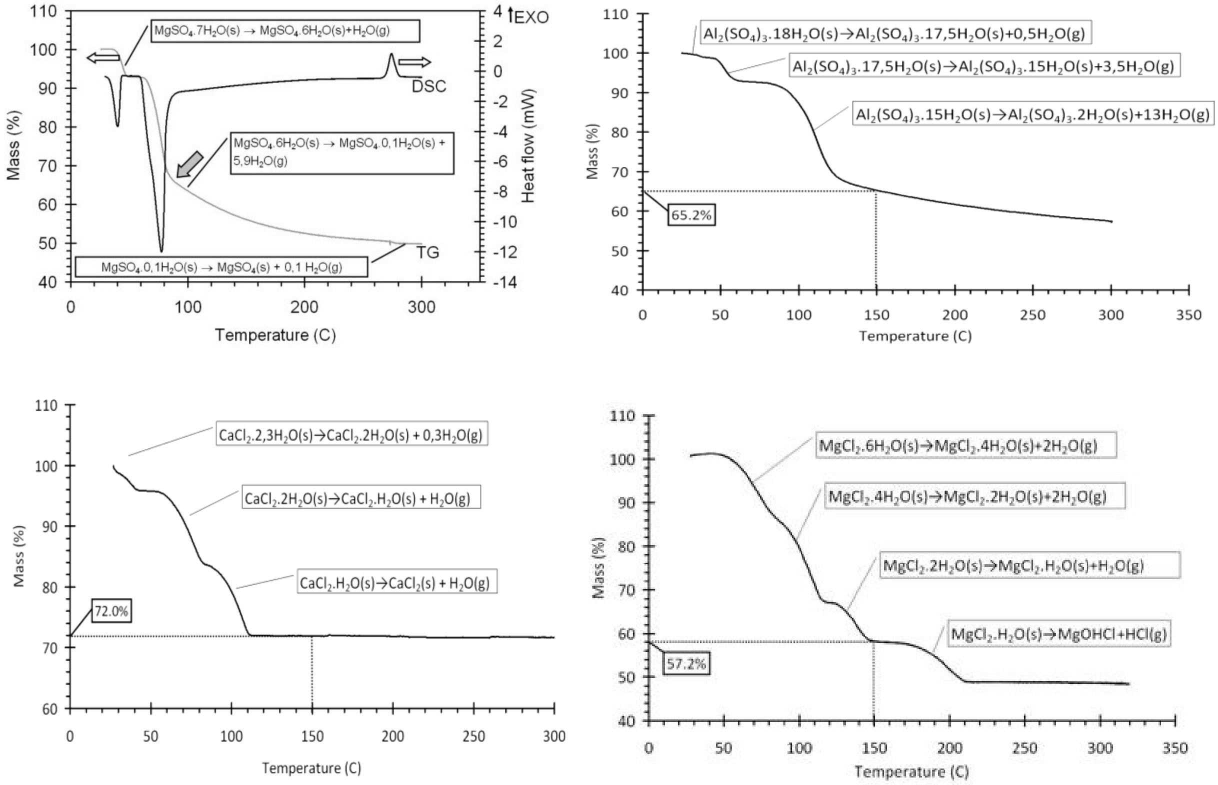

Figure 2: TGA results for selected salt hydrates (a) $MgSO_4x7H_2O$, (b) $Al_2(SO_4)_3x18H_2O$, (c) $CaCl_2x6H_2O$, (d) $MgCl_2x6H_2O$. Heating rate is 1 °C/min. Fig a: moist atmosphere (23 mbar water vapour pressure), Figures b,c,d: dry nitrogen atmosphere.

Next, hydration experiments were carried out. After drying the salts in an oven at 150°C for four hours, the salts were hydrated again in a closed reactor setup, as shown in Figure 3. During the hydration, two different temperature settings were applied; one setting with both the sorbent bed and the evaporator at 25°C, and one setting with the sorbent bed at 50°C and the evaporator at 10°C (a situation that would be more representative for actual applications, in which e.g. a tap water storage would have to be heated up from 50°C to 65°C). The results of these hydration experiments are shown in Figure 4.

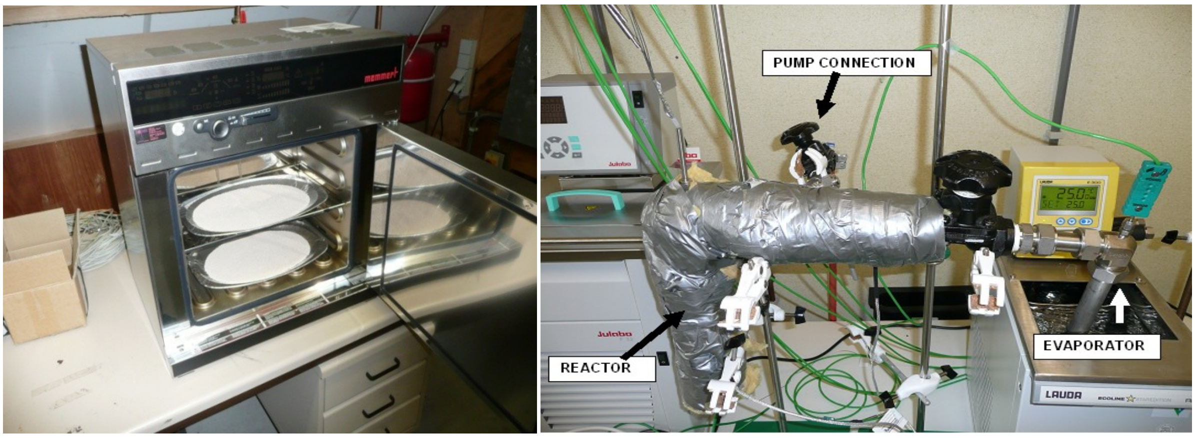

Figure 3: (left) Drying of salt hydrates in the oven, (right) Hydration of the salt in the evacuated setup.

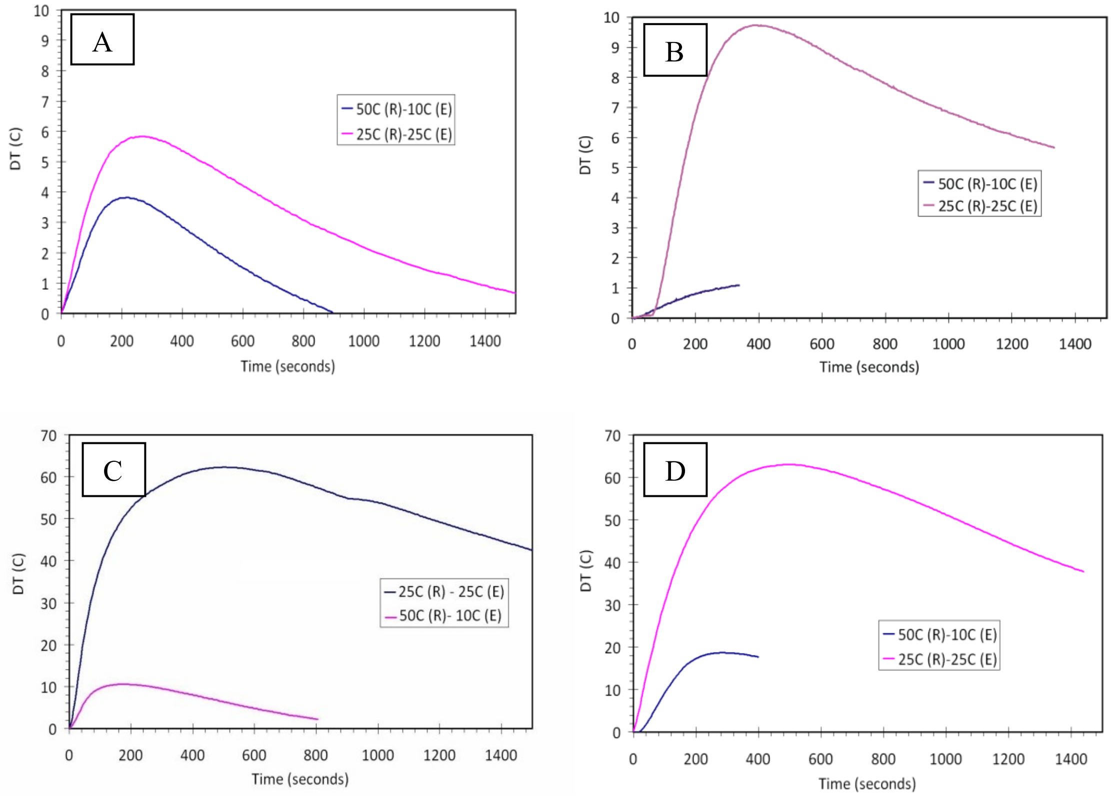

Figure 4: Hydration results for selected salt hydrates (a) $MgSO_4x7H_2O$, (b) $Al_2(SO_4)_3x18H_2O$, (c) $CaCl_2x6H_2O$, (d) $MgCl_2x6H_2O$.

As can be seen, the magnesium chloride hexahydrate ($MgCl_2.6H_2O$) provided the highest temperature step on hydration. From these results, $MgCl_2.6H_2O$ was identified as the most promising of the tested materials for application as seasonal heat storage in the built environment.

REACTOR CONCEPT SELECTION

For a thermochemical seasonal storage, different reactor concepts are possible. Four basic types can be discerned, based on the distinction between open (atmospheric) and closed (evacuated) sorption systems, and between packed bed reactors and reactors in which the thermochemical material is in motion. For the latter case, typically a system with a separate reactor is examined, through which the material is flowing, in order to minimize the auxiliary energy required for the material transport.

At ECN, all four reactor types were evaluated, and the open atmospheric system (as shown in Figure 1) was selected because of its simplicity and potentially low cost. A small labscale prototype was built, that can contain about 300 grams of thermochemical material. The reactor was subsequently insulated and used for hydration experiments. A 20 slpm air flow with 12 mbar vapour pressure was flown through the open sorption reactor. The results are shown in Figure 5. As can be seen, on hydration, a temperature rise in the sorbent bed was found of about 20°C. Furthermore, the figure shows the two temperature fronts moving though the bed: first a high temperature front due to the fact that the whole reactor content is quickly heated up by the convection of the reaction heat, followed by a much slower low temperature front, indicating that the hydration of the thermochemical material has been completed, after which the material is cooled down by the cold incoming airflow.

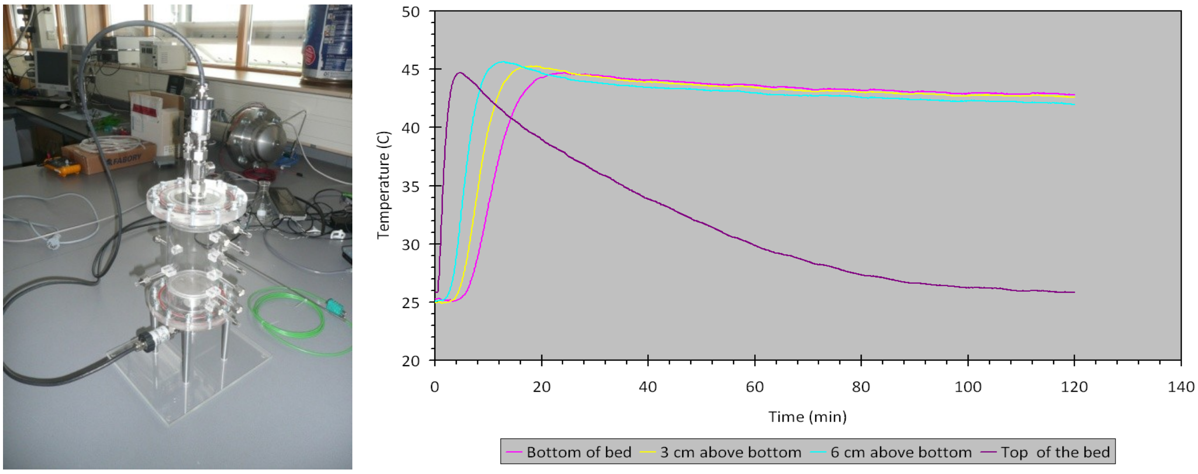

Figure 5: Open reactor (left) small prototype, (right) reactor temperatures during hydration with 20 slpm moistened air flow (12 mbar vapour pressure).

However, during the experiments with this storage system, the top layer of the hygroscopic salt hydrate was found to agglomerate during the heat discharge process (hydration). The agglomeration reduces the bed porosity and the ability to reabsorb water. To overcome this problem, a composite material consisting of $MgCl_2.6H_2O$ and a carrier material has been developed at ECN. This composite material was tested under practical conditions in an small open fixed bed storage system with a capacity of 300 grams. The results are positive, showing improved stability and low pressure drop. In the following reactor measurements, this composite material is used.

REACTOR UPSCALING

In order to investigate the feasibility of this technology for application as seasonal heat storage, it is important to upscale the small test reactor towards a full system. In the following paragraphs, the first results for this upscaling are shown. First, the homogeneity of the flow through the reactor was examined. Next, a first trial reactor was built for first preliminary tests. Finally, an open sorption storage system was built including an upscaled reactor.

Flow distribution

In order to obtain full hydration of the thermochemical material, it is important to have a sufficiently uniform flow through the reactor. In order to evaluate the flow distribution in a practical system, hydration experiments were carried out in a thin box. This box was fitted with connections at the bottom and the top and then the box was filled with the composite material. Next, moist air was flown through the box reactor, and the temperature profile was recorded by infrared camera.

The result is shown in Figure 6a. Clearly, a strong non-homogeneous temperature field appears. Next, a header was constructed in the box and a new hydration experiment was carried out. The result is shown in Figure 6b. As can be seen, a much more homogeneous flow is obtained, but still the temperature distribution shows a peak in the centre of the box reactor, which is ascribed to the injection jet. From these experiments, it is concluded that not only a header should be present to create a homogeneous flow distribution in the bed, but also a baffle plate to avoid an injection jet in the bed.

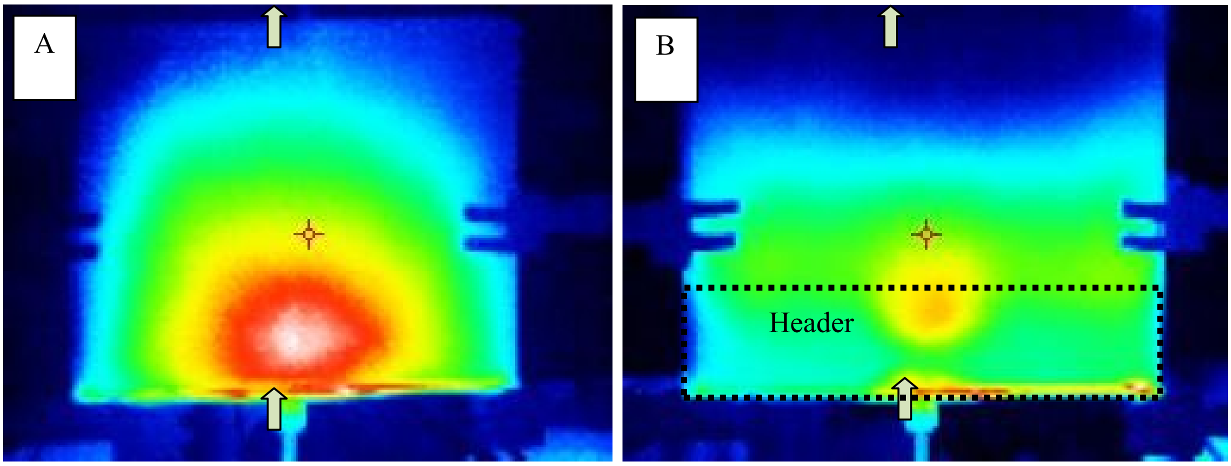

Figure 6: IR recordings of hydration in box reactor (a) without entrance air channel, (b) with entrance air channel.

First results reactor upscaling

Based on the results shown in the previous paragraph, a quick-and-dirty trial reactor has been built with a storage capacity of 3,5 kg. A schematic for this reactor is shown in Figure 7. A hydration test was carried out in this trial reactor to check the performance of a reactor with such a flow configuration. The temperature in the reactor was measured on hydration of the composite material with a moist nitrogen flow (vapour pressure roughly 12 mbar), as shown in Figure 8. Note that the two thermocouples at the entrance show similar temperature profiles, indicating a homogeneous distribution of the incoming air at the reactor entrance. Again, the fast heating front and the slow cooling front can be discerned in the measurement results. As can be seen, the 3.5 kg reactor content was able to heat up the incoming air for more than 24 hours. A rough indication of the energy output over the first 23 hours is obtained by integrating the power in the air 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.

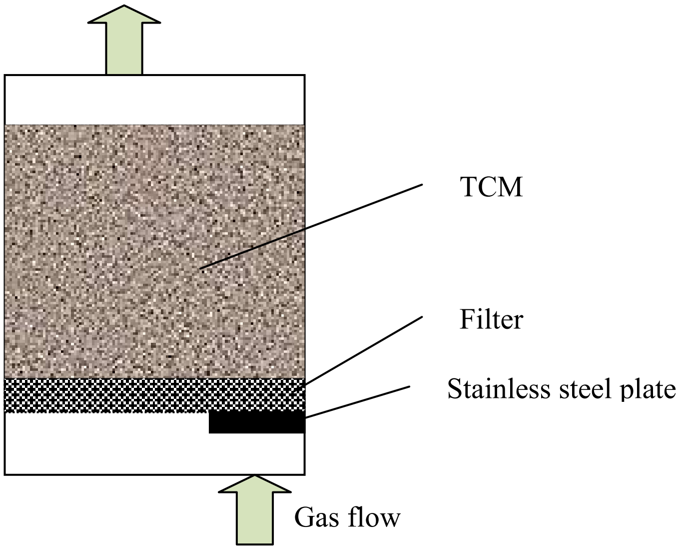

Figure 7: Schematic for the 3.5 kg trial reactor.

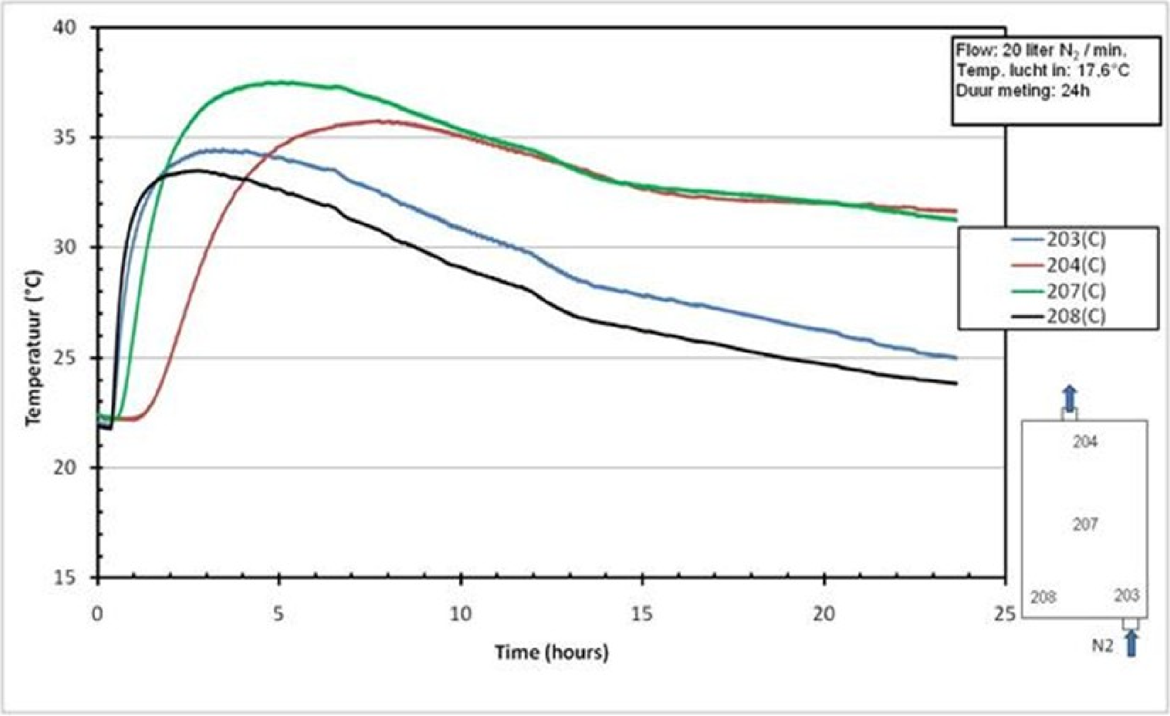

Figure 8: Temperatures on hydration of 3.5 kg of composite material in the trial reactor.

First preliminary results upscaled prototype storage system

Presently, a new reactor system setup is under construction, containing an upscaled reactor with a packed bed capacity of 10 liters. This time the setup concerns 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 load), the heat exchangers and the fan. A schematic of the new reactor system setup is shown in Figure 9. Photographs of the setup are shown in Figure 10.

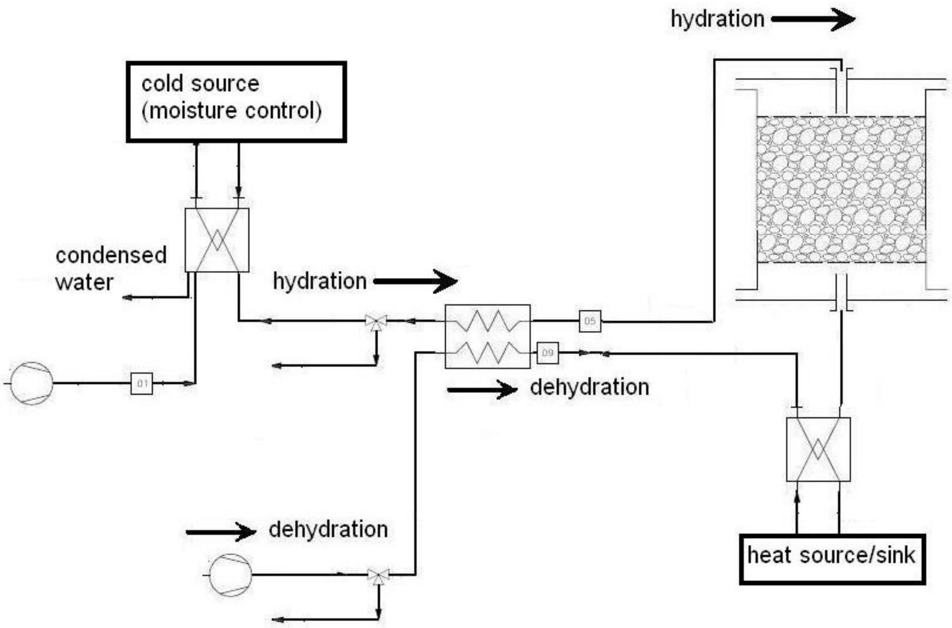

Figure 9: Schematic of upscaled reactor system.

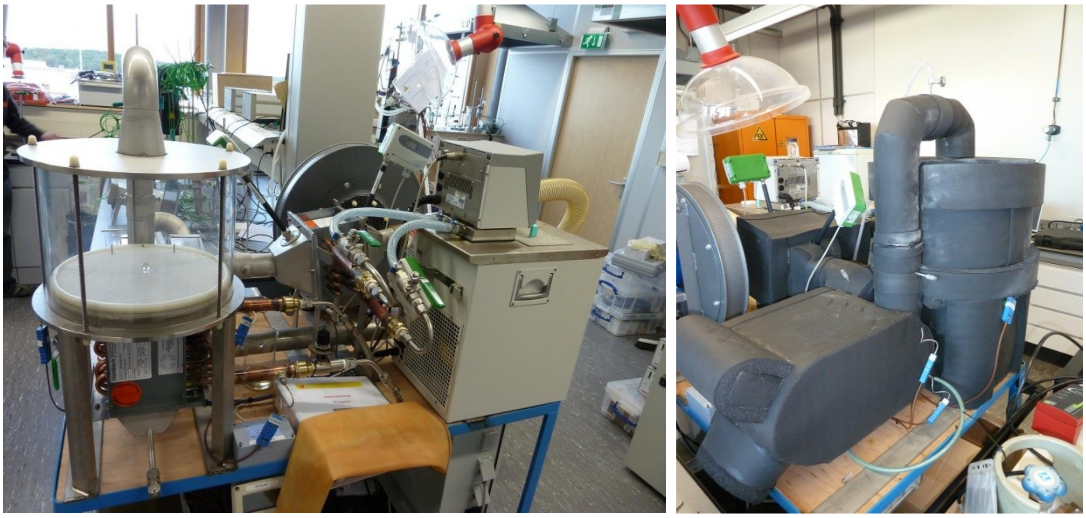

Figure 10: Photographs new prototype reactor system, (a) before and (b) after insulation.

So far, only the first preliminary measurements with this new system have been carried out. First, a reference measurement was carried out in the empty reactor, to establish the reference performance of the reactor without salt in the hydration configuration (taking into account air leakage, thermal capacity, heat exchanger efficiency, etc). Ambient air was driven through the system at a rate of 580 liter/min. The thermostatic bath (the heat source/sink in Figure 9) was fixed at a temperature of 50°C and the system temperatures were measured. The results are shown in Figure 11. As can be seen from this figure, the temperature in the reactor stabilised at roughly 30°C, which means that a temperature drop of 20°C occurs in the circuit between the heat source and the reactor. This was found to be largely due to air leakage from the system; the air tightness of the system will be improved during the next phase of the research.

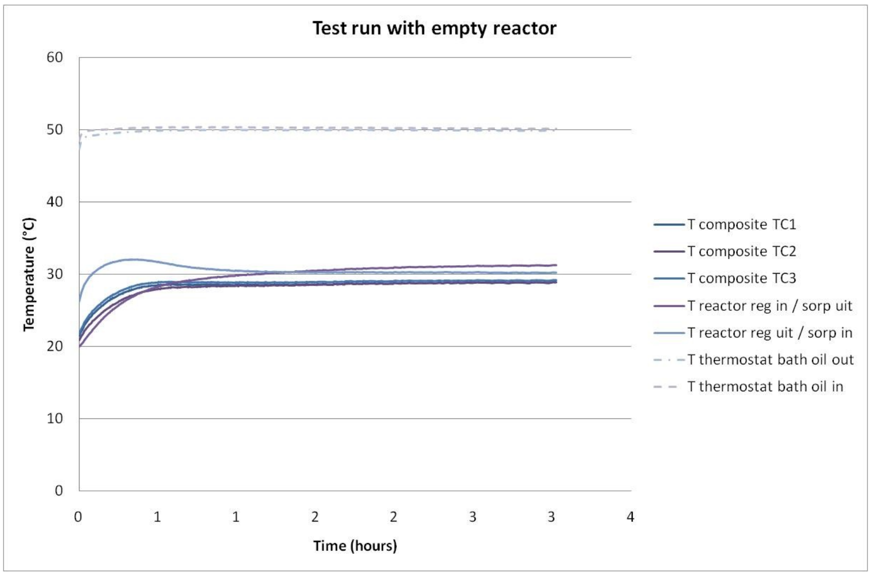

Figure 11: Reference measurement with empty reactor in hydration configuration.

With this system, a dehydration experiment was carried out. An air flow of 580 liter/minute was heated up to 130°C by means of the heat source thermostat bath, and subsequently flown through the reactor. The measured temperatures are shown in Figure 12. Note that the reactor is now in the dehydration configuration, which means that the airflow is now in the opposite direction as compared to the aforementioned reference experiment (see Figure 9). The reactor bed contains about 5 kg of composite material. The thermocouples TC1, TC2 and TC3 are all in the lower side of the bed, near the hot air entrance. Figure 12 shows clearly that the material is dehydrating, as can be seen from the dent in the temperature rise at about 110°C (roughly corresponding to the TGA data shown previously in Figure 2). After dehydration, the composite material did not show any degradation, as far as could be detected by visual inspection.

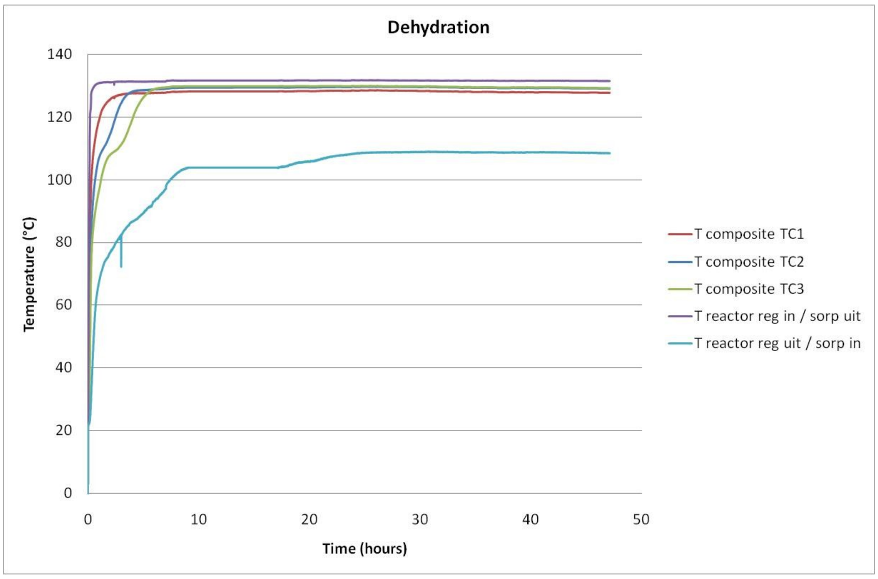

Figure 12: Dehydration of $MgCl_2x6H_2O$ in the new TC reactor system (hot air inflow temperature: 130°C, flowrate: 580 liter/min, reactor content 5 kg composite material.

Finally, a first hydration measurement was carried out, hydrating the material that was dehydrated in the abovementioned dehydration experiment. The air humidity was kept at roughly 10 mbar. As can be seen in Figure 13, the temperature in the reactor rises to about 45°C, which is 15°C higher than was found in the reference measurement shown in Figure 11. Therefore, it may be concluded that the resulting temperature rise in the system is similar to the temperature rise observed in the trial reactor (shown in Figure 8), and therefore the composite material behaves as expected. The effect of the hydration on the temperature is further illustrated by the peaks that occur in Figure 13 on switching on the evaporator. This evaporator was applied because the lab air was very dry at the time of measurement (about 6 mbar vapour pressure) and therefore a separate evaporator was required to obtain the desired vapour pressure of 10 mbar. Clearly, the water vapour in the air has a large effect on the output temperature.

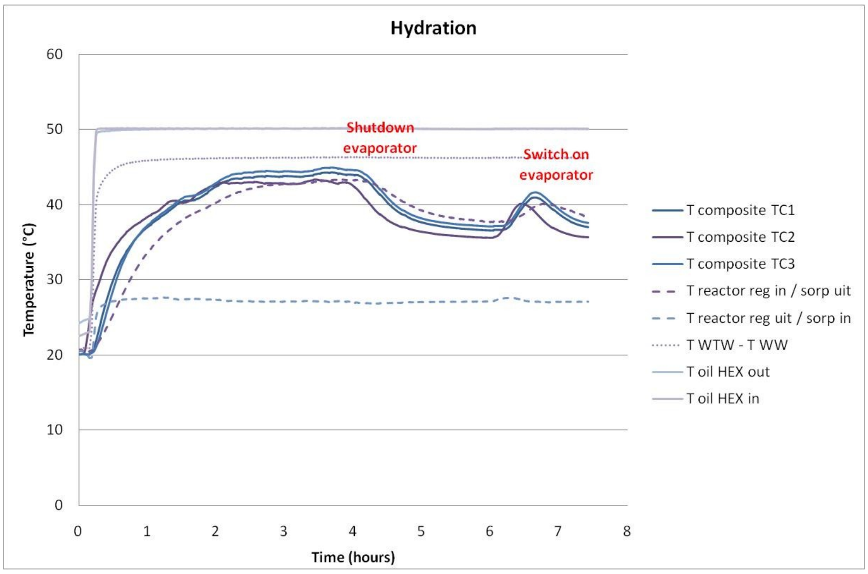

Figure 13: Hydration of $MgCl_2x6H_2O$ in the new TC reactor system (reactor content is the material that was dehydrated in Figure 12), flowrate: 580 liter/min.

CONCLUSION AND OUTLOOK

Thermochemical heat storage provides new opportunities for long term heat storage such as seasonal heat storage. Low cost materials have been identified that have sufficiently high energy density, can produce sufficient temperature step to be used for heating purposes and have sufficiently fast kinetics to generate the desired power.

The selected material, which is a composite based on $MgCl_2x6H_2O$ with a carrier material, has been hydrated and dehydrated in an open reactor system. The first measurements on a small labscale prototype have been completed successfully, and the focus is now on upscaling the reactor system. Presently, a prototype system is tested containing a reactor vessel with a capacity of 10 liters. The aim is to optimize this system and use the results to prepare the development of a field test prototype.

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