Low temperature chemical heat storage – an investigation of hydration reactions

F. Bertsch*, B. Mette*, S. Asenbeck*, H. Kerskes*, H. Müller-Steinhagen* +

* Institute for Thermodynamics and Thermal Engineering (ITW), University of Stuttgart, Germany
Pfaffenwaldring 6, 70550 Stuttgart, Germany
Tel.: +49-(0)711-685-63279, Fax: +49-(0)711-685-63503
Email: bertsch@itw.uni-stuttgart.de

+ Institute for Technical Thermodynamics (ITT), German Aerospace Center (DLR)

Abstract
Two different salt hydration reactions have been studied with respect to possible low temperature heat storage applications. First results of experiments with magnesium sulfate monohydrate and copper sulfate monohydrate, hydrated by a moist air flow, are presented. Emphasis has been placed on the point of reaction equilibrium regarding temperature and humidity, which can be approximated theoretically from literature data, and on the achievable temperature lift. The experimental data are in good agreement with the theoretical equilibria. At high humidities and temperatures of about 40 °C, both sulfates yield feasible reaction rates. Nevertheless, an energy-efficient provision of water vapor at these conditions is essential.

Keywords: thermo-chemical heat storage, salt hydrate, magnesium sulfate, copper sulfate, solar thermal

1. Introduction
The technology of thermal energy storage is a key element for reaching the German and European objectives with respect to climate protection and reduction of fossil energy demand. An efficient storage of low-temperature heat is essential for applications with a time shift between energy provision and energy demand, such as the use of solar thermal energy or combined heat and power plants. In this context, using the heat of reversible chemical reactions to realize chemical heat storage promises highly efficient short and long term stores with a high energy density and relatively small heat losses. In a first study at ITW the potential of different salt to salt hydrate reactions were investigated in a packed bed reactor.

Activities in the field of chemical heat storage
The probably best developed and most known project using low temperature thermo-chemical heat storage is the sorption store developed by the company UFE-Solar and Fraunhofer ISE. Due to technical problems this concept has not been commercialized until now. The concept of a closed adsorption of water vapor to silica gel was further developed by AEE-Intec together with ISE and other partners within the European project “Modestore” [12]. A pilot plant was commissioned in a single-family house by AEE-Intec in 2003. The concept of a low loss, long term storage was demonstrated successfully. However, the achieved effective energy density of 50 kWh/m³ was only about 50 % of the theoretical value. This can be explained by the process design itself as the sorption temperature decreases with increasing
charge. Thus the maximum achievable temperature lift of 50% charged silica-gel is too low to drive a typical radiator heating system and is hence not suitable for practical applications.

From a design point of view the open adsorption has many advantages. The flow through a sorption store with humid air leads to an inhomogeneous discharging of the storage material with distinct adsorption fronts. Thus the outlet air temperature remains approximately constant on a high level. Projects from ZAE-Bayern [13] and ITW [11] have shown that a charging of up to 85% of the storage material can be obtained. The storage energy density of the sorption materials was 130 kWh/m³ which is about two times higher than the storage density of a water store with the same volume ($\Delta T = 50$ K, which is 58 kWh/m³).

Using the heat of reaction of a reversible gas-solid reaction offers the potential of an even higher storage density. Within a joint project of the Institute of Technical Thermodynamics (ITT) of the German Aerospace Center (DLR), ITW is investigating the technical feasibility of chemical heat storage for low-temperature applications, whereas high temperature applications are investigated by ITT.

The hydration reactions of an anhydrated salt ($\text{MgSO}_4$, $\text{CuSO}_4$) have been investigated in a packed bed reactor. The experiments were carried out under various flow conditions of the air (temperature, partial pressure of water vapor). With equilibrium calculations the results obtained in these experiments have been analyzed.

2. Materials and methods

The schematic set-up of the test facility used to carry out the hydration experiments is shown in Figure 1. The reactor has a length of 20 cm and a diameter of 3.5 cm. The piping towards the reactor can be heated to the desired inlet temperature of the reactor. The air flow temperature is measured at the inlet of the reactor. The temperature distribution in flow direction inside the reactor is measured with three thermocouples at 5 cm, 10 cm and 15 cm respectively. These thermocouples have been calibrated to an uncertainty of ±0.1 K.

![Figure 1: Schematic sketch of the test rig used for the hydration and dehydration experiments](image-url)
The inlet and outlet humidity is measured by two capacitive moist sensors (hygrotest 650, version 4, testo). Piping and reactor are insulated with at least 5 cm of glass-wool or Armaflex® respectively. Copper(II)-sulfate-penta-hydrate (CuSO₄*5H₂O), purity > 98.5 % and magnesium-sulfate-hepta-hydrate (MgSO₄*7H₂O), purest grade, both from the company “Carl Roth” where used as salt hydrates. They have been dehydrated in the test rig at a maximum temperature of 200 °C. From thermo-gravimetric analysis it is known that at this temperature monohydrates are formed [7, 8]. The volumetric flow of the air for all experiments was 1.5 m³/h. If not stated differently the mass of the probe was 100 g monohydrate.

In Figure 2 pictures of the used materials are shown.

![Figure 2](image)

Figure 2: Pictures of the used materials. (a) MgSO₄*1H₂O, (b) CuSO₄*1H₂O, (c) MgSO₄*7H₂O, (d) CuSO₄*5H₂O

3. **Experimental investigations and results**

Magnesium-sulfate-monohydrate (MgSO₄*H₂O) has a high potential as chemical storage material. Including the condensation heat of water vapor, a theoretical storage density of 2.3 GJ/m³_heptahydrate (633 kWh/m³_heptahydrate) can be obtained. This is about 11 times higher than the storage density of a water store with the same volume (ΔT = 50 K). In Table 1 different hydration experiments with magnesium sulfate monohydrate are shown. In these experiments MgSO₄*H₂O was flown through by humid air with a flow rate of 1.5 m³/h. Depending on the inlet temperature and humidity a maximum temperature lift of 30 K has been observed.

In Figure 3 the inlet temperature and reactor temperatures at heights of 5 cm (T1), 10 cm (T2) and 15 cm (T3) of experiment 4 (Table 1) are plotted against time. As the outlet temperature is almost equal to T3, only T3 is displayed in figure 3. The temperature increases almost uniformly over the reactor length to a peak of about 55 °C. With increasing charge, the temperature lift decreases simultaneously. No reaction front was formed. A slow but constant reaction rate has been observed even after 7 hours. The same shapes of curves, but different temperature lifts were observed in the other five experiments.
Table 1: Summary of the experiments with magnesium sulfate monohydrate and humid air, $\vartheta_{in}$ is the inlet temperature of the reactor, $\varphi$ the relative humidity of the inlet air flow, $p_{\text{H}_2\text{O}}$ the water vapor pressure of the inlet air flow and $\Delta T_{\text{max}}$ the maximum measured temperature lift.

<table>
<thead>
<tr>
<th>No.</th>
<th>$\vartheta_{in}/^\circ\text{C}$</th>
<th>$\varphi/%$</th>
<th>$p_{\text{H}_2\text{O}}/\text{mbar}$</th>
<th>$\Delta T_{\text{max}}/\text{K}$</th>
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<td>60</td>
<td>60</td>
<td>119.6</td>
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The uniformly decreasing temperature in the reactor can be explained by a decreasing reaction rate. This indicates an increasing transport inhibition of water vapor towards MgSO$_4$·xH$_2$O (x≤6) inside the crystals. It was further observed that the lower the temperature and humidity at the reactor inlet, the slower the reaction takes place. In experiment No. 1 a temperature lift of about 1 K was still observed after 10 hours, whereas for experiment No. 6 a temperature lift was observed just for 1.5 hours. After each experiment the mass of the probe has been determined. For all experiments, the increase of weight was between 3 and 4 mol water per mol magnesium sulfate monohydrate. The fully hydrated state was not reached.

Many authors report that MgSO$_4$·7H$_2$O melts or boils in its crystal water before degrading to lower hydrates (e.g. [7, 10]). This leads to crystal growth and bonding. In the experiments carried out at ITW this phenomenon has been avoided by performing the dehydration of MgSO$_4$·7H$_2$O in a packed bed reactor. The air flow, which helped to transport the water out of the reactor, and the slow heating rate successfully, inhibited crystal growth and bonding.

There are different hydrates of Magnesium sulfate, i.e. mono-, bi-, tetra-, penta-, hexa and heptahydrate, even though not all of these hydrates are stable or crystalline [4,5]. It is not known/described if and under what conditions during the hydration reactions from MgSO$_4$ to MgSO$_4$·7H$_2$O intermediates are formed. From thermodynamic data (e.g. [1, 2, 3, 4, 5, 9])
Equilibrium curves of magnesium sulfate and its different hydrates can be approximated using the van’t Hoff equation:

\[
\frac{\ln K}{T} = \frac{\Delta H_R}{RT^2}
\]  

(1)

where \( K \) is the equilibrium constant, \( \Delta H_R \) the enthalpy of reaction, \( T \) the absolute temperature and \( R \) the gas constant. The equilibrium constant can be calculated with Gibb’s equation:

\[
\Delta G_R = -RT \ln K
\]

(2)

where \( \Delta G_R \) is the Gibbs free energy of reaction. Although 6 different hydrates have been described in literature, sufficient thermodynamic data to calculate the equilibrium curve are only available for mono-, hexa- and hepta hydrate. In Figure 4 these equilibrium curves are depicted. Displayed in Figure 4 are also the reactor inlet conditions of the air flow (temperature, partial pressure of water) of each experiment and the maximum temperature lift achieved.

In experiments number 1, 2 and 3 the reactor inlet temperature was comparatively low. Furthermore, the inlet conditions are very close to the equilibrium of magnesium sulfate hexa- to heptahydrate. Both effects result in a slow reaction rate, a long hydration time and a moderate temperature lift. In experiment 4 and 5 the higher inlet temperature favors the hydration of the anhydrate and a higher reaction rate, a shorter hydration time and a higher temperature lift is observed. The highest temperature lift of 30 K is obtained in experiment 6. However, a fully hydrated state of the magnesium sulfate cannot be achieved under these conditions as the reactor inlet condition is to the right of the equilibrium curve of hexa- to heptahydrate.

Figure 4: Equilibrium curves of MgSO₄ and its hydrates and the reactor inlet conditions of the air flow (point 1 to 6) for the different experiments. [1, 2, 4] were used to calculate the equilibrium curves at atmospheric pressure

With increasing hydration of the salt, a decreasing reactor temperature is observed. (cf. figure 3). This is due to the approaching of the reaction equilibrium from magnesium sulfate hexa- to heptahydrate as the hydration of the salts proceeds. A decreasing reaction rate is the result. Furthermore, the maximum achievable reactor temperature is limited by the
equilibrium of the intermediates. Magnesium sulfate monohydrate can absorb water at a higher temperature than a more hydrated salt such as magnesium sulfate hexahydrate.

However, to obtain information about the thermal performance of the hydration reaction, in further experiments not the maximum achievable temperature lift has to be determined but the reaction rate at a constant temperature. This requires an isothermal reactor.

A typical low-temperature domestic space heating system requires forward temperatures of about 40 °C. At this temperature promising results regarding reaction rates and the state of equilibrium are observed. However, a high water vapor pressure is needed.

Experiments with copper sulfate monohydrate were accomplished since the reaction from copper sulfate mono- to pentahydrate offers a theoretical storage density of 2.1 GJ/m³pentahydrate or 574 kWh/ m³pentahydrate. This is about 10 times higher than the storage density of a water store of the same size (at ΔT = 50 K). In Table 2 the different reactor inlet conditions (temperature, humidity) of these experiments are shown. A maximum in the temperature lift can be observed in experiment No. 4. The characteristics of the temperature distribution inside the reactor during the hydration were similar to those observed during the experiments with magnesium sulfate (cf. Figure 3).

Table 2: Summary of the experiments with CuSO₄·H₂O and humid air, \( \vartheta_{\text{in}} \) is the inlet temperature of the reactor, \( \varphi \) the relative humidity of the inlet air flow, \( p_{\text{H}_2\text{O}} \) the water vapor pressure of the inlet air flow and \( \Delta T_{\text{max}} \) the maximum measured temperature lift.

<table>
<thead>
<tr>
<th>No.</th>
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<th>( \varphi /% )</th>
<th>( p_{\text{H}_2\text{O}} /\text{mbar} )</th>
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During the hydration from copper sulfate mono- to pentahydrate crystal growth and agglomeration has been observed. While dehydrating CuSO₄·5H₂O in the packed bed reactor these agglomerates and crystals where destroyed and a fine powder of CuSO₄·1H₂O has been obtained (see Figure 2b).

After each experiment, the probe mass was determined. The increase of weight for experiments 1, 2, 3 and 4 was between 3.5 and 4 mol water per mol copper sulfate monohydrate. Thus it is possible to almost fully hydrate CuSO₄·H₂O under these reactor inlet conditions. In experiment 5 an uptake of less than 1 mol fraction of water was observed. The theoretical equilibrium curves of copper sulfate and water vapor can be calculated using equations (1) and (2) together with thermodynamic data [9]. The results are shown in Figure 5. Depicted are also the reactor inlet conditions of the airflow during the experiments and the maximum measured temperature lifts. The decrease of the temperature lift at high inlet temperatures and water vapor pressures can be explained by the equilibrium states. However, according to the equilibrium curve CuSO₄ mono- to trihydrate, no reaction should have been observed in experiment 5. The fact that a reaction took place might be due to two reasons. Firstly, during the dehydration of the hydrated salt in the test rig not only copper sulfate monohydrate has been formed but also copper sulfate. Secondly, the theoretical equilibrium might not fully characterize the used material.
Concerning the equilibrium curves and reaction rates of the experiments, the temperature interval between 30 °C and 40 °C seems to be appropriate using copper sulfate as storage material. Yet the maximum temperature lift observed was only 11 K. But as stated before this is not a measure of the thermal performance of the system. A sufficient reaction rate of the experiments was only observed using high water vapor pressures and temperature around 40°C.

5. Conclusion

The hydration reactions of magnesium sulfate and copper sulfate have been studied in an open hydration circuit using humid air flow. Magnesium sulfate monohydrate and copper sulfate monohydrate are promising candidates for thermo-chemical storage materials. Dehydrating the salts in an open circuit has the advantage that crystal growth and bonding can be prevented effectively. Hence, during the experiments, the materials where cycle stable.

The equilibria of the sulfates with humid air have been approximated with literature data. The hydration experiments have shown that for both, magnesium- and copper-sulfate-monohydrate, a high water vapor pressure is needed for a sufficiently high reaction rate. The reaction of copper sulfate monohydrate with humid air is limited by the equilibrium to a maximum operating temperature of 60 °C. Although higher temperature lifts and operating temperatures were observed using MgSO₄, this is not directly correlated with a faster reaction rate. To determine the reaction rate, further research has to be done in micro- and macro-scale to understand the reaction kinetics and mass transfer processes, especially with respect to the different hydrates of magnesium sulfate.

However, a water vapor pressure of more than 13 mbar cannot be provided easily from ambient air during the heating period. Hence the application of magnesium sulfate or copper sulfate as the only thermo-chemical storage material seems to be critical. Further material research has to be done. One possible way to overcome this obstacle could lie in composite materials which will be part of future research activities at ITW.
Acknowledgments

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Nomenclature

- $\Delta T$ $K$ temperature difference
- $\vartheta$ °C temperature
- $\varphi$ % relative humidity
- $p_{H_2O}$ bar partial pressure of water
- $K$ - equilibrium constant
- $R$ J mol$^{-1}$ K$^{-1}$ ideal gas constant
- $\Delta G_R$ kJ mol$^{-1}$ Gibbs free energy of reaction
- $\Delta H_R$ kJ mol$^{-1}$ enthalpy of reaction

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