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Calorimetric studies of thermochemical heat storage materials based on mixtures of $MgSO_4$ and $MgCl_2$

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ABSTRACT

Attapulgite granulate impregnated with mixtures of $MgSO_4$ and $MgCl_2$ hydrates was investigated for suitability as a composite thermal energy storage material. These mixtures were chosen because of the very different deliquescence relative humidities of the salts. The thermochemical heat storage of these materials was characterized by measurements of isothermal heat of sorption and thermogravimetry (TG). The salt mixtures showed a different sorption behavior compared to pure $MgSO_4$. The reduction of the deliquescence relative humidity of the mixture by the partial substitution of $MgSO_4$ by $MgCl_2$ increases the capacity of condensation and therefore the released heat. The energy density of the composite heat storage material containing a salt mixture of 20 wt% $MgSO_4$ and 80 wt% $MgCl_2$ was 1590 kJ/kg measured by calorimetry (at 30 °C/85% RH) with a desorption temperature of 130 °C.

1. Introduction

The storage of unutilized solar energy is an important factor to increase the efficiency of renewable energy and therefore to save fossil fuels. For this purpose, micro- and mesoporous materials with high storage capacity based on the heat of adsorption of water vapor, e.g. modified zeolites, aluminophosphates (ALPO) and silicoaluminophosphates (SAPO) have been widely investigated and characterized [1,2]. While zeolites offer the advantage of a high temperature lift they also require high charging temperatures, typically above 470 K. The molecular sieves ALPO-18 and SAPO-34 show a medium temperature lift and a lower charging temperature [2]. However, due to high synthesis costs they are currently too expensive for application as heat storage materials.

Another group of thermochemical heat storage materials are composite materials [2–4] made of porous materials impregnated with hygroscopic salt hydrates. These materials have the advantage of a low desorption temperature (up to 130 °C), a low price and simple production method. The desorption temperature of 130 °C is realizable by solar collectors and is sufficient for desorption and charging the storage materials [5]. Therefore, the materials appear to be interesting for the utilization of a day/night or seasonal heat storage.

The use of these materials is based on the exothermic reaction of a salt in a low state of hydration with water vapor to form either a higher hydrated form or a salt solution inside the pores. The water uptake depends on the deliquescence relative humidity (DRH). If the relative humidity (RH) of the environment exceeds the DRH, the salt absorbs water and dissolves until reaching equilibrium, i.e. until the water activity of the solution equals the relative humidity. At relative humidities below the DRH, the salt picks up water vapor forming a higher hydrated state but no solution. Both cases are shown in the following equations.

$$\text{Salt}(s) + H_2O(g) \leftrightarrow \text{hydrated form}(s) \quad \text{for RH} < \text{DRH} \qquad (1)$$

$$\text{Salt}(s) + H_2O(g) \leftrightarrow \text{solution}(l) \quad \text{for RH} > \text{DRH} \qquad (2)$$

The resulting heat of sorption is in case (1) the sum of the heat effects of the water vapor condensation and the heat of reaction of the hydration. Diffusive water transport at the reaction interface may often be the rate limiting step in solid–gas–solid reactions. For example, in the system $MgSO_4$–H_2O kinetic hindrance of the hydration of kieserite ($MgSO_4{\cdot}H_2O$) to higher hydrates was observed [6,7]. Investigation of the sorption heat of $MgSO_4{\cdot}7H_2O$ dehydrated at 130 °C showed that the thermodynamically stable product, i.e. $MgSO_4{\cdot}7H_2O$, could not be obtained at 30 °C and 85% RH [8]. Magnesium sulfate has a high hydrothermal stability and does not decompose at elevated temperatures and water vapor pressures but the slow rate of the rehydration reaction is disadvantageous for heat storage applications.

In case (2) a higher RH compared to the DRH of the salt will result in an additional sorption of water and the heat of condensation increases the total release of heat. The disadvantage of this process is the formation of a salt solution that may affect the hosting material. Especially halides show a great tendency

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to decompose under hydrothermal conditions. Through hydrolysis reactions strong acids such as HCl will be formed. Metal parts of adsorber units can corrode under the influence of these acidic solutions [9].

To improve the performance and stability of heat storage materials both reactions may be combined. A hydrothermally stable salt with high DRH (e.g. magnesium sulfate) may be mixed with a small amount of a deliquescent salt to realize advantageous properties. The dehydrated magnesium sulfate hydrate can partly dissolve in a solution of a deliquescent salt and higher hydrate states will be formed by reaction in solution. The hydration is no more a solid–gas–solid reaction and the kinetic hindrance is overcome. Therefore mixtures containing $MgSO_4$ (high DRH of 90% RH at 30 °C) and $MgCl_2$ (low DRH of 33% RH at 30 °C) were chosen in the present work. Using common cation (Mg^{2+}) mixtures avoids undesired reactions between the two salts.

This paper presents results of the heat storage properties of a composite material (salt mixtures inside a porous host material). Several influencing factors were investigated such as the salt mixing ratio, the variation of the measurement conditions and the influence of the salt content.

2. Experimental

2.1. Materials

Attapulgite granulate with an open porosity of 74.3%, a BET surface area of 106 m^2/g and an average pore diameter of 0.08 μm (Hermsdorfer Institut für Technische Keramik, Germany) was used as porous host material. The granulate was impregnated with salt solutions containing $MgSO_4$ and $MgCl_2$ in the desired mixing ratios and were dried at 40 °C to constant mass. Using this procedure, salt contents of the composite materials from 19 to 43 wt% were obtained. In the case of impregnation with the pure $MgSO_4$ solution, the state of hydration after drying at 40 °C was determined by thermogravimetry (TG) yielding $MgSO_4{\cdot}7H_2O$. Phase identification after impregnation with the mixed solutions was difficult due to the fact that both salts have different hydrated states. Furthermore, the drying characteristics were influenced by the very different deliquescence relative humidities of the salts at every mixture ratio.

2.2. Methods

The heat of sorption was measured in an open system in a circulation cell using a Calvet-calorimeter C 80 (Setaram) coupled with a humidity controller Wetsys (Setaram). The preparation of the dehydrated samples and the sorption measurement were done within the calorimeter, by using gas circulation cells. After placing about 0.75 g of the composite material in the experimental cell it was heated to the desired desorption temperature (130 and 100 °C, respectively) at a rate of 2 K/min. A dwell time of 2 h was adjusted to reach equilibrium. The water vapor evaporated during the dehydration was removed in a flow of dry air (5% RH at 30 °C) at a flow rate of 50 ml/min. Subsequently, the dehydrated material was cooled down at the same flow rate of dry air (5% RH). After achieving a constant heat flow at the sorption temperatures of 30 and 40 °C, respectively, the sorption reaction was induced by a sudden increase in the relative humidity to the desired value (i.e. 75% and 85% RH, respectively) and the heat flow was measured. The total heat of sorption was determined by integration of the heat flow curve. Table 1 summarizes the experimental conditions.

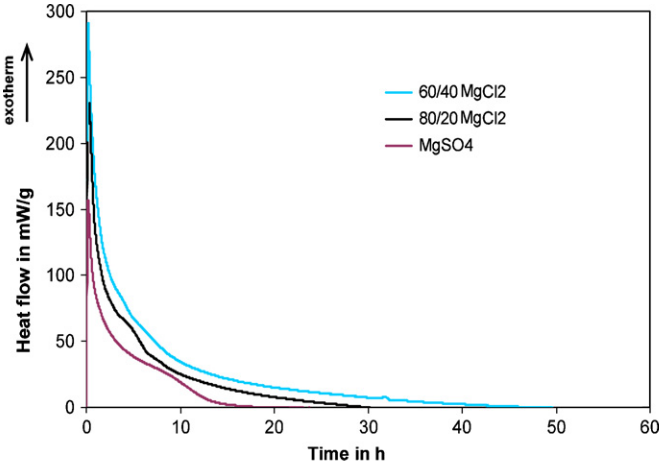

Fig. 1. Heat flow curves of attapulgite granulate impregnated with different salt mixtures at 30 °C and 85% RH.

Thermogravimetry was applied to determine the water content of the materials and salt hydrates using a Setsys 16/18 device (Setaram). The material samples were dehydrated completely at a heating rate of 10 K/min in air atmosphere to calculate the total amount of water. In addition, the water content of pure $MgSO_4$ and $MgCl_2$ hydrates were determined to obtain the hydration states at the desorption temperature of 130 °C.

3. Results and discussion

3.1. Influence of the salt mixing ratio

The influence of the salt mixing ratio was measured after dehydration at 130 °C and subsequent sorption at 30 °C and 85% RH.

The heat flow curves of the composite (attapulgite granulate hosting different salt/salt mixtures) are shown in Fig. 1. The hydration of a dehydrated $MgSO_4$ hydrate follows the reaction after Eq. (1) and took the shortest time to reach the equilibrium (about 18 h). For the salt mixtures the reaction follows Eq. (2), i.e. if a salt solution is formed, the time to reach the equilibration was much longer (up to 50 h; Fig. 1). The released heat at the beginning of the measurement was clearly higher than that of pure magnesium sulfate. This behavior is caused by the differences between the water vapor partial pressure of the dehydrated salt or salt mixture and the humid air. Table 2 summarizes the results of the heat of sorption measurements at 30 °C and the total salt content of the composite heat storage materials. For comparable total salt contents the heat of sorption increases with increasing weight fraction of $MgCl_2$ at similar conditions.

If RH < DRH, the maximum enthalpies of hydration for every mixing ratio may be calculated according to Eq. (1) if the hydration states of the educt phases are known. TG measurements

Table 1
Sorption conditions.

Condition	Temperature of desorption (°C)	Sorption temperature (°C)	Humidity (% RH)
A	130	30	85
B	130	30	75
C	130	40	75
D	100	40	75

Table 2
Heat of sorption and salt content of the composite material depending on the mixing ratio of the salt.

Mass ratio $MgSO_4/MgCl_2$	Salt content at 40 °C (wt%)	Heat of sorption (kJ/kg material)
100/0	31.7	610
90/10	26.6	720
80/20	27.2	880
70/30	26.7	920
60/40	28.6	1060
50/50	29.3	1100
40/60	28.6	1150
30/70	33.2	1320
20/80	32.8	1600
10/90	30.7	1620

Table 3
Heat of sorption and sorption conditions of a heat storage material with a mixture of 20 wt% $MgSO_4$ and 80 wt% $MgCl_2$.

Condition	Temperature of desorption (°C)	Measurement conditions	Heat of sorption (kJ/kg material)
A	130	30 °C–85% RH	1590
B	130	30 °C–75% RH	1430
C	130	40 °C–75% RH	1070
D	100	40 °C–75% RH	1100

with pure single salts yielded water contents of $MgSO_4{\cdot}1.3H_2O$ and $MgCl_2{\cdot}1.8\ H_2O$ after dehydration at 130 °C. At 30 °C the thermodynamic stable end products of the hydration reaction are $MgSO_4{\cdot}7H_2O$ and $MgCl_2{\cdot}6H_2O$, respectively. Then, the hydration heat is the difference of the standard enthalpy of formation of the product phase and the sum of the standard enthalpies of formation of the educt phases with the standard enthalpy of formation of gaseous water. The enthalpies of formation of the educt phases were obtained by interpolation from the known standard enthalpies of formation of $MgSO_4{\cdot}H_2O$ and $MgSO_4{\cdot}2H_2O$ [10] as well as $MgCl_2$ and $MgCl_2{\cdot}2H_2O$ [11] at 25 °C. The values of $MgSO_4{\cdot}1.3H_2O$ and $MgCl_2{\cdot}1.8H_2O$ were calculated to be −1694.0 and −1215.3 kJ/mol, respectively. The enthalpy of formation of gaseous water (−241.8 kJ/mol) was taken from Atkins [12].

$$MgSO_4{\cdot}1.3H_2O + 5.7H_2O \leftrightarrow MgSO_4{\cdot}7H_2O$$

$$h = -2.25\ \text{kJ/g}\ (-324\ \text{kJ/mol})$$

$$MgCl_2{\cdot}1.8H_2O + 4.2H_2O \leftrightarrow MgCl_2{\cdot}6H_2O$$

$$h = -2.13\ \text{kJ/g}\ (-272\ \text{kJ/mol})$$

To compare these calculated heats of hydration with the measured sorption heats, the experimental values of the composite materials had to be corrected by subtracting from the measured sorption heat of the composite materials the adsorption heat of the host material. The latter was determined in an independent experiment as 120 kJ/kg. Finally, the heats of sorption were recalculated by referring the heat effect to the net mass of the salt mixtures in the composite materials.

Fig. 2 shows the corrected experimental heats of sorption of the salt mixtures as well as the calculated values for the heats of hydration in dependence of the salt mixture ratio. The deliquescence relative humidity of the salt mixtures is also shown. The DRH is the relative humidity (RH) over saturated salt solution and was determined by water vapor pressure measurements of every salt mixing ratio.

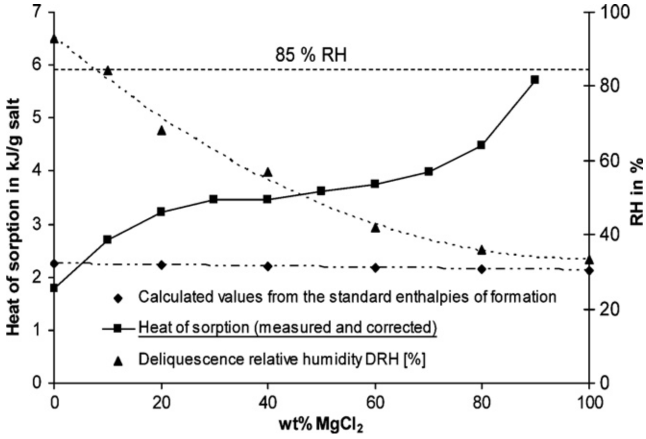

Fig. 2. Heat of sorption at 30 °C and 85% RH related to the composition of the salt mixture.

With increasing substitution of $MgSO_4$ by $MgCl_2$ the DRH of the salt mixtures decreases because of the lower deliquescence relative humidity of $MgCl_2{\cdot}6H_2O$. Every DRH of a salt mixture except that of pure $MgSO_4{\cdot}7H_2O$ is lower than the 85% RH in the sorption experiment. Under this condition the reaction follows Eq. (1) and the measured heat of sorption (1.8 kJ/g) is somewhat lower than the calculated heat of hydration for the thermodynamically stable product $MgSO_4{\cdot}7H_2O$. Most likely, this difference between measured and calculated value is caused by the kinetic hindrance leading to incomplete hydration as mentioned above.

Higher ratios of $MgCl_2$ will result in lower heats of sorption due to the lower enthalpy of formation of $MgCl_2{\cdot}6H_2O$. However, the reduction of the DRH in the chloride-rich mixtures causes the formation of a solution, i.e. an additional condensation of water vapor, which implies a significant increase in the measured heat release as well. If the relative humidity of 85% exceeds the deliquescence relative humidity of the salt mixture, the reaction follows Eq. (2) and more dehydrated magnesium sulfate can dissolve in the solution. A substitution of only 10 wt% $MgSO_4$ by $MgCl_2$ increases clearly the measured heat compared to the calculated heat of sorption. It can be seen that the measured heat of sorption at 85% RH and 80 wt% $MgCl_2$ is twice as much than the calculated value for the formation of the solid salt hydrate.

The increased amount of condensed water will result in salt solutions which can escape out of the porous material. Leakage of salt solution might be avoided by using appropriate salt mixtures and by adapting the porous material regarding pore size and pore distribution.

3.2. *Variation of the measurement conditions*

Table 3 compares the heats of sorption at different temperatures of desorption and measurement conditions.

The variation of the sorption conditions (temperature and relative humidity) on the isothermal sorption shows a decrease of the integral heat of sorption at higher sorption temperatures and lower relative humidity. At lower humidities (condition B) the difference between the water vapor partial pressure of the salt hydrate and that of the humid air is smaller, hence, there is less condensation of water. Higher sorption temperatures (condition C) reduce the heat of condensation of water vapor. At lower relative humidities lower states of hydration can occur and less water will be absorbed.

The decrease of the desorption temperature from 130 to 100 °C (condition D) has only a minor effect on the release of heat. This temperature reduction is very beneficial for the technical application because apart from the lower desorption the hydrothermal load of the material is significantly decreased.

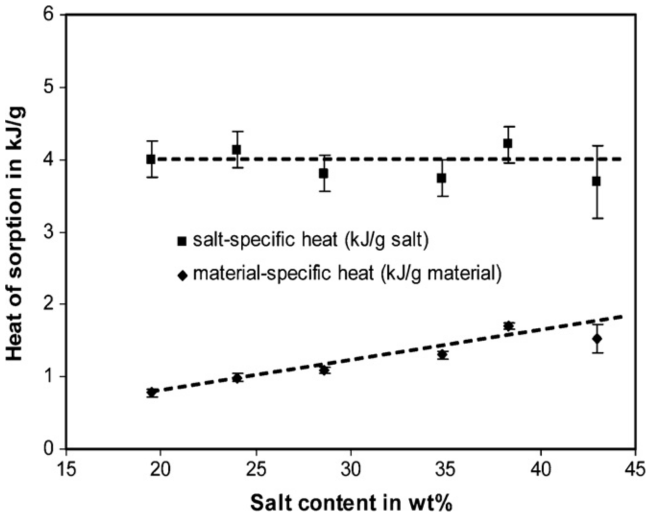

Fig. 3. Heat of sorption in dependence of the salt content.

3.3. *Influence of the salt content*

To study the influence of the salt content on the heat of sorption the host material was impregnated with different concentrations of a solution containing a mixture of $MgSO_4$ (60 wt%) and $MgCl_2$ (40 wt%). Fig. 3 shows the influence of the salt content on the heat of sorption (measurement condition A). For salt contents up to 38 wt% the precisions of the measurements of the composite materials were generally ±0.05 and ±0.2 kJ/g for 43 wt%, respectively.

The utilization of more concentrated solutions results in a higher salt content of the composite material and therefore, increases the material-specific heat of sorption proportionally. The salt-specific heat is approximately constant at an average value of 4000 kJ/kg (± 0.25 kJ/g). At higher salt contents (above 38 wt%) a loss of precision (±0.5 kJ/g) of the measurements was observed. This might be caused by pore clogging or the formation of salt crusts on the composite surface resulting in reduced rates of water vapor transfer. Particularly in the case of the material impregnated with a saturated solution, yielding a salt content of 43 wt%, superficial salt crusts were observed. Since the results presented here indicate that the increase of the salt content increases the heat release proportionally, ongoing work is aimed at determining a maximum salt content using cyclic desorption and sorption.

4. Conclusions

Salt hydrate mixtures of magnesium sulfate and magnesium chloride were studied for the application in composite materials for thermochemical heat storage. It is shown that the partial substitution of $MgSO_4$ by the chloride, i.e. a salt with a lower DRH, will result in higher heat of sorption. This higher heat release with increasing amount of $MgCl_2$ is the result of the increased absorption of water in the concentrated salt solution. The higher heat release at the beginning of the measurement of the mixtures leads to a higher temperature lift, which is an important factor for thermal storage. The measured sorption heats of a composite material of attapulgite impregnated with a mixture of 20 wt% $MgSO_4$ and 80% $MgCl_2$ of 1590 kJ/kg at 30 °C and 85% RH (1100 kJ/kg at 40 °C/75% RH) are sufficient for an application as solar thermal energy storage materials. For the practical application of the composite material, the maximum salt content and the optimum mixing ratio of the two salts regarding the working condition of the heat exchanger or heat storage system need to be determined in future hydrothermal cyclic sorption and desorption investigations. Mixtures with a high rate of sulfate and a low desorption temperature should be used, because of the corrosion tendency of the chlorides.

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