Calorimetric investigation of magnesium sulfate hydration in porous materials

**Kirsten Linnow[1], Konrad Posern[2], Tanya Talreja[1], Michael Niermann[1],
Christian Kaps[2] and Michael Steiger[1]**

[1] Department of Chemistry, University of Hamburg (Germany)

[2] Chair of Building Chemistry, Bauhaus Universität Weimar (Germany)

Abstract

The sorption behavior of dehydrated magnesium sulfate in porous glasses with pore diameters from 1.7 µm to 7 nm was investigated by using isothermal calorimetry. The kinetic hindrance of the formation of the thermodynamically stable product $MgSO_4 \cdot 7H_2O$ was not overcome at 85 % RH and 30 °C in the material with the largest pores. In contrast, in pores below 173 nm the high water uptake clearly indicates the formation of a solution. The released heat (Q_r) can be calculated as the sum of the heat of hydration (Q_{hyd}), the heat of condensation (Q_c) and the heat of solution (Q_{sol}). The water uptake and the overall released heat both increase with decreasing pore size. Although high energy densities up to 0.95 GJ/m³ were found for the material composed of Vycor glass (d_m = 7 nm) and $MgSO_4$, this composite does not seem to be suitable as heat storage material due to the formation of a solution and the high humidity of 85 % RH required for the release of heat. Porous carbon was used as an alternative host material for $MgSO_4$. Isotherms of the water vapor uptake of a porous carbon composite with three different loads of $MgSO_4 \cdot H_2O$ were determined and are discussed in this paper. An energy density of 0.74 GJ/m³ can be achieved without formation of a solution at 72 % RH.

Key-words: thermochemical heat storage, salt hydration, magnesium sulfate, influence of pore size

1. Introduction

Magnesium sulfate is a promising candidate for the application of a salt hydrate as thermal energy storage material, due to the high theoretical energy density of 2.2 GJ/m³. This calculation is based on the enthalpy of reaction per mole of salt for the hydration of $MgSO_4 \cdot H_2O$ to $MgSO_4 \cdot 7H_2O$ ($\Delta_{hyd}H$ = –323 kJ/mol, Grevel et al. 2012) and the molar volume of bulk $MgSO_4 \cdot 7H_2O$ (147 cm³/mol). The release of the stored heat in total is limited by incomplete hydration (Posern and Kaps 2008, Linnow et al. 2014) as well as by the simple reason that the crystals clump together during hydration, which leads to a lowering of the air flow through a storage tank severely hindering the release of the stored heat. To avoid such complications the idea arose to disperse the salt in porous host materials. The volumetric energy density becomes then a function of porosity and the pore filling as depicted in Figure 1 for the complete hydration of $MgSO_4 \cdot H_2O$ to $MgSO_4 \cdot 7H_2O$. Obviously, the design of a composite material is only economically feasible, if its energy density significantly exceeds the values typically obtained using water vapor sorption with zeolites (dotted area in Fig. 1). Hence, highly porous materials with a high pore filling are required. However, up to now the sorption behavior of salts dispersed in porous materials is not well understood. Aristov and Vasiliev (2006) reported an increased water sorption due to the dispersion of the crystals in nanosized pores up to 16 nm. However, a systematic investigation of the influence of a wider range of pore sizes and the influence of pore filling is rarely found. In a first research project we studied the influence of pore sizes from 1.7 µm down to 7 nm meadian pore diameter in porous glasses on the hydration behavior of $MgSO_4 \cdot H_2O$ and the released heats at 30 °C and 85 % RH were determined by isothermal calorimetry. It turned out that a solution was formed in pores with

d_m = 173 nm and smaller although the deliquescence humidity of $MgSO_4 \cdot 7H_2O$ (89 % RH, 30 °C, Steiger et al. 2011) was not exceeded. In addition it was found that the released heat (Q_r), measured by isothermal calorimetry, can be treated as the sum of the heat of hydration (Q_{hyd}), heat of condensation (Q_c) and heat of solution (Q_{sol}). Although high energy densities up to 0.95 GJ/m³ were obtained for composite composed of Vycor (d_m = 7 nm) and $MgSO_4$, this material does not seem to be suitable as heat storage material for two reasons. First, the formation of a solution leads in turn to the uncontrolled transport of the liquid possibly resulting in efflux of the salt from the interior of the porous host matrix. Second, the high relative humidity of 85 % required for the complete release of the stored heat might be not always available.

This study deals with the design of composite materials of high energy densities. The influence of the pore filling on the water vapor sorption behavior of $MgSO_4 \cdot H_2O$ dispersed in porous carbon was investigated as a first step. Composite materials of a highly porous carbon with spherical pores of 737 nm in diameter with three different loads of $MgSO_4 \cdot H_2O$ were synthesized (Wang et al. 2008). At low pore filling (11 % with respect to the $MgSO_4 \cdot 7H_2O$) the formation of a solution was achieved at about 35 % RH. The humidity, required to achieve the hydration state of $MgSO_4 \cdot 7H_2O$, increases with increasing pore filling. A reasonable energy density of 0.74 GJ/m³ was achieved for the composite with the highest load of 40 % at 72 % RH.
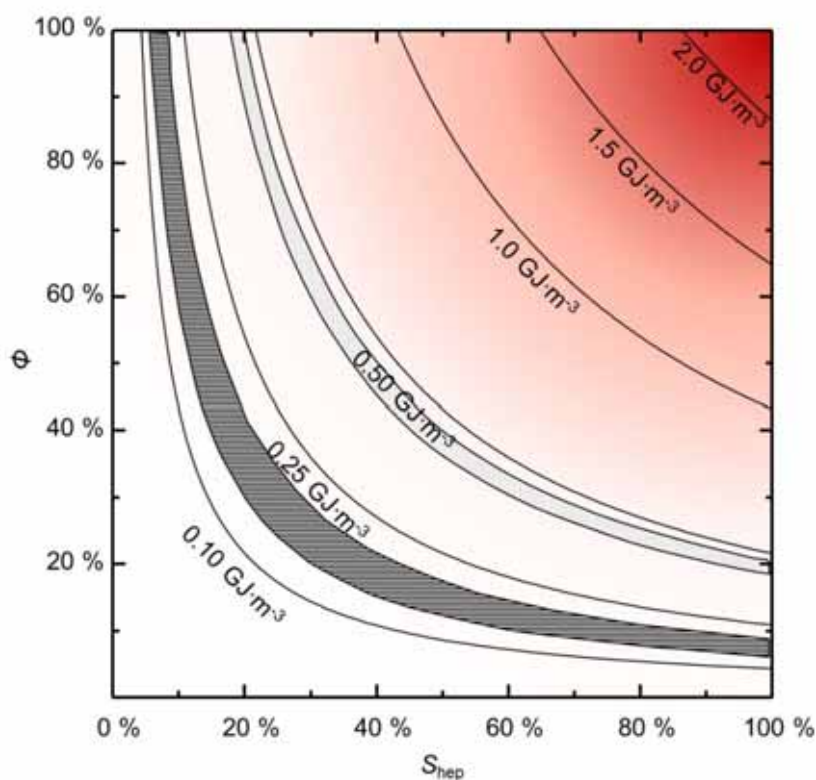
Figure 1: Volumetric energy densities (isolines) of monolithic composite materials composed of porous materials filled with $MgSO_4 \cdot H_2O$ as function of porosity ϕ and pore filling S_{hep}. The upper right corner represents the energy density for the complete hydration to $MgSO_4 \cdot 7H_2O$ of bulk $MgSO_4 \cdot H_2O$. The hatched area represents typical values for water based sensible heat storage and the dotted area represents typical values for water vapor sorption with zeolites.

2. Materials and Methods

2.1 Impregnation of the porous host matrix

Weighed amounts of crushed porous glasses were impregnated with a solution of 1.2 mol/kg $MgSO_4$, filtered and dried at 40 °C for three days in a drying cabinet before measuring the overall heat of reaction of each sample.

Porous carbon with spherical macro pores (d_m = 737 nm) and a porosity ϕ_m = 1.93 cm³/g (i.e. 81 %), determined by mercury porosity intrusion, and a minor contribution of ϕ_m = 0.03 cm³/g (i.e. ϕ = 1 %) of

mesoporosity in the range 4–11.8 nm, determined by nitrogen physisorption, was used. Three different $MgSO_4·H_2O$ loads were used to measure the water vapor sorption isotherms. The samples of the porous

carbon were treated differently, one was impregnated with a solution of 1.3 mol/kg $MgSO_4$ filtered and excess solution was dabbed with a paper tissue before drying at 200 °C to constant weight to ensure that dehydration to $MgSO_4·H_2O$ was achieved. To achieve higher loads the second and third portion were impregnated with a saturated solution of $MgSO_4$ (4.1 mol/kg) at 100 °C and filtrated before drying at 200 °C. This procedure was repeated twice for the third portion to achieve the highest load.

2.2 Instrumentation

Overall heats of reaction were determined at 30 °C and 85% RH in a gas circulation cell using a calorimeter C80 connected to the controlled humidity generator Wetsys (Setaram Instrumentation, France). Samples of approximately 1.2 g of each composite material were heated in the cell to 130 °C. The dwell time of two hours was adjusted to obtain a constant heat flow at the desorption temperature. In the next step, the desorbed material was cooled to 30 °C at 5% RH. When a constant heat flow signal (ca. 0 mW) was achieved, the humidity was increased to 85% RH and the resulting heat flow was measured. The overall heat of reaction (Q_r) was determined by integration of the heat flow curve.

A water vapor sorption test system SPSx-1μ (ProUmid, Germany) was used to measure the water vapor isotherm of the carbon–$MgSO_4$ composites at 23 °C. Isotherms were recorded from 0–84 % RH in steps of 3 % RH. The samples were kept at each humidity until constant weight was achieved.

3. Results and discussion

3.1 Influence of pore size

The total water content expressed as molar ratio of water per mole $MgSO_4$ (x) after hydration at 85 % RH and 30 °C is given in Table 1. The water content provides evidence that in large pores the kinetic hindrance of the formation of the thermodynamic stable phase, $MgSO_4·7H_2O$, was not overcome. Only in the materials with pore diameters of 173 nm and below, the water content x is higher than 7. Due to the reasonable assumption that the thermodynamic stable crystalline compound $MgSO_4·7H_2O$ is formed, the higher water content indicates the formation of a solution and the overall reaction that occurs in the composites therefore is:

$$n MgSO_4·x_A H_2O + n_w H_2O(g) \rightarrow n_{cr} MgSO_4·7H_2O + n_{sol} Mg^{2+} + n_{sol} SO_4^{2-} + n_{w,sol} H_2O(l) \text{ (eq. 1)}$$

Considering the concentration of a saturated solution (3.24 mol $MgSO_4/kg^{-1}$ water) at 30 °C (Steiger et al. 2011) it is possible to calculate the partitioning between the crystalline solid and the saturated solution using a simple mass balance approach for both $MgSO_4$ and water. This calculation reveals that in the material with $d_m = 173$ nm 27 % of the water is bound in the crystalline hydrate. For the remaining materials this value was 25 % ($d_m = 96$ nm) and 51% ($d_m = 45$ nm), and, only 10 % of the water is present in the crystalline phase in the Vycor glass composite ($d_m = 7$ nm). However, not only the heat of hydration but also the heat of adsorption and the heat of solution contribute to the overall heat effect. These contributions were calculated using the partitioning of water and assuming a thermochemical cycle including the formation of $MgSO_4·7H_2O$, adsorption of the remaining water in the porous substrates and the partial dissolution of the crystalline $MgSO_4·7H_2O$ in the adsorbed water. The average enthalpy of hydration ($\Delta_{hyd}H_0 = -53.9$ kJ/mol water vapor) was taken from Grevel et al. (2012). The enthalpy of dissolution of a saturated solution at 30 °C (20.5 kJ/mol $MgSO_4$) was obtained by combining experimental enthalpies of solution at low concentration and 30 °C (Cappellina and Napolitani 1966) and heats of dilution at 30 °C calculated with an ion interaction model (Steiger et al. 2011). In lack of exact enthalpies of adsorption for the host materials, the enthalpy of condensation (–43.8 kJ/mol at 30 °C) was used instead as the enthalpy of adsorption approaches the enthalpy of condensation with increasing surface coverage. The small differences of the measured heat (Q_r) and the sum of the calculated heats (Q_{cal}) as given in Table 1 column 7 show that the overall heat of reaction can be treated as the sum of the heat of hydration (Q_{hyd}), heat of condensation (Q_c) and heat of solution (Q_{sol}).

Tab. 1: Water content and released heats of the composite materials at 85 %RH and 30 °C.

d_m (nm)	x	Q_r (J)	Q_{hyd} (J)	Q_c (J)	Q_{sol} (J)	Q_r-Q_{cal} (J)	$\Delta_r H_0$ (kJ/mol)
$1.7 \cdot 10^3$	6.12	-458	-402	0	0	-56	-63.1
$1.7 \cdot 10^3$	6.55	-240	-224	0	0	-16	-59.3
173	8.31	-502	-407	-78	4	-21	-55.1
96	10.32	-353	-193	-117	5	-48	-57.7
96	8.64	-445	-358	-83	4	-8	-53.5
45	9.78	-572	-447	-174	8	+41	-47.7
45	9.95	-554	-425	-176	8	+39	-47.7
7	15.10	-653	-299	-382	18	+10	-46.8
7	14.81	-620	-289	-356	17	+8	-47.0

Even though theoretical considerations about the influence of a confinement on the thermodynamics have been published by Steiger (2005, 2009) little is known about the real behavior of salts in confinement. Nonetheless, the formation of a solution was observed in all materials with pore diameters equal to or below 173 nm although the deliquescence humidity (DRH) of bulk $MgSO_4 \cdot 7H_2O$ was not exceeded. Due to the small pores capillary condensation the partial dissolution of the salt can occur in very small pores (7 nm). The formation of a solution in the macroporous materials with pore diameters in the range 45–173 nm is surprising. In general, two competitive effects on the solubility of salts in confinement can be discussed. One effect is the concave curvature of the meniscus of an unsaturated filled pore which yields a decrease of the pressure in the pore solution according to the Laplace equation. This leads to a decrease of the solubility and, consequently, to an increase of the deliquescence humidity. Due to the formation of a solution in the macroporous materials below the DRH of the bulk salt the pressure drop can be excluded as driving force for the water uptake at humidities below the DRH. The second effect can be described as the influence of the crystal size or inter-crystalline porosity formed by the agglomeration of small crystals in a pore. Solubility increases with decreasing size below about 100 nm (Steiger 2005), which in turn leads to a decrease of the DRH, i.e. an increased water uptake. If the inter-crystalline pores are small enough that capillary condensation can take place, the water uptake can also be increased by this effect. However, currently the morphology and the size of the crystals and the inter-crystalline pore space in the hydrated state are unknown. Nevertheless, small crystal size and very narrow inter-crystalline void volumes may well be the reason for the formation of a solution below the DRH of the bulk salt.

The energy densities (ρ_E), calculated from the measured overall heat of reaction, for the glass composites are listed in Table 2. The pore filling (S_{hep}) was calculated under the assumption that $MgSO_4$ is present as $MgSO_4 \cdot 7H_2O$. It is important to note that at 85 % RH a solution was found in addition to $MgSO_4 \cdot 7H_2O$, therefore the real pore filling at 85 % RH is higher than given in Table 2. The energy density increases with increasing porosity (ϕ) and as expected with increasing pore filling. The energy density of the Vycor-composites ($d_m = 7$ nm) exceeds the theoretical value calculated for the respective porosity (34 %) and pore filling (see Figure 1). The increased energy density is the result of the excess water content of more than 7 moles H_2O per mole $MgSO_4$. Although the high energy densities of the Vycor composites of 0.88 GJ/m^3 and 0.95 GJ/m^3, respectively, seem to be sufficient for the application as a heat storage material, this composite is still far from being a satisfactory heat storage material for two major reasons, the formation of a solution within the pores and the high humidity needed for the heat release. However, as a result of this investigation it becomes clear that total water uptake and the degree of of hydration are a function of pore size, pore filling and applied humidity. Moreover the energy density is a function of the total porosity.

Tab. 2: Porosity (ϕ), theoretical pore filling ratio (S_{hep}) with respect to MgSO$_4$·7H$_2$O and energy density at 85 % RH and 30 °C.

d_m (nm)	S_{hep} (%)	ϕ (%)	ρ_E (GJ/m³)
$1.7 \cdot 10^3$	66	41	0.46
$1.7 \cdot 10^3$	34	41	0.25
173	38	22	0.19
96	77	29	0.60
96	91	29	0.61
45	64	43	0.63
45	65	43	0.64
7	72	34	0.88
7	80	34	0.95

3.2 Water vapor sorption isotherms

Impregnation of the porous carbon resulted in composites with mass ratios 0.20, 0.58 and 0.74 MgSO$_4$·H$_2$O per gram carbon. These salt contents correspond to pore fillings of 11 %, 32 % and 40 %, respectively, calculated assuming that the MgSO$_4$·7H$_2$O is present in the pores. The water vapor sorption behavior of the composites compared to the unloaded carbon is depicted on the left side in Figure 2. The water uptake is expressed as mass ratio (i.e. in g water per g carbon). The carbon itself shows a water uptake of 10 % at 84 % RH clearly exceeding the porosity of the mesopores (0.03 cm³/g). It should be stressed that the water vapor sorption in hydrophobic porous carbon is controlled by the formation of water clusters which adsorb on existing polar sites on the carbon walls and the pore filling is not only a question of pore width and surface area but also of surface chemistry (Thommes et al. 2014). The water uptake of the composites clearly exceeds the water uptake of the carbon indicating that hydration of the salt takes place also at low humidities. The water uptake increases with increasing load of the carbon with MgSO$_4$. However, the right diagram shows that the water content per mole of salt decreases with increasing pore filling. The black line in the right diagram represents the calculated equilibrium water uptake of MgSO$_4$·H$_2$O, which is the thermodynamically stable phase up to 48.3 % RH at 23 °C. From 48.3 % to 49.6 % RH MgSO$_4$·6H$_2$O is the stable phase and above 49.6 % the hydration should yield MgSO$_4$·7H$_2$O. However, deviations from equilibrium were observed during hydration of bulk MgSO$_4$·H$_2$O at 66 % RH (Linnow et al. 2014). It was found that the hydration was incomplete due to the formation of a product barrier layer below the deliquescence humidity of the monhydrate. Above 90.7 % RH MgSO$_4$·7H$_2$O deliquesces and forms a solution.

The isotherms show that the salt confined in the pores of the carbon picks up water below the hydration equilibrium humidities of the MgSO$_4$·H$_2$O and MgSO$_4$·6H$_2$O (48.3 % and 49.6 %). As discussed above this may be caused by small crystal sizes and secondary porosity. The water uptake curve of the sample with 11 % pore filling rapidly increases up to 7 mol H$_2$O where an inflection point and a change in the slope of the curve is observed. The water uptake curve can then be described as nearly proportional at higher humidities where a solution is formed. A slight step at 35 % RH is visible for the higher salt contents of 32 % and 40 %, which is slightly above the humidity where the slope of the sample with the lowest salt content changed. A second step is found above the equilibrium humidity of MgSO$_4$·H$_2$O and MgSO$_4$·6H$_2$O at about 51 % RH, but the water content indicates that the hydration was not complete at this moment in time, although the humidity was kept constant for 200 hours. A pronounced step occurs at 54 % RH where the water content exceeds 6 mole H$_2$O per mole MgSO$_4$. Subsequently, there is only a slightly increase of the water content with increasing humidity. Since the behavior of the salt in confinement is not yet fully understood, an explanation for the observed influence of the pore filling on the water uptake isotherms cannot be provided.

In general, regarding the release of heat, a high water uptake is desirable. On the other hand however, the possible discharge of the salt from the porous substrate as a consequence of the formation of a solution has to be avoided in order to achieve satisfactory cycling stability of the composite material. Accordingly, the maximum water content should be limited to 7 mole water per mole MgSO$_4$ or expressed in other words to
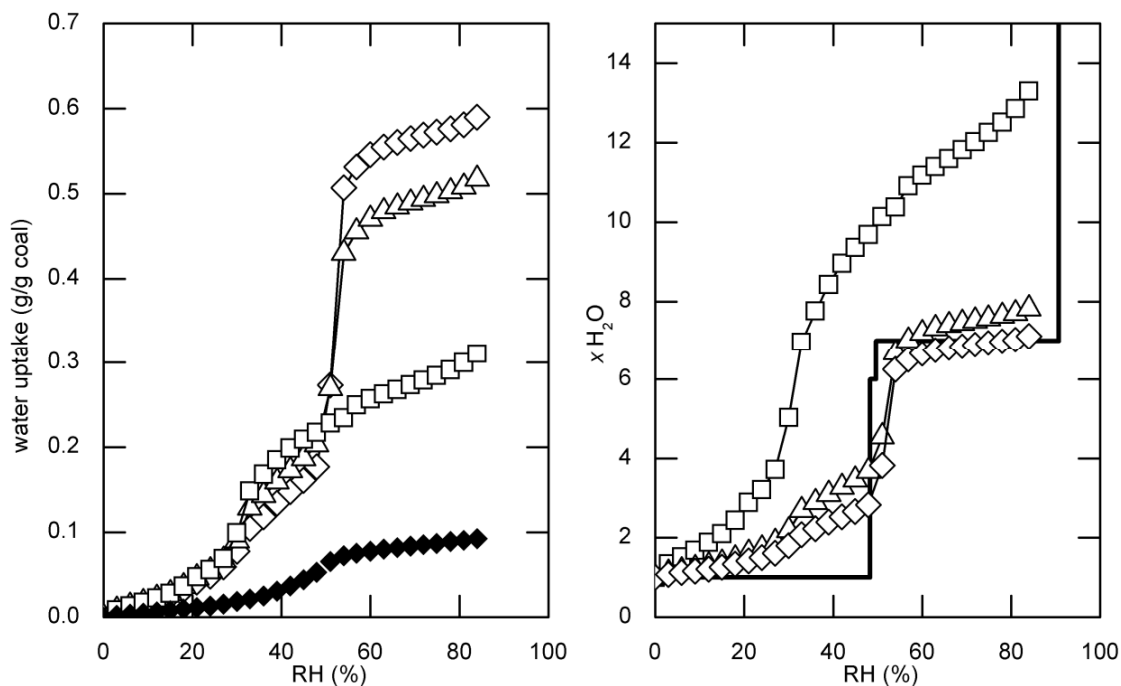
Figure 2: Water vapor sorption isotherms of carbon–MgSO$_4$ composites at 23 °C. The water uptake is expressed as mass ratio of water and carbon in the left diagram, whereas in the right diagram the water content is expressed as molar ratio of water and MgSO$_4$. Filled diamonds represent the water vapor sorption behavior of the unloaded macroporous carbon, open squares, triangles and diamonds represent the water vapor sorption isotherms of the carbon with 11 %, 32 % and 40 % pore filling with MgSO$_4$·7H$_2$O (S_{hep}). The black line in the right diagram represents the thermodynamic prediction of the sorption behavior of MgSO$_4$·H$_2$O.

the last crystalline state at which the complete hydration to MgSO$_4$·7H$_2$O was achieved. Obviously, an upper limit for the relative humidity not only depends on the pore size but also on the pore filling of the material and has to be investigated for each composite material. Relative humidities at which the hydration state of MgSO$_4$·7H$_2$O was achieved without formation of a solution are listed in Table 3. In addition, the volumetric energy densities for the composite materials were calculated by using the enthalpy of hydration. As expected the energy densities increase with increasing pore filling, but surprisingly the humidity required for the complete hydration increases with increasing pore filling. In general the energy densities are higher than typical values of a water based sensible storage tank as given in Figure 1 and the energy density of the composite filled with 40 % MgSO$_4$·7H$_2$O is quite good compared to typical values of zeolite adsorption heat storage systems.

Tab 3: Humidity at which the hydration to MgSO$_4$·7H$_2$O is achieved and corresponding energy density of the carbon–MgSO$_4$ composites (d_m = 737 nm, ϕ = 82 %) as a function of pore filling (S_{hep}).

RH (%)	S_{hep} (%)	ρ (GJ·m^{-3})
33	11	0.19
54	32	0.53
72	40	0.74

4. Conclusions

In conclusion, it is shown that the overall released heat increases with decreasing pore size due to the higher water uptake. In pores with diameters equal to or below 173 nm a solution is formed. The overall heat of reaction can be treated as the sum of the heat of hydration, the heat of condensation and the heat of solution. The average enthalpy of reaction ($\Delta_r H_0$) decreases slightly with increasing water uptake, as a consequence of a decreasing contribution of the hydration enthalpy and an increasing contribution of the heat of solution. To avoid salt transport the formation of a solution is unwanted. Hence, the complete hydration to MgSO$_4$·7H$_2$O

without formation of a solution is desirable although more heat can be released by increasing the humidity to allow a higher water uptake. It turns out that the complete hydration to the $MgSO_4 \cdot 7H_2O$ is not only a function of the pore size but also a function of the pore filling. Therefore it can be concluded that the relative humidity and pore filling need to be optimized for each composite material. It is shown that an energy density of 0.74 GJ/m^3 can be reached without the formation of a solution at 72 % RH in a highly porous carbon–$MgSO_4$ composite of a pore filling of 40 % with respect to $MgSO_4 \cdot 7H_2O$. As a careful forecast on upcoming results and as a conclusion of the two investigations presented in this paper, the design of $MgSO_4$–composite materials with satisfactory energy densities at about 50 % RH appears to be achievable by adjusting the parameters pore size, pore filling and humidity.

Acknowledgement

5. References

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