

SALT MIXTURES IN POROUS CERAMICS FOR THERMOCHEMICAL STORAGE OF LOW TEMPERATURE HEAT

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1. Introduction

Long term storage of solar heat or transformation of solar heat into could demands often a thermochemical process with materials having a low charging temperature to meet the requirements of simple inexpensive solar collectors. A number of storage materials are available such as silica gel or so called composites (Levitskij et al. 1996, Jänchen et al., 2004, 2005) hosting a hygroscopic salt hydrate. Those salt hydrates, showing a high potential for thermochemical heat storage, may have disadvantages like slow hydration/dehydration kinetics (magnesium sulfate as an example) or a too low value of the deliquescence relative humidity (DRH) typically for halides. The latter leads to liquefaction of the salts at rather low relative humidity already and may result in leakage problems.

We have therefore investigated a new approach of utilization of salt hydrates in porous hosts by using a mixture of salts (Posern and Kaps, 2010) to prevent the disadvantages of the single salts.

2. Materials and Methods

Attapulgite and mullite of different porosity served as hosts for a mixture of 40% Mg-chloride and 60% Mg-sulfate. The texture of the supports has been characterized by scanning electron microscopy (REM) and mercury intrusion.

The hydration and dehydration properties of the mixed salt composites have been studied by thermogravimetry (TG) and differential thermoanalysis (DTA) after hydration at controlled humidity and room temperature. Gravimetric isotherm measurements at different temperatures have been carried out to study the hydration and dehydration properties in more detail using a McBain balance.

Stability tests have been performed by repeated cycles of hydration/dehydration under conditions of an open storage system. Finally mullite based honeycomb structures with a defined pore size distribution have been developed and tested in an open lab-scaled thermochemical storage.



Fig. 1: Honeycomb structure of a composite storage material mullite/salt mixture for a lab-scaled open thermochemical storage

The storage consists of a vaporizer delivering an airstream of controlled humidity connected with the main part of the storage hosting the storage material of about 1.5 L volume. Figure 1 shows the arrangement of the honeycomb structures set later into the main part of the storage. An adjustable exhauster completes the lab-scaled storage. The apparatus is equipped with sensors for temperature, humidity and air flux measurements.

3. Results and Discussions

3.1 Texture of the materials

The composites have been prepared using a standard impregnation method to get a salt amount between 9 and 21wt% (hexahydrate based, cf. Table 1). The amount of salt correlates with the controlled established texture of the porous supports due to the results of the SEM (cf. Fig. 2 as an example), the mercury intrusion (cf. Table 1) and TG measurements (not shown). The maximum salt volume accommodated amounts to $\frac{1}{4}$ of the pore volume of the support as can be seen from Table 1, column 4 and 5.

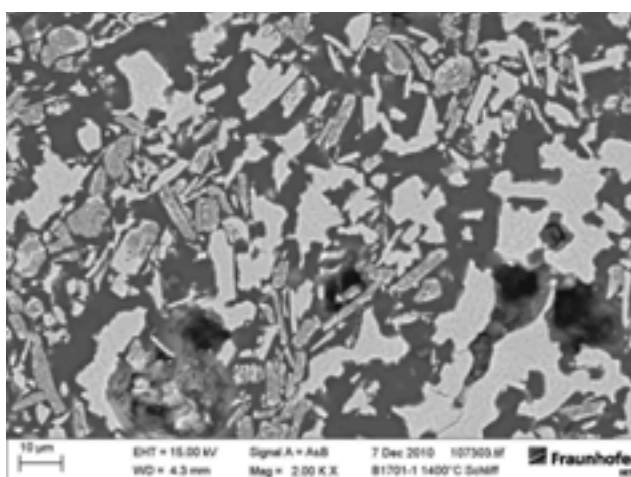


Fig. 2: SEM image of the porous mullite (B 1701) impregnated with $Mg(SO_4)/MgCl_2$, average pore diameter 4.19 μm , dark areas resin filled pores, bright areas aluminosilicate framework

Tab. 1: Characteristic data of the composite materials based on different porous mullite and attapulgite (amount in wt% is based on the hexahydrate of the salts)

Sample	Salt amount in wt%	Pore diameter in μm	Pore volume in cm^3/g	Salt volume in cm^3/g
B 1535 (attapulgite)	21.5	0.4	0.661	0.168
B 1555 (mullite)	8.4	0.30	0.207	0.056
B 1580 (mullite)	8.9	8.15	0.219	0.060
B 1688 (mullite)	16.8	13.21	0.503	0.124
B 1701(mullite)	20.3	4.19	0.599	0.156
B 1704 (mullite)	21.4	-	-	-

3.2 Hydration/dehydration properties

The water uptake at RH=79% and room temperature (under static conditions) amounts to up to 0.25 g water/g composite. According to the TG and DTA results more than half of the hydrate water (and heat) can be utilized upon charging at 80°C. Thus, mullite or attapulgite based composites may be suitable for low temperature (solar heat) applications.

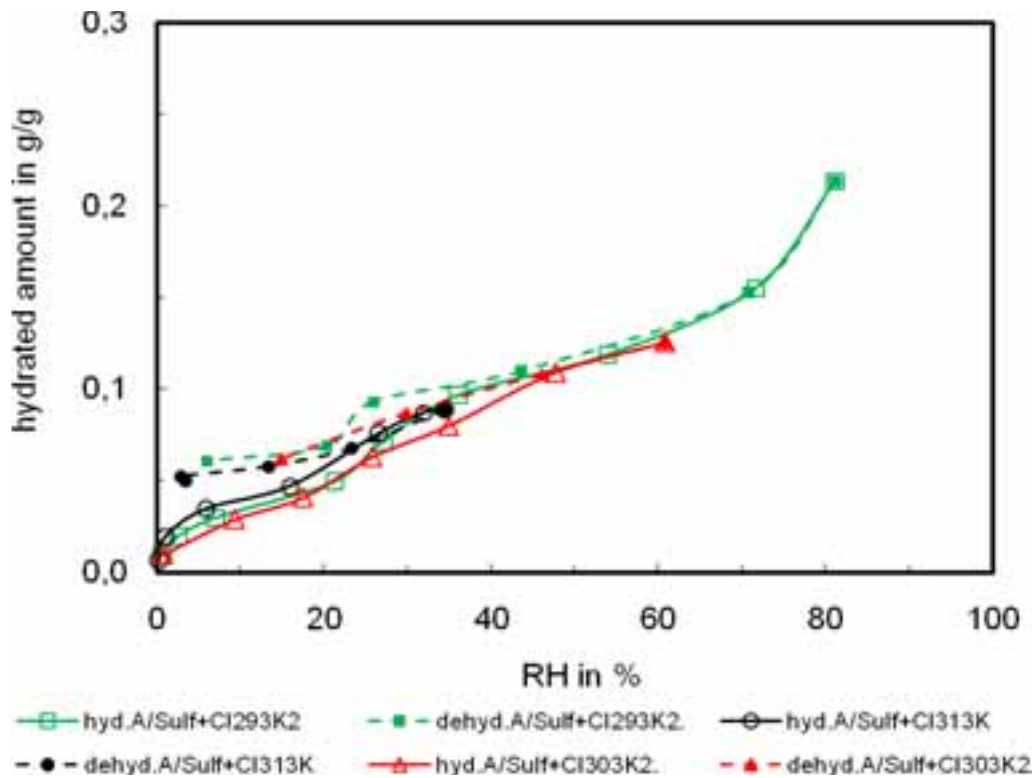


Fig. 3: Isotherms hydration/dehydration of B 1535 (attapulgite/salt mixture) at 293, 303 and 313 K, filled symbols and dashed lines denote dehydration. (Activation prior to the isotherm measurements has been performed at 150°C in high vacuum.)

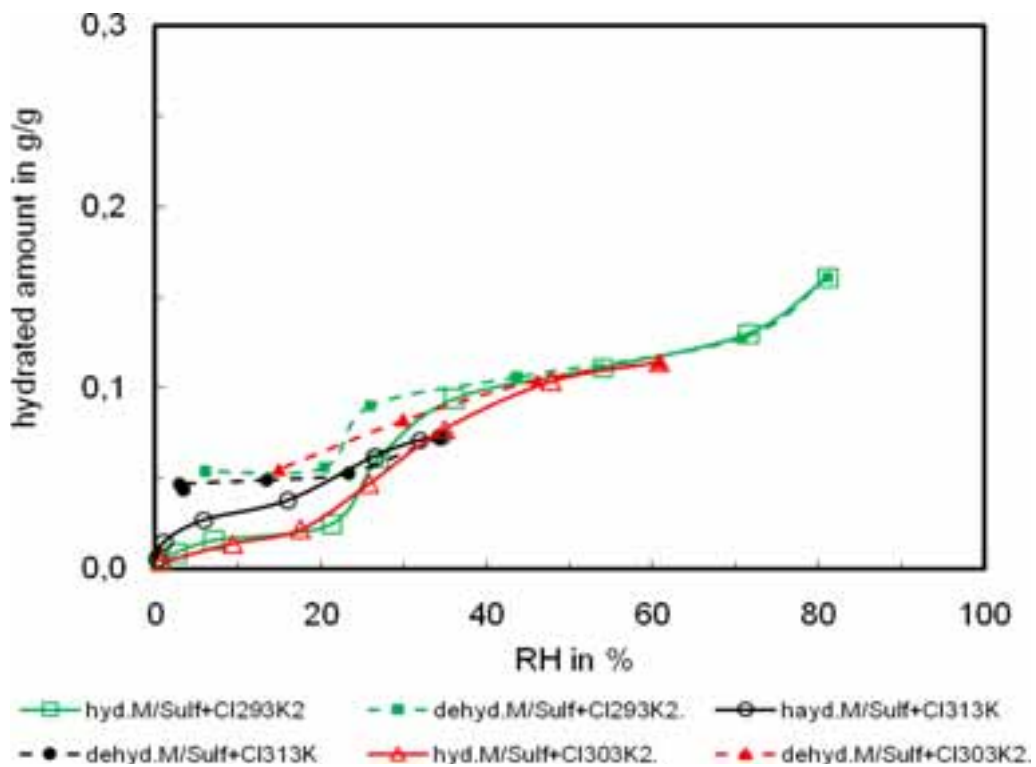


Fig. 4: Isotherms hydration/dehydration of B 1704 (mullite/salt mixture) at 293, 303 and 313 K, filled symbols and dashed lines denote dehydration. (Activation prior to the isotherm measurements has been performed at 150°C in high vacuum.)

A more detailed investigation of the hydration/dehydration behavior has been carried out by isotherm measurements on attapulgite- and mullite samples with the same amount of salt. Unfortunately the pore size distribution is not comparable. It is hard to prepare mullite samples having simultaneously small pores and a bigger pore volume or volume of salt, respectively. So it has to be taken into account that the pores of attapulgite are significantly smaller than for mullite which might influence the size of the crystals in the pores.

A set of Isotherms for different temperatures is given in the Fig. 3 and 4 for both the attapulgite and mullite samples. It is plotted the amount hydrate water vs. the relative humidity. As can be seen the hydration branches (solid lines) of the isotherms fall more or less into one bundle of curves as it has to be. Some deviation can be found for mullite (Fig. 4) between the curves of the higher temperature (313 K) and the two lower once (293, 303 K). This could be due to some kinetic effects of the hydration process.

Another (kinetic) effect may be the reason for the hysteresis found between hydration (solid lines) and dehydration (dashed lines) for both materials. A closer look to the isotherms reveal a different hydration/dehydration behaviour above RH=50% (reversible) and below RH=50% (not reversible). According to Posern and Kaps (2010) the deliquescence relative humidity (DRH) of the 60/40 wt% mixtures (sulphate/chloride) amounts to about 50%. Consequently, the more “liquid” part of the isotherm is reversible.

3.3 Cycle stability

Cyclic hydration/dehydration tests reveal sufficient hydrothermal stability for charging temperatures below 150°C. Figure 5 shows, as an example, the hydration capacity vs. the number of cycles for dehydration at 150°C. Some degradation is obvious, however, cyclic hydrothermal treatment at 250°C leads to much faster degradation of the material. Just a few cycles hydration/dehydration reduce the hydration capacity dramatically. Thus, charging of those storage material should be performed at $T < 150^\circ\text{C}$.

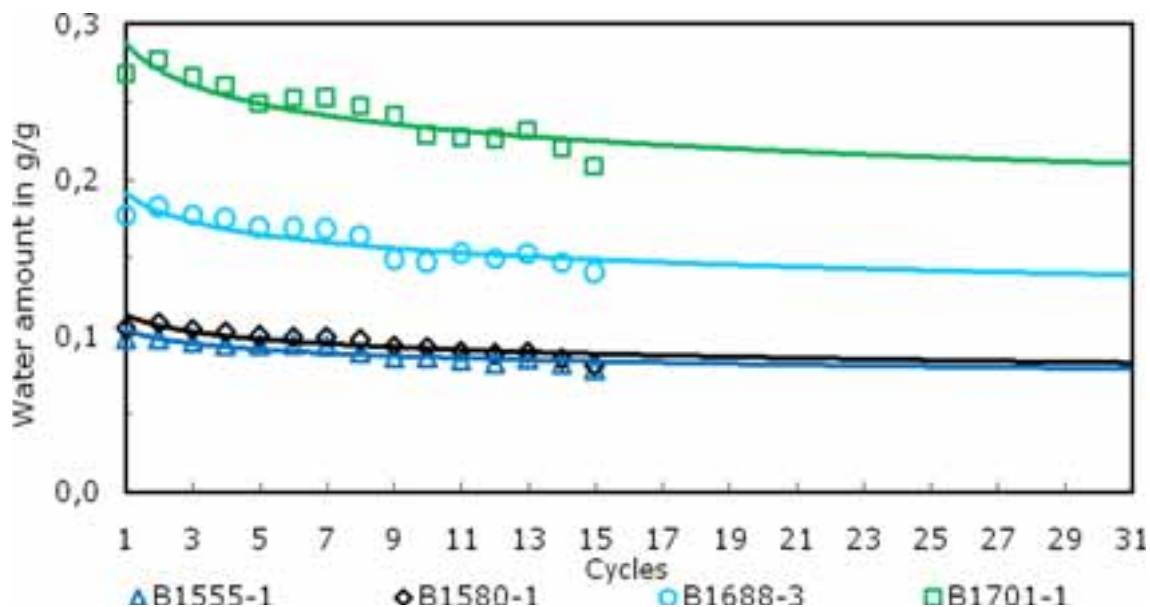


Fig. 5: cycles hydration/dehydration of mullite/salt mixtures, dehydration at 150°C, hydration at room temperature with RH=79%

3.4 Storage tests

Because of the temperature influence on the thermal/hydrothermal stability of the composites used the charging temperature in the storage was kept below 150°C as can be seen in Fig. 6 (green stepwise rising

curve). Fig. 6 shows the changes of temperature and humidity in the storage as function of. time upon dehydration of the composite. The stepwise course of temperature inside the storage material indicates successive dehydration of individual hydrates of different strength as know from thermogravimetric measurements. Corresponding steps can be found in the isotherms of hydration and dehydration as well (Fig. 4). The charging process ended at constant temperature in the storage material and corresponding matching values of air stream humidity in and out. This was the case after roughly 110 min.

First results of the discharging measurements are summarized in Table 2. Table 2 compares the mullite based composite with attapulgite based materials. Generally, no significant difference between supports of different nature can be found so far. The amount of water taken by the material determines the quantity of energy released. More experimental work has to be done to get more reliable data on the influence of support and the ratio of salt mixture on the storage capacity which is still low compared with silica gel for instance.

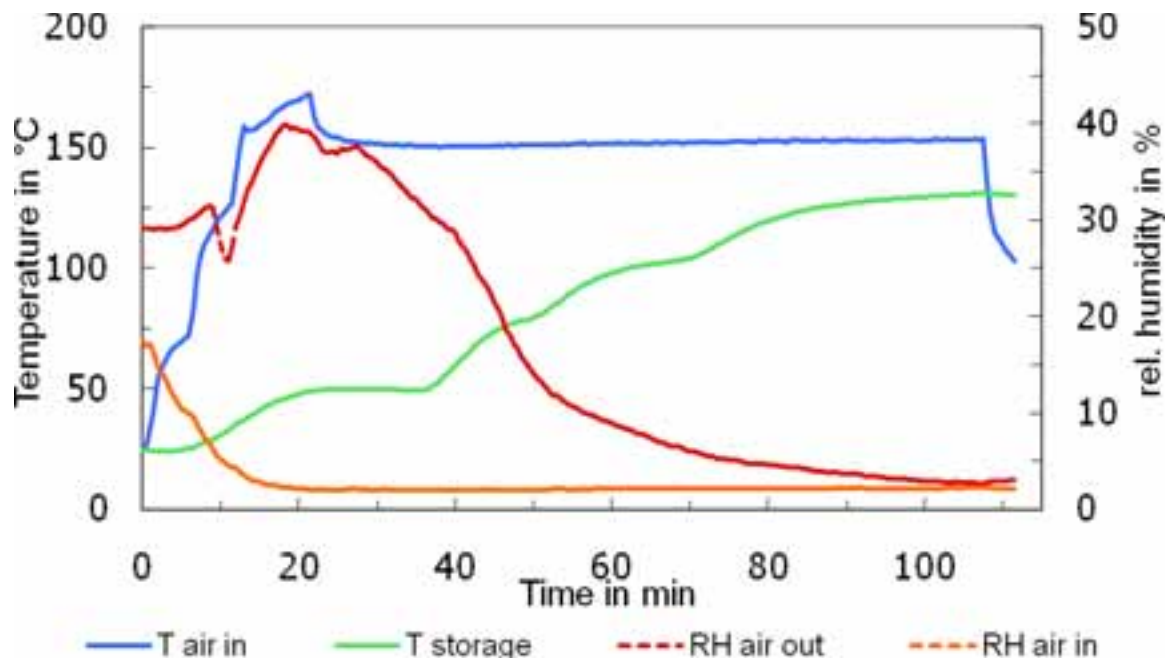


Fig. 6: charging mode of the honeycomb structure of mullite in the open storage,

Tab. 2: Results of the storage experiments in closed (attapulgite) and open systems (honey comb structure mullite).

Material	Charging-temperature in °C	Water uptake in g/g	T _{max} storage in °C	Energy density in kJ/kg
At/MgSO ₄	150	0,063	55	223
At/MgSO ₄ /MgCl ₂	130	0,178	70	477
Mu/MgSO ₄ /MgCl ₂	130	0,080	65	(230)

4. Conclusions

Porous ceramics could be prepared with mean pore diameters varying between 0.3 and 13 μm with corresponding pore volumes of 0.2 to 0.6 cm³/g. About ¼ of this pore volume of the support can be filled by a hygroscopic salt mixture MgCl₂/MgSO₄ using a saturated solution for the impregnation procedure.

The isotherms at 293-313 K show a stepwise curve due to formation of individual hydrates with different strength upon rising humidity. The part of the hydration/dehydration isotherms above 50% relative humidity is reversible whereas the piece below this humidity shows a hysteresis due to the DRH value of the salt mixture of about 50%. Most probably kinetic effects cause the hysteresis at $RH < DRH$ where solidification of the salt mixtures occurs.

The hydrothermal/thermal stability of the composite salt mixture/ceramics in high relative humidity is limited to temperatures up to 150°C.

First tests of a honeycomb structure in an open storage system confirm to some extent suitability of the chosen combination mullite/salt mixture for low temperature utilization of heat. The useable storage capacity, however, remains low so far.

5. Acknowledgements

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