# Thermophysical analysis of sorption materials for thermal energy storage

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## Conclusion

This work demonstrates the application of thermophysical measurement methods to evaluate sorption material properties like sorption isotherms, enthalpies, kinetics, specific heat, thermal conductivity and decomposition temperatures. Different composite material candidates based on zeolites with different inorganic salt fractions where compared.

It could be shown that the measured thermophysical data on the real storage material provides valuable information for the design process of a thermal energy storage reactor.

**Fig. 1: TG/sDSC system**

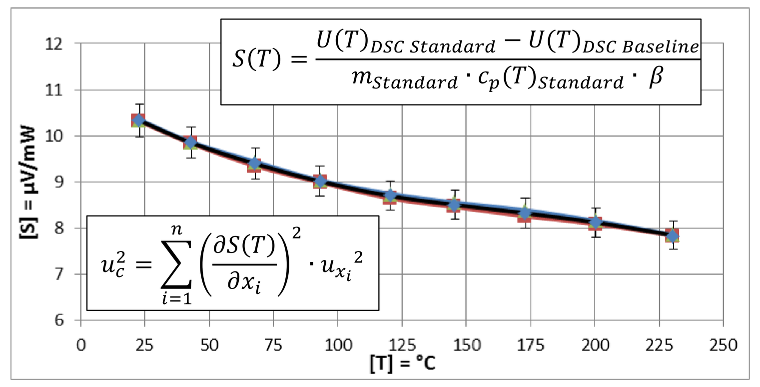


**Fig. 2 DSC sensitivity uncertainty assessment**

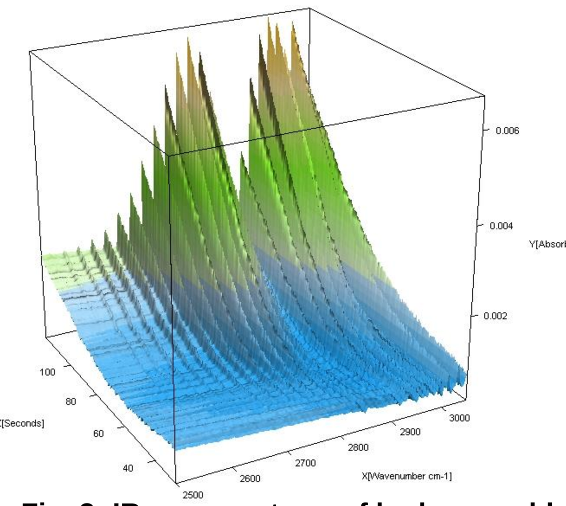

**Fig. 3: IR gas spectrum of hydrogen chloride**

**Fig. 4: THB sensor in Z4A particles**


## REFERENCES

1. U. Hammerschmidt, V. Meier, "New Transient Hot-Bridge Sensor to Measure Thermal Conductivity, Thermal Diffusivity, and Volumetric Specific Heat", International Journal of Thermophysics, Vol. 27, No. 3, May 2006
2. DIN 51007, "Thermal analysis; differential thermal analysis; principles"; June 1994
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4. G. Englmair, B. Zettl, D. Lager: "Characterization of a rotating adsorber designed for thermochemical heat storage processes", EUROSUN2014, International Conference on Solar Energy and Buildings, 16. - 19. September 2014, Aix les Bains


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## Introduction

Main criteria when sorption material candidates should be selected for a specific thermal energy storage (TES) application are:

- Sorption Isotherms
- Energy density or sorption enthalpies
- Kinetics
- Specific heat of the sorbent
- Thermal conductivity of the sorbent
- Decomposition temperatures
- Cycling stability

These process depended and material specific properties are needed in the beginning of a TES design process to identify, if the needed thermal power and capacity can be achieved by the investigated sorbent material. Furthermore the measured material properties of the real used material can be implemented into physical motivated reactor models for simulation based design.

The following sections should show, how Thermogravimetry (TG), Differential Scanning Calorimetry (DSC), Infrared spectroscopy (FTIR) and the Transient Hot Bridge method (THB) could be used to characterize these properties. In this poster mainly the results for a synthetic zeolite 4A are described.

## Materials

Additionally to synthetic zeolite products a natural clinoptilolite and different composite materials based on natural zeolite and inorganic salts have been considered for application.

**Zeolites**
- natural clinoptilolite; particle size 0,2 - 5mm
- synthetic zeolite 4A, pore size 0,4nm, particle size: 1,6 2,5 mm

**Inorganic salts**:
- $CaCl_2$, $SrBr_2$, $MgCl_2$, $MgSO_4$, LiCl

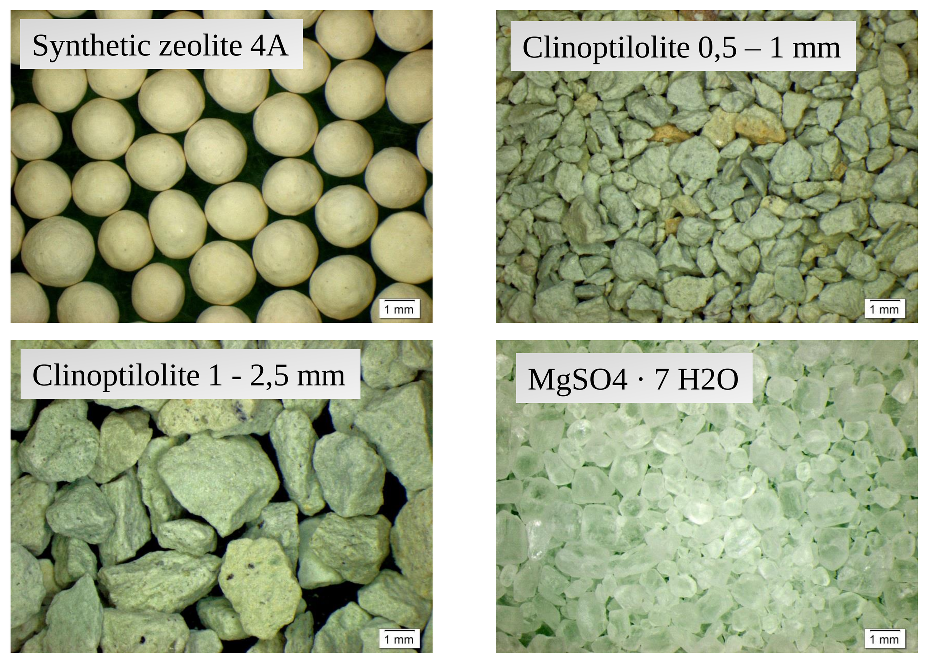


**Fig. 5: Investigated storage material candidates**

## Methods

**Thermogravimetry with simultaneous DSC (TG/sDSC)**
For sorption isotherm and isobar measurements a TG/sDSC (NETZSCH STA 449F1, s. Fig. 1) and a connected humidity generator (ProUmid MHG32) was used.
Prior to the sorption measurements several reference sapphire measurements were done to identify the system sensitivity and the associated uncertainty (s. Fig. 2).
The sorbent material was filled into a Pt-Rh crucible without lid and measured using an $N_2$ atmosphere with different partial pressures of water vapor.
A preceding desorption step with a specified duration of 120 minutes at a maximum temperature of 230°C was done. Afterwards the water uptake and heat flow at three different temperatures (34, 52, 76°C) and two different partial pressure water vapor (6, 12, 24 mbar) is measured (s. Fig. 6) and the integral of the heat flow signal is evaluated.

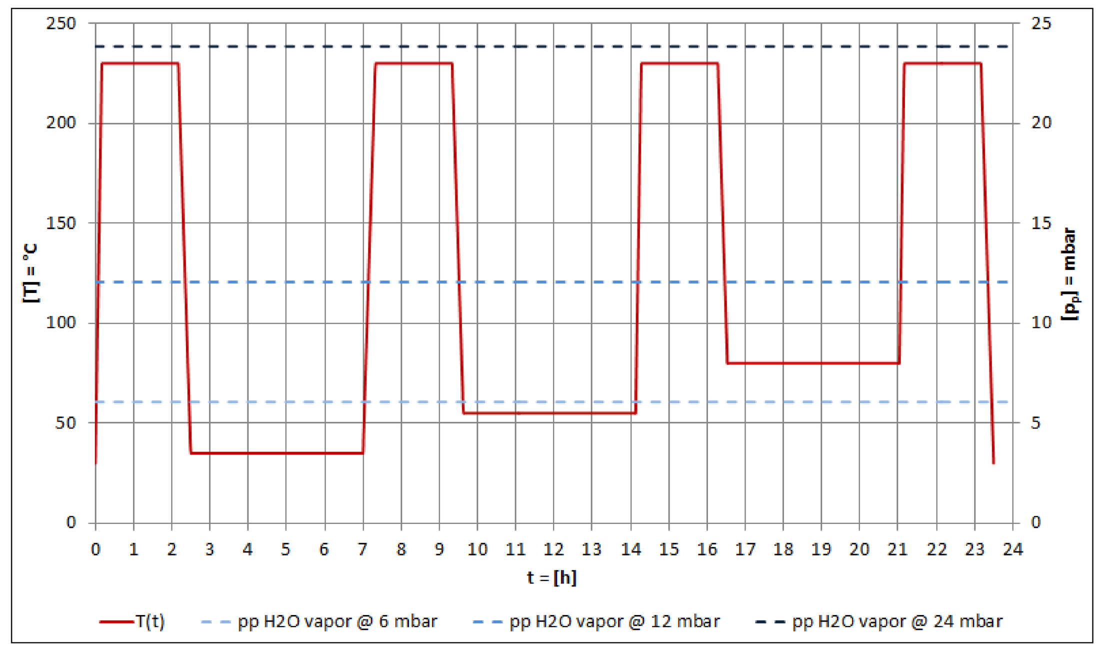


**Fig. 6: Temperature program and water vapor pressure**

**Gas analysis with FTIR**
During the desorption step a simultaneous FTIR gas analysis is done to identify evolved gases from the sample. The STA system is connected via a heated transfer line to the exhaust gas of the STA furnace.

**Transient Hot Bridge**
The effective thermal conductivity of the bulk solids was measured with the transient hot bridge method. The sensor is placed in a packed bed of the sorbent material (s. Fig. 4) and measured under defined temperature and humidity conditions.

[1] U. Hammerschmidt, V. Meier; 2006

**DSC**
Pure DSC measurements with a hf-DSC (NETZSCH DSC 404C) between 20°C and 300°C with a heating rate of 20 K/min under He atmosphere were done to evaluate the specific heat of the sorbent material. To identify the measurement uncertainty, three baselines and three sapphire measurements under the same system conditions were done. Specific heat $c_p(T)$ was determined by the $c_p$ ratio method.

[2] DIN 51007, 1994

## Results

**Sorption isotherm and enthalpy:** The TG/sDSC results for the zeolite 4A can be seen in Fig. 7 where the adsorbed amount of water and the measured adsorption enthalpy (in relation to the initial mass after desorption) is depicted. A comparison to the calculated values by Fischer 2009 is also shown.

| T | $p_{p\ H2O}$ | $\Delta m$ | $\Delta H_{Ads}$ |
|---|---|---|---|
| °C | mbar | % | J/g |
| 34 | 6,1 | 17,5 | 489,5 |
| | 12,1 | 18,6 | 645,9 |
| | 23,9 | 19,3 | 660,9 |
| 52 | 6,1 | 16,1 | 428,3 |
| | 12,1 | 17,2 | 576,8 |
| | 23,9 | 17,8 | 603,3 |
| 76 | 6,1 | 13,6 | 316,1 |
| | 12,1 | 15,2 | 501,4 |
| | 23,9 | 16,0 | 518,4 |

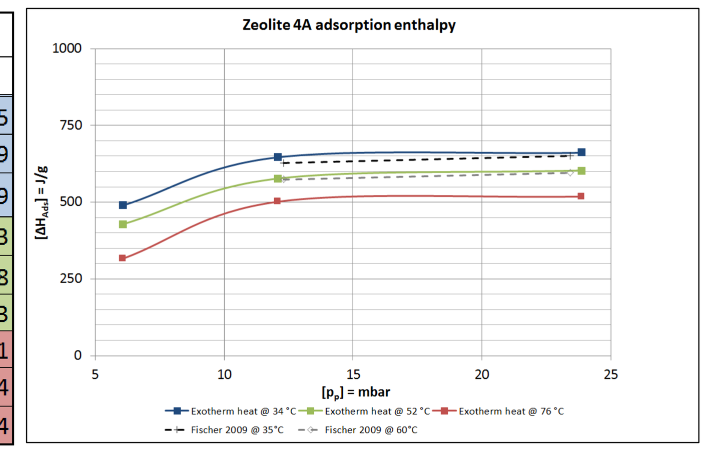


**Fig. 7: Z4A sorption isotherms and heat of adsorption**

[3] Fischer, 2009

**Sorption kinetics:** Fig. 8 shows the measured kinetic behavior of the heat flow and the adsorbed amount of water of a packed bed for zeolite 4A.

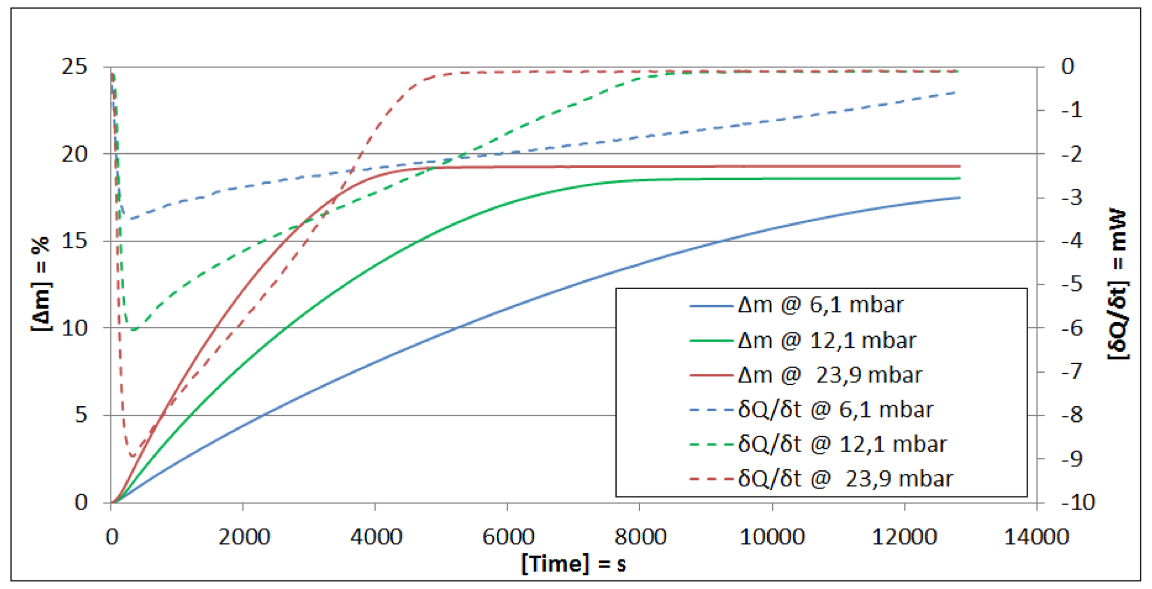


**Fig. 8: Kinetic behavior of the heat flow and mass change of Z4A**

**Decomposition:** Clinoptilolite impregnated with $CaCl_2$ showed hydrolysis to hydrogen chloride in the evolved gas FTIR analysis at 110°C (s. Fig. 3). This result specifies the upper temperature limit for a TES application based on this candidate.

**Transient Hot Bridge:** Measured thermal conductivity of zeolite 4A at room conditions (T=22°C; rh=50%):
$\lambda$=0,152 W/m·K, $u_c(\lambda)$ =9,5·$10^{-3}$ W/m·K

**Specific heat:** Fig. 9 represent $c_p(T)$ of zeolite 4A

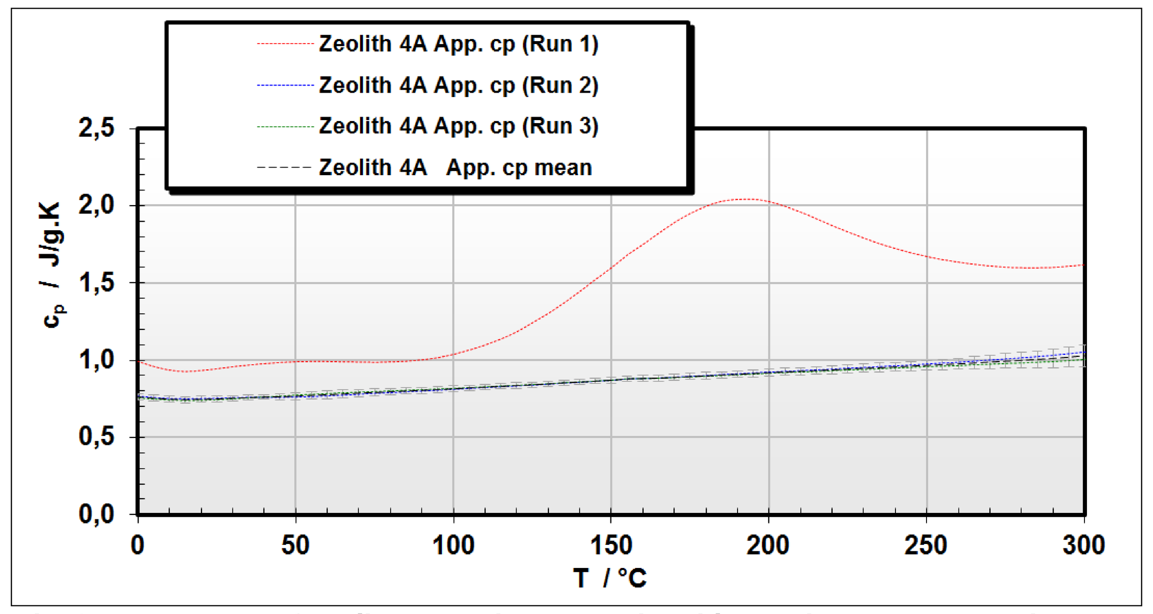


**Fig. 9: Apparent $c_p$ of zeolite 4A; red: evaporation, blue and green: pure sorbent**

[4] Englmair, Zettl, Lager; 2014