NATURAL ZEOLITES IN THERMAL ADSORPTION STORAGE AND BUILDING MATERIALS FOR SOLAR ENERGY UTILIZATION IN HOUSES

Jänchen J.[1]*, Herzog T.H.[1] Thrun E.[2]
*Author for correspondence
[1]Technical University of Applied Sciences Wildau,
Wildau, 15754, Germany,
[2]ZeoSolar e.V. Berlin
Berlin, 12489, Germany
E-mail: jochen.jaenchen@th-wildau.de

ABSTRACT

Two natural zeolitic tuffs of different European origin were studied for thermal adsorption storage application and as possible additives in plaster. The water adsorption behavior and the thermal adsorption storage properties were checked by thermoanalysis and in a lab-scaled storage of 1.5 L volume. The storage capacities achieve about half of the capacities of synthetic zeolites. The mixing properties in standard plaster showed to be very suitable for use. From our thermoanalytical results we estimated for an additive content of 20 wt.% thermal effects of 30-50 kJ/kg plaster. The thermal effect of Micronal® in plaster amounts to 20 kJ/kg plaster if the possible concentration of 10 wt.% is taken into account. Thus, the zeolitic tuff have a better thermal effect than the BASF product Micronal® containing an organic phase change material (PCM) as active component.

INTRODUCTION

A smooth utilization of thermal solar energy for climate control in buildings requires short- and/or long term thermal adsorption storage or energy transformation methods. Natural zeolites are well known for different applications in agriculture, purification of water, drying of air and technical gasses. Some attempts have been made in the past to utilize those minerals for thermal adsorption storage [1]. Beginning in ancient times in Italy up to present, zeolitic tuffs played an important role as construction materials or cementing agent [2].

Because of the relative inexpensive and broad availability of natural zeolites (cf. for example in Greece [3] or in Serbia and many other countries [2]) we proved its use in buildings for energetic reasons. This paper presents therefore (building on previous work [4]) results of the water adsorption properties and of the thermal adsorption storage performance of Greek and Serbian natural zeolitic tuffs.

EXPERIMENTAL SECTION

The zeolitic tuffs used in this study are from the Metaxades-Petrota region in the northeast of Greece [3] and from the Vranjska Banja deposit in Serbia. These deposits consist of rather pure zeolites such as clinoptilolite (HUE) or mordenite (MOR) with a notable water adsorption capacity. The crystallographic structure and the channel network of both zeolites are shown in Figure 1. Morphological information of two of the Greek samples may easily be obtained from Figure 2.
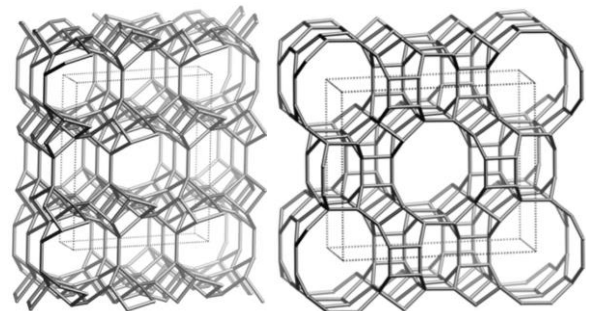
Figure 1 Structure of HUE (clinoptilolite, left) and MOR (mordenite). The dotted lines denote the size of the unit cell.

The composition and texture of the materials were characterized by XRD and scanning electron microscopy (SEM). The hydration and dehydration properties were determined by thermogravimetry (TG) and differential thermoanalysis (DTA) using a Netzsch STA 409 apparatus partially under simulated conditions close to these at a building wall. Hydrothermal stability tests were performed by repeated cycles of hydration and dehydration at elevated temperatures and with appropriate swing of relative water vapor pressure.
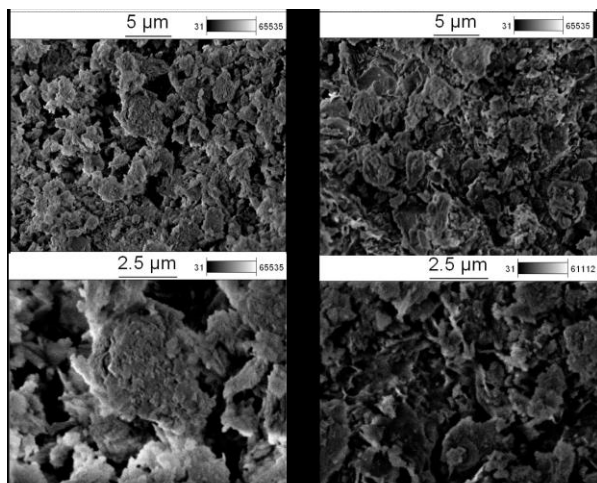
Figure 2 SEM of the natural zeolitic tuffs from Greece, sample type D_b (left), sample type F (right).

We also checked the processing properties of the zeolite grains in plaster by preparing samples of plaster on a wall. About 20 wt.% of zeolite could be easily mixed with the standard plaster slurry. Finally, the potential storage materials were tested in open lab-scaled thermal adsorption storage of 1.5 L volume corresponding with about 1 kg of zeolite grains. The charging temperature was set on 200°C (for more details compare reference [5]).

RESULTS AND DISCUSSIONS

### Adsorption Behaviour and Storage Properties

Beside the structural and morphological information of the samples already given above, Table 1 lists some other characteristic data of zeolitic tuffs such as the grain size, the summarized zeolite content and the water sorption capacities.

Table 1 Characteristic data of the materials

Sample	Grain size in mm	Zeolite content in wt.%	Water capacity at RH 79% (TG) in g/g
Greek type D_b	2.4-3.3	94.5*	0.161
Greek type D_m	2-2.4	85.9*	0.155
Greek type F	1-2	77.0*	0.140
Serbian type	1-3	71.1**	0.143

*clinoptilolite and mordenite, ** clinoptilolite

The characterization of the natural zeolite by chemical analysis and XRD confirm relatively high purity of the materials. The zeolite content of the Greek materials varies between 94% and 77 % depending on the type. The zeolite concentration of the Serbian material amounts to 71%. This is less zeolite as found for the Greek tuffs because of other nonporous components such as feldspar, plagioclase and quartz. As can be seen from Table 1 the water adsorption values are related to that fact with amounts of about 0.16-0.14 g/g as determined by TG.
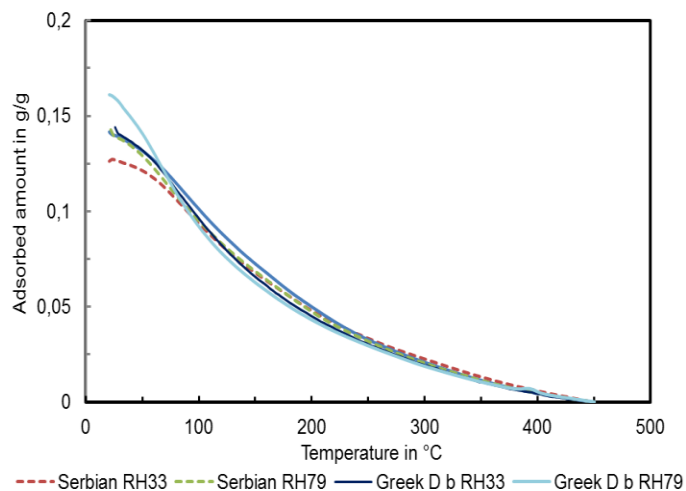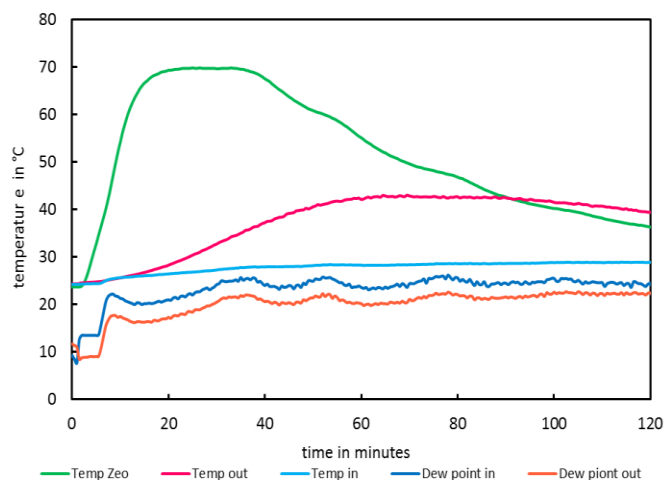

Figure 3 TG profiles of the natural zeolitic tuffs from Greece and Serbia upon water sorption at different RH values.

Further, the TG results in Figure 3 differ correspondingly too, despite differences in RH for saturation prior to the TG experiment. The maximum water adsorption capacities for the Serbian zeolite and Greek type D_b, however, are just half of the adsorption capacity of modern synthetic molecular sieves.

Consequently, 13XBF, which consist of binder free beads, adsorbs 0.316 g/g at the same conditions and the specific energies differ accordingly and amount to about 166 Wh/kg for 13XBF and roughly 90 Wh/kg for the natural materials [5]. This may spoil the storage suitability of the natural zeolites in terms of energy density but this disadvantage might be compensated by substantial lower prices for the zeolitic tuffs. While granulated standard products of synthetic zeolites cost 2000-4000 €/t the natural zeolitic tuffs with a certain particle size distribution and high zeolite content may cost about 200-400 €/t.

The Figures 4, 5 and Table 2 tell something more in detail about the results of the storage tests by adsorbing water vapor. The figures show profiles over time of the temperatures in the middle of the zeolite bed and of the humid air stream in and the dry outlet stream. Further, the diagrams show the dew point of the in- and outlet. Regardless of differences in the water flux no substantial differences in the storage behavior can be observed according to the results in Table 2. The maximum temperature and the adsorption capacity related to the true zeolite concentration in the storage don't differ significantly. The adsorption capacity in the storage (a in Table 2) corresponds well with TG data in Figure 3 for T=25-200°C (200°C is the charging temperature of the storage).

However, a closer look to the values in the Figures 4 and 5 reveal some impact of the flux on the dew point difference in/out, the outlet temperature and the breakthrough time. In the case of the higher flux ($1.3 \cdot 10^{-4}$ kg s^{-1} m^{-2} water, Figure 4) the outlet temperature is higher but the dew point difference is les (Figure 5 with $0.9 \cdot 10^{-4}$ kg s^{-1} m^{-2} water). The higher flux allows a higher reaction rate (adsorption of water and release of heat)

Figure 4 Results of the storage tests (discharging by water adsorption) on the natural zeolitic tuffs from Greece type D_b (higher flux).
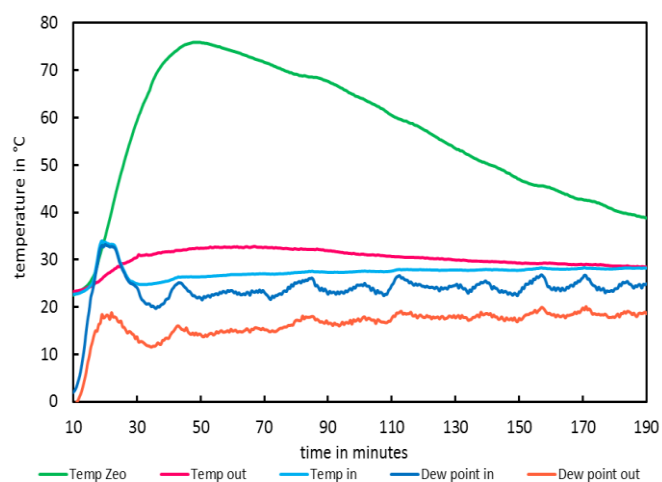

Figure 5 Results of the storage tests (discharging by water adsorption) on the natural zeolitic tuffs from Serbian type (lower flux).

Table 2 Results of the adsorption and storage tests, adsorption capacity, a (related to sample) and a_z (related to pure zeolite) and maximum temperature in the storage, T_{max}

Sample	a in g/g	a_z in g/g	T_{max} in °C
Greek type D_b	0.10	0.106	70
Serbian type	0.07	0.098	75

and thus heat up the outlet air to some more extend. So, higher flux may be applied for heating applications and lower for drying purpose.

Another important data of the storage materials is the hydrothermal stability. The results are presented in Figure 6. Harsh conditions have been applied to get information about the stability by a lower number of cycles. As demonstrated the adsorption capacity does not decrease much after about 30 cycles confirming high hydrothermal stability.
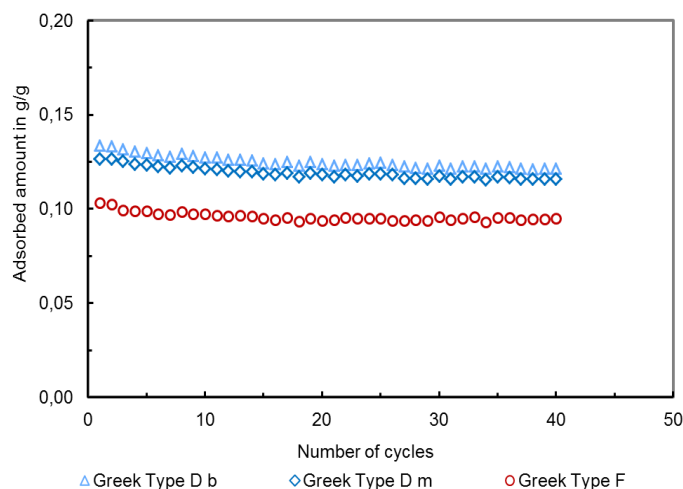

Figure 6 Test of hydrothermal stability by cycles adsorption (25°C, RH=10%) and desorption (350°C, RH=18%).

Zeolite Tuffs as Additive in Building Material

The ability of the zeolitic tuffs to adsorb and desorb humidity upon diurnal cycles of temperature swing and humidity change with corresponding heat consumption or heat release makes these materials suitable for controlling the local environment on building walls.

We simulated the environmental changes at the wall by an adapted heating program in our DTA facility. We assumed two different temperature levels (50°C and 80°C) possibly develop at the outer surface of the walls because of thermal radiation by the sun. The temperature profile of the measurements is shown in Figures 7 and 8. The sample is heated in a dry nitrogen stream of 70 ml/min with 10 K/min. up to 50°C followed by 20 min. dwell time and another increase to 80°C waiting another 20 min. at constant temperature. Finally the sample was desorbed completely at 450°C to obtain the dry weight.
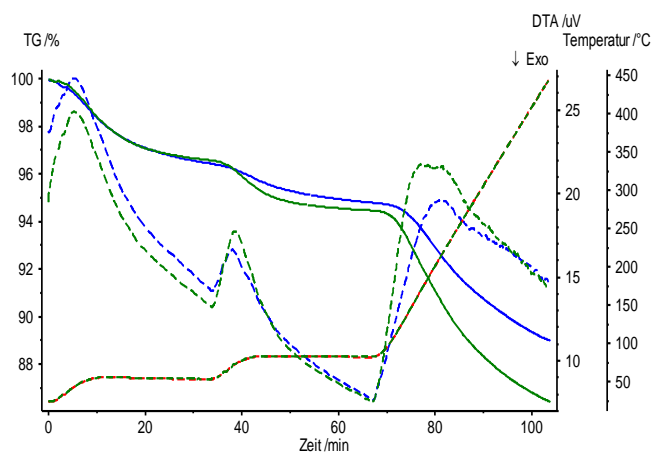
Figure 7 TG (solid lines) and DTA (dashed lines) profiles of two different natural zeolites from Greece: type F (blue, top curve) Type D_b (green) upon water saturation at 79% RH.
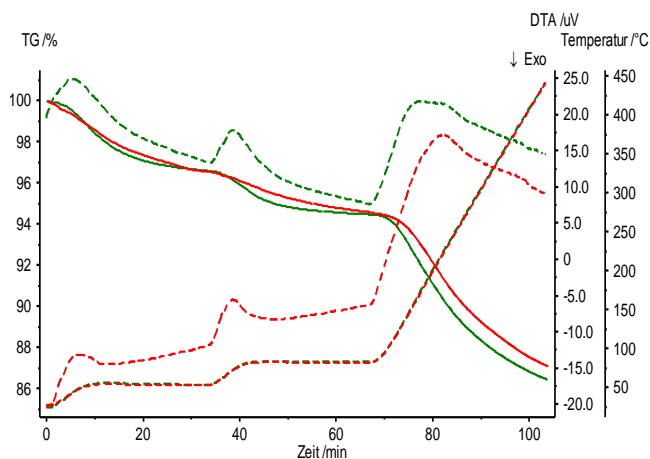
Figure 8 TG (solid lines) and DTA (dashed lines) profiles with isothermal parts at 50°C and 80°C of Greek type D_b (geen), Serbian type (red, top curve) upon water saturation at 79% RH.

Figure 7 compare the water desorption behavior of the two Greek zeolite types D and F. Figure 8 relates the TG and DTA profiles of the Greek zeolite D_b and the Serbian material. As can be seen, the Greek types D_b and F differ slightly up to 80°C rather than the Greek and Serbian materials. The latter behave very similar up to 80°C in terms of the water amount released (cf. Table 3, second column). Accordingly the heat evolved upon water uptake and release should be the same. The DTA curves in Figure 8 indicate this heat consumption by endothermic peaks for the water desorption. This heat consumption would delay the warming up of the wall covered with zeolite containing plaster.

To get some quantitative data of the potential for cooling and heating of the building walls we calculated the integral heat of desorption and adsorption based on our water release data and the differential molar heats of adsorption given by Isirikyan for clinoptilolite [6]. The heat curve shows in the regarding interval of loading heats of adsorption of about 60 kJ/mol water (=3.33 kJ/kg water).

Table 3 Results of the thermoanalytical tests as building materials; adsorption capacity of pure zeolite sample, $a_{80°}$, and adsorption heat release/consumption of plaster with 20% zeolite, Q_1 for T=50° and Q_2 for T=80°C.

Sample	$a_{80°}$ in g/g	Q_1 in kJ/kg	Q_2 in kJ/kg
Greek type D_b	0.063	30	50
Serbian type	0.063	30	50
PCM Micronal®	n/a	20*	20*

*Melting heat at 25°C

So we estimated from our thermogravimetric results and the integral heats of adsorption the thermal effect of zeolitic tuffs in plaster (cf. Table 3). For an additive content of 20% a significant higher thermal effect can be expected with 30 kJ/kg plaster as it is claimed for Micronal® from the BASF with about 20 kJ/kg containing 10% of an organic phase change

material (PCM). Heating up to 80°C may have an even better result for the zeolite as shown in Table 3, fourth column. Micronal ® is based on the PCM RT 25 (Rubotherm) and has a heat of fusion of 206 kJ/kg which was the bases of our calculations.
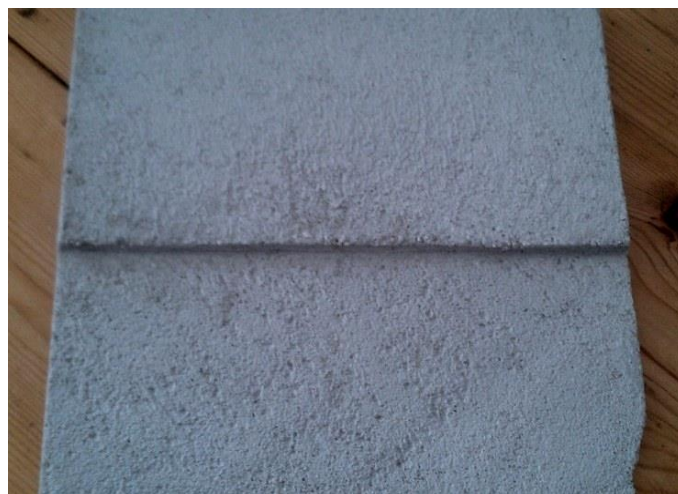
Figure 9 Sample of plaster with 20% Greek natural zeolitic tuffs from Greece type D_m.

Finally we prepared plaster with 20 wt.% of zeolitic tuff (grain size 2-2.4 mm) as a first trail. It was easy to replace parts of the standard ingredient sand by zeolite grains (not so different to sand as the PCM is) to get plaster with regular processing properties. The result is demonstrated in Figure 9.

Sezemanas et al. [7] investigated the influence of the natural zeolite clinoptilolite on the properties of plaster in more detail. They found that clinoptilolite ensures adequate hydration of cement minerals and compacts the structure slightly. The compressive and flexural strength of hardened plaster increases. Drying shrinkage, water vapor resistance factor and coefficient of capillary absorption remained unchanged. This findings in [6] emphases improved use of the modified plaster beside its ability of environmental control by the zeolites additives as reported in this paper.

As an open question remains the long term stability and chemical tolerance of the zeolite grains in the plaster.

CONCLUSION

The natural zeolites from the Metaxades-Petrota region or Vranjska Banja deposit are promising low-cost additives in plaster to improve the natural control of temperature and humidity in buildings. The PCM Micronal® can control the temperature too but do not have any positive effect on the humidity of the wall. Different to this organic PCM the inorganic zeolite is nonflammable and do not contribute to fire hazard.

The thermal adsorption storage properties are compared with synthetic zeolites limited because of their lower adsorption capacities and storage densities. Further, the rather high

charging temperature (desorption of the water) could be restrictive in terms of solar applications. This may spoil the storage suitability of the natural zeolites in terms of energy density but might be compensated by substantial lower prices.

Generally the use of natural zeolitic tuffs in regard of solar thermal application should be focused on building materials for environmental control. Solar thermal energy storage and solar cooling (heat pumps) may be a good option for natural zeolites taking into account the low costs.

ACKNOWLEDGEMENT

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