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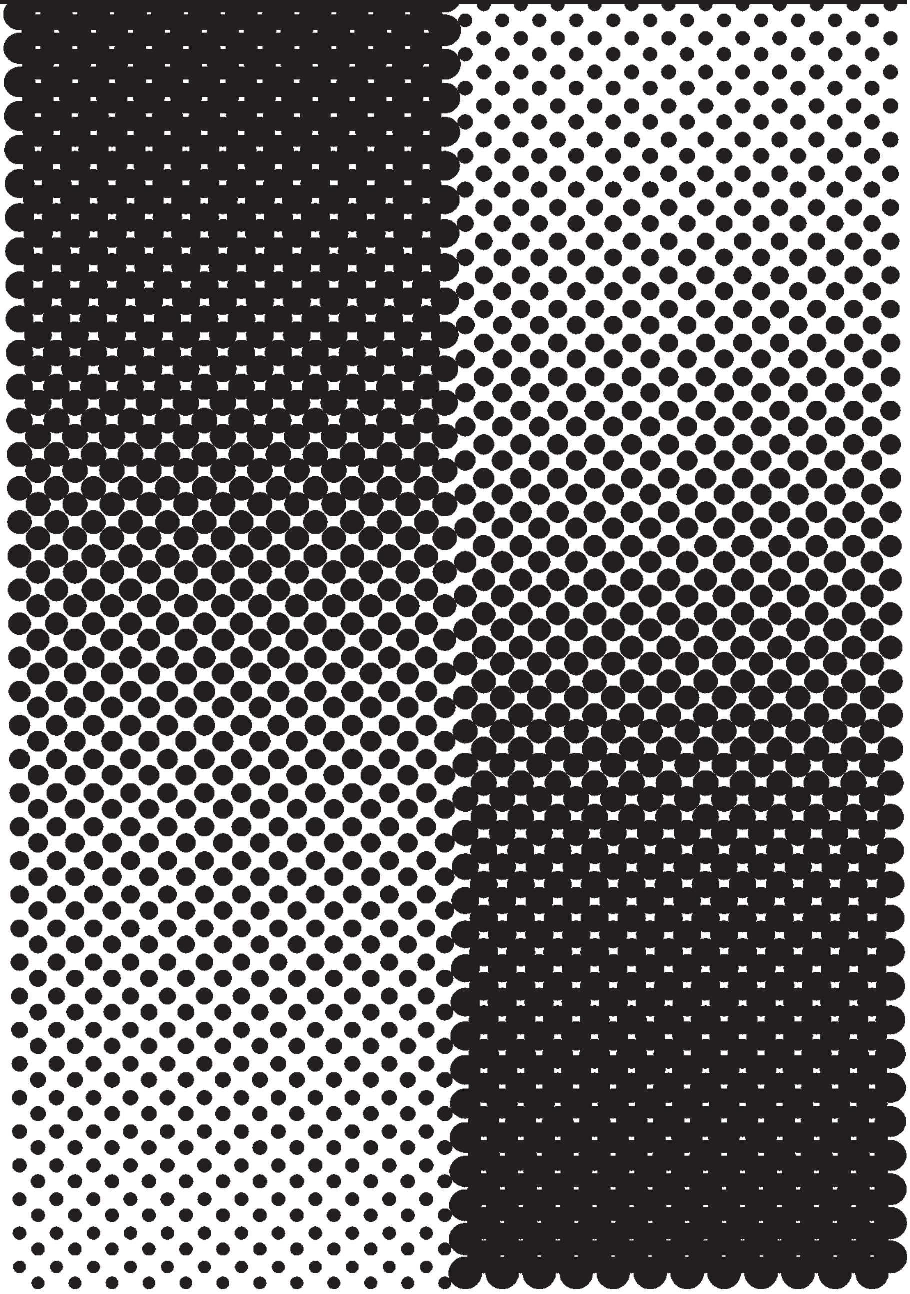

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DYNAMIC HEAT OF ADSORPTION OF WATER VAPOUR ON ZEOLITIC TUFF AND ZEOLITE 4A BY FLOW MICROCALORIMETRY

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ABSTRACT

In this study a practical method for measurement of heat of adsorption of water vapour on adsorbents was developed to evaluate the feasibility of substitution of a zeolitic tuff with zeolite 4A in air drying and heat pumps. The change of heat of adsorption with inlet humidity of the air passing through the calorimeter was investigated. Samples were characterised by X-ray diffraction and thermal gravimetric analysis techniques. Specific heats of the zeolitic tuff and zeolite 4A were measured as 1.01 and 1.42 J/g K, respectively. Adsorption isotherms fitted to the Langmuir model with regression coefficient 0.93 and 0.94 with monolayer capacities, X_m 9.68% and 26.35% H_2O for the zeolitic tuff and zeolite 4A, respectively. The energy storage intensity was measured in the range 48–97 J/g and 464–201 J/g for the tuff and zeolite 4A, respectively. Heat of adsorption of zeolite decreased with surface coverage and it was in the range 1750–2835 and 1104–2640 J/g H_2O for the zeolitic tuff and zeolite 4A, respectively.

Keywords: microcalorimeter, heat of adsorption, zeolite, water vapour adsorption, specific heat.

AIMS AND BACKGROUND

Microcalorimeter is a quite important apparatus for measurement of heat of adsorption, of enthalpy of liquid, specific heat of solid, characterisation and water adsorption of an adsorbent, investigation of reaction kinetics and following metabolic events in living cells.

Groszek et al.[1] reported that the flow adsorption microcalorimetry was a powerful tool for investigation of adsorption and the assessment of its mechanism, as it provided a straightforward route to information concerning energetic aspects of the process.

Brown and Grozsek[2] determined heat of adsorption of ammonia on a zeolite catalyst and acid activated clay catalyst by flow adsorption microcalorimetry. Heat of irreversible adsorption of NH_3 was found as 41 and 88.2 kJ/mol NH_3 for zeolite

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Na–Y and H–Y, respectively. Due to high value of heat of adsorption adsorbent was diluted with sand.

Water vapour adsorption on different adsorbents was investigated by flow adsorption microcalorimetry. Simultaneous determinations in the flow adsorption microcalorimeter of the amounts and heats of adsorption designed to discover to what extent the adsorption of water vapour on a heterogenous carbon and carbon molecular sieve was influenced by the presence of nitrogen and methane at atmospheric pressures and how the differential heats of displacement of these gases by water change with increasing uptake. Equilibration of sample with ice and water was done[3].

Differential scanning calorimetry (DSC) has been used to study the thermal effects during adsorption of water on different zeolite NaA samples. Calibration of DSC was needed. The fraction of heat which flows to the sensor depends on the thermal properties of the sample and of the gas phase[4]. The calibration factor, CF, will compensate for this effect, and is defined as the ratio between the real melting heat and the measured melting heat:

$$\mathrm{CF} = \frac{(\Delta H_{\mathrm{m}})_{\mathrm{real}}}{(\Delta H_{\mathrm{m}})_{\mathrm{meas.}}} \qquad (1)$$

Calibration factors determined with pieces of gallium, indium or tin on top of different zeolite NaA samples. Values of calibration factors were found to be between 0.77 to 1.17. The gas flow through the DSC cell consisted of pure nitrogen (2 lh^{-1}) or a nitrogen/water mixture, saturated in an evaporator filled with ice (p_w~4.6 mm Hg), also at a flow rate of about 2 l h^{-1} (measured at room temperature). Sometimes higher water vapour pressures were used by evaporation at room temperature (p_w~17.5 mm Hg). Heats of adsorption calculated from the measured peak areas and calibrating factors were between 3111 to 3944 J/g H_2O (Ref. 4).

Gorbach et al.[5] measured and modelled water vapour adsorption on zeolite 4A. Both corresponding models of equilibria and kinetics of water vapour adsorption on zeolite 4A as a function of water vapour concentration measurent were presented.

Extensive studies on various adsorbents have shown that zeolites have some favourable properties for energy storage over other adsorbents. This is mostly due to the shape of their adsorption isotherms and the amount of heat of adsorption[6]. Local zeolitic tuff from Bigadic, Turkey, rich in clinoptilolite was investigated for the possible utilisation in energy storage[7]. The samples were identified by X-ray analysis and their properties related to energy storage applications were determined by Ulku[7]. The dynamic behaviour of a column packed with local zeolite mineral, mainly clinoptilolite, was examined under adiabatic conditions by Ulku and Ozkan[8]. The change in the energy density of clinoptilolite was investigated depending on inlet air properties (temperature, humidity, and velocity), particle diameter of adsorbent and bed height. It has been proposed that the local zeolite mineral (mainly clinoptilolite) can be used as adsorbent in energy recovery applications.

Comparison of the zeolitic tuff with commercial syntetic zeolites was made as dessicant materials in packaging applications. While two different types of commercial zeolites adsorbed 18–19% water at 10% relative humidity at 25°C the zeolitic tuff adsorbed 9.4%. The values were 20–21 and 11.5 % for 20% relative humidity[9].

The low thermal conductivity of zeolites limited their use in adsorption heat pumps. Thus, studies were made to maximise heat transfer area by forming very thin layers at the outside of the heat exchanger tubes used in heat pumps to increase the heat transfer efficiency[10]. Thermal conductivity of natural zeolites from the Gordes region was 0.26 W/m K and studies were made to increase the thermal conductivity by adding fillers such as Al, $Al(OH)_3$ and graphite, and it was found that Al addition up to 40% increased the thermal conductivity to 1.2 W/m K (Ref. 11).

Qui et al.[12] reported that the heat capacity of zeolite 4A is in the temperature range 37 to 311 K. The heat capacities shows no anomalies in this temperature range interactions. Drebushchak et al.[13] measured heat capacity of heulandite in an adiabatic vacuum calorimeter.

In this study, development of a practical method for measurement of heat of adsorption of water vapour on adsorbents by using a Seteram C-80 microcalorimeter was aimed at. Local zeolitic tuffs from Gordes, Turkey, and zeolite 4A were used as adsorbents. Air at different relative humidities was passed through samples in microcalorimeter cell, and heat of adsorption was measured at 30°C.

EXPERIMENTAL

Materials. Local zeolite from Gordes, Turkey, and Aldrich 4A zeolite having 5 mm average particle size were used in the experiments. Natural zeolite samples were characterised by using a Philips x-pert X-ray diffractometer with Cu K_a radiation.

Adsorption isotherms. The adsorption isotherms of natural and synthetic zeolites at 30°C were obtained by using the temperature and humidity controlled chamber (Angelantoni Industry). The samples were dried at 175°C in a vacuum furnace (Nuve EV-018) for 2 h. A sensitive balance was placed into the chamber. When the chamber reached to desired temperature and relative humidity, the zeolite sample was placed into the chamber. Sensitive balance was held in the chamber in 10–60% humidity range and weighing the sample was done inside the chamber. Then for 70 to 90% humidities, sensitive balance was placed outside the chamber and the samples equilibrated in the chamber were weighed outside to protect the balance from high humidities.

Microcalorimetry. A Seteram C-80 microcalorimeter (Seteram Instruments, France) was used to measure the heat of adsorption. This calorimeter is based on the Calvet heat flow principle. The temperature ranges was from 20 to 300°C with aluminium or nickel O-ring and to 200°C with teflon O-ring, and the heating rate was from 0.01 to 2 K/min. It consisted of two cells, one was the sample cell, the other was the reference cell. These were placed in the thermostated calorimetric block, which was controlled by using a temperature controller. Two identical and independent heat flux detectors consisting of conductive thermocouples connected the vessels thermally to the block, so that vessel temperature was always as close as possible to that of the block.

Specific heat measurement. Specific heat of the zeolite samples was measured by using a-Al_2O_3 standard (Aldrich) by a C-80 calorimeter. Heating runs with 0.05°C/min were done for blank, a-Al_2O_3 and the zeolite sample for this purpose.

Control of air relative humidity in microcalorimeter experiments. The humidity of air was controlled by mixing dry and saturated air streams obtained by passing ambient air through a silicagel packed column and wash bottle filled with water, respectively, as seen in Fig. 1.

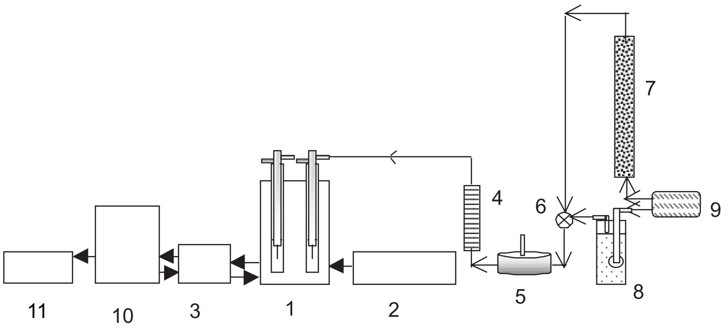

Fig. 1. Experimental set up: 1 – microcalorimeter (Seteram C-80); 2 – power module; 3 – control panel (CS 32); 4 – flowmeter; 5 – humidity probe; 6 – humidity control valve; 7 – silicagel packed column; 8 – wash bottle; 9 – air pump; 10 – computer; 11 – printer

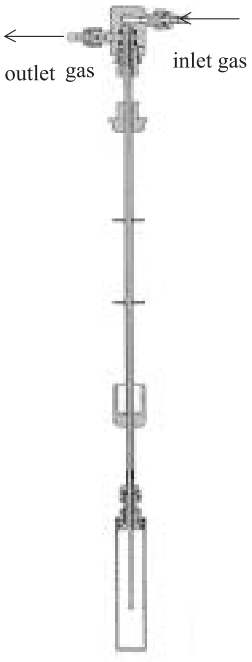

Fig. 2. Gas circulation vessel

Measurement of heat of adsorption. Gas circulation vessels shown in Fig. 2 were used to perform the heat of adsorption measurement. Sample was put into the sample cell and the cell was placed in microcalorimeter. Although it is known that zeolites should be degassed at 400°C to obtain complete dryness, since teflon seals of the cell were resistant up to 200°C, the samples were dried at 175°C. This outgassing temperature could also be achieved practically in regeneration of the adsorption columns and heat pumps. While the sample was kept at 175°C for 2 h, dried air, obtained by passing through the silica gel packed column, was sent to sample cell at ambient temperature. Then the sample was cooled to 30°C with dry airflow. Finally, zeolite samples were subjected to adsorption of water vapour by passing air at a constant relative humidity at 30°C at 380 cm^3 /min rates. Relative humidity range 20 to 90% at room temperature was investigated in this study. The experiments done are as tabulated in Table 1. A blank experiment without any sample was also done to see heat capacity effect and it was found as negligible. The heat of adsorption was found from the area of the exothermic peak recorded by microcalorimeter.

Table 1. Experiments for adsorption heat measurements

Sample type	Ambient temperature (°C)	Sample mass (mg)	Air flow rate (cm^3 min^{-1})	Air relative humidity (%)
Natural zeolite	25.7	513	380	30
(tuff)	27.6	513	380	40
	24	513	380	70
	23.4	513	380	90
Zeolite 4A	27.1	256.8	380	30
	29	256.8	380	40
	26.7	52	380	70
	25	52	380	90
Blank test	22	–	380	90

Calibration of microcalorimeter. Microcalorimeter was calibrated by measuring the heat of fusion of benzoic acid and indium. Aluminium oxide from Aldrich is filled into the sample cell. Benzoic acid from Lachema was placed on a-aluminium oxide and the sample cell was placed in the microcalorimeter. Since melting point of benzoic acid is 122.4°C, the microcalorimeter was heated from ambient to 110°C with the rate 1°C/min, between 110 to 130°C with the rate 0.1°C/min. Benzoic acid melted at 122.4°C and the measured heat of fusion (DH_f) value, 34.08 cal/g, was very close to the literature value of 33.89 cal/g (Ref. 14). Calibration factor was found to be 1.03 using the values above and equation (1). The same calibration experiment was done for indium. Melting point of indium is 156.6°C, the microcalorimeter was heated from ambient to 150°C with the rate 1°C/min, between 150 to 170°C with the rate 0.1°C/min. Indium melted at 159.28°C and the measured heat of fusion (DH_f) value, 6.88 cal/g, was very close to the literature value of 6.81cal/g (Ref. 14). Calibration factor was found to be 1.01 using the values above and equation (1).

TGA analysis. TGA analysis of the samples equilibrated with 75% humidity at 25°C was made by heating them up to 175°C at 1°C/min rate and keeping them at this temperature for 2 h simulating the outgassing process in a C-80 microcalorimeter. Then they were heated up to 1000°C at 10°C/min rate.

RESULTS AND DISCUSSION

In the powder X-ray diffraction diagram of the tuff shown in Fig. 3, characteristic peaks of clinoptillolite at 2q values 9.92, 22.43, 25.8, 30.05, and 32 were observed[15]. Thus, the tuff was rich in natural zeolite clinoptillolite. The presence of quartz, montmorrilonite and illite was reported in the same tuff by other researchers.

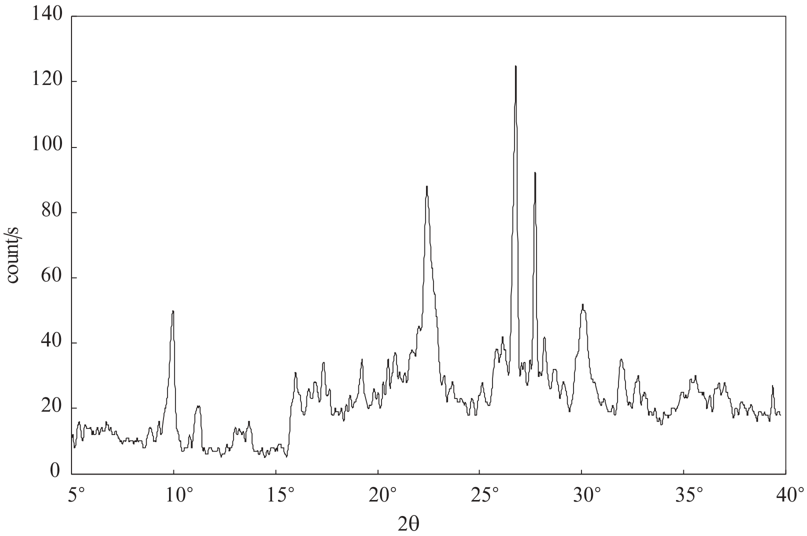

Fig. 3. X-ray diffraction analysis of natural zeolite (tuff)

The specific heat of the samples was found as 1.014 and 1.42 J/g K for the zeolitic tuff and zeolite 4A, respectively. They were comparable with the literature values. The specific heats of heulandite and zeolite 4A was found as 1.10 J/g K by Drebushchak et al.[13] and 0.92 J/g K by Qui et al.[12], respectively.

State of the samples outgassed in the calorimeter at 175°C was determined by TGA analysis as seen in Fig. 4. No further mass loss was observed by heating the samples for 2 h at 175°C. 2.54 and 3.04% mass loss occured between 175 and 700°C for the zeolitic tuff and zeolite 4A, respectively. Thus, it can be concluded that the outgassed tuff and zeolite 4A in the calorimeter at 175°C, already contain 2.59 and 3.04% H_2O, respectively.

Adsorption isotherms. The adsorption isotherms at 30°C for the outgassed samples at 175°C for 2 h are shown in Fig. 5. No data could be obtained up to 20% relative humidity by the method used in this work. As seen in Fig. 6 the isotherms fitted to the Langmuir model shown by equation (2) with regression coefficient 0.93 and 0.94 with monolayer capacities, X_m, 9.68 and 26.35% for the tuff and zeolite 4A, respectively. The monolayer capacity of zeolite 4A at 25°C was close to the ones found by previous researchers[5] as seen in Fig. 5. For natural zeolite an apparent

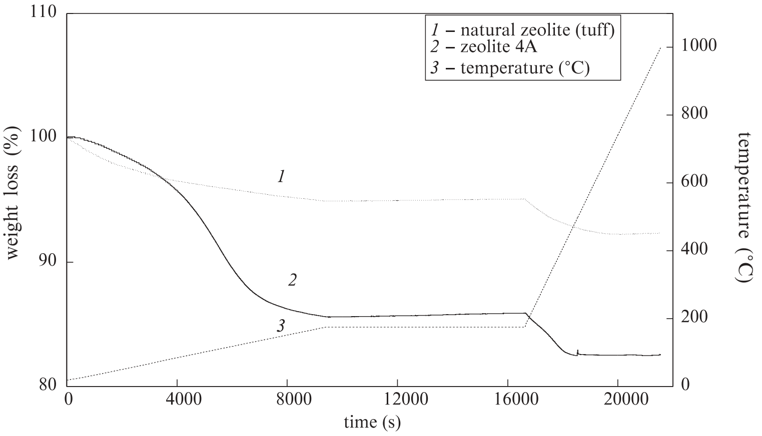

Fig. 4. TGA analysis of natural zeolite (tuff) and zeolite 4A

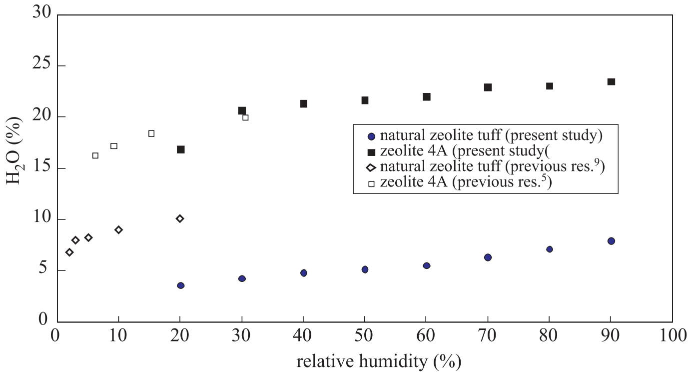

Fig. 5. Adsorption isotherms of natural zeolite (tuff) and zeolite 4A

adsorption isotherm was determined in the present study. Lower adsorption capacity was observed due to moisture adsorption during the transfer of the sample from outgassing oven to constant humidity chamber. In Fig. 5 the data obtained by Ozkan[9] under vacuum had higher values than found in the present study made in air.

$$\frac{1}{X} = \frac{1}{bX_{\mathrm{m}}} \frac{1}{\mathrm{RH}} + \frac{1}{X_{\mathrm{m}}} \qquad (2)$$

where X represents solid moisture percent, RH – percent relative humidity at 30°C, and b – the Langmuir constant which values were found as 0.023 and 0.260 natural zeolite and zeolite 4A, respectively.

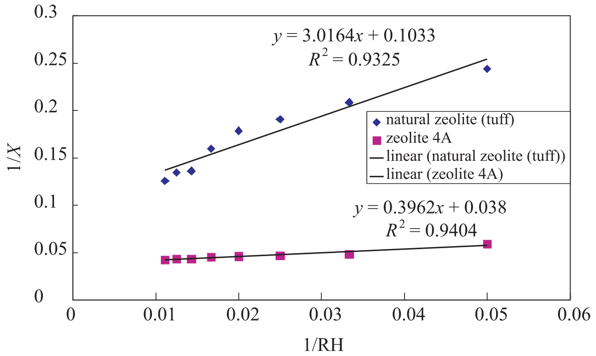

Fig. 6. Langmuir adsorption isotherm model of natural zeolite (tuff) and zeolite 4A

Heat of adsorption. The heat flow versus time curves for experiments done at different relative humidity at constant air flow rate are shown in Figs 7 and 8. The heat of adsorption in the sample cell heats the air passing through the cell from ambient

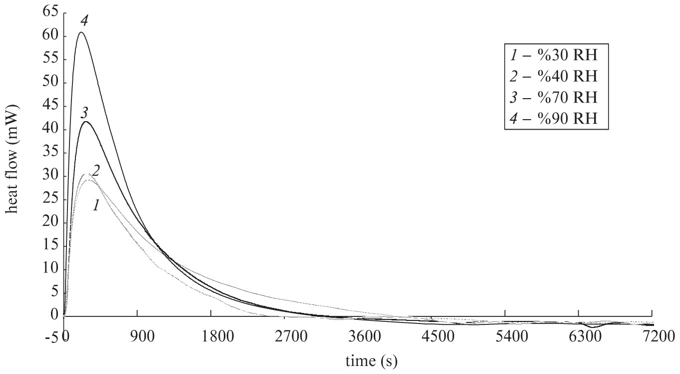

Fig. 7. Heat of adsorption peak of natural zeolite (tuff) at different air relative humidity with constant air flowrate (380 cm^3 min^{-1}) at 30°C

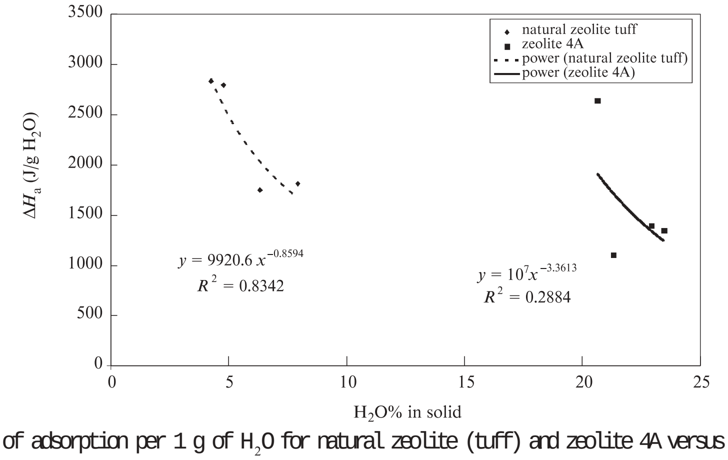

Fig. 8. Heat of adsorption per 1 g of H_2O for natural zeolite (tuff) and zeolite 4A versus solid moisture content

temperature to 30°C, the sample and calorimeter, and excess of this heat seen as an exothermic peak on the heat flow versus time curve.

The exothermic peak area should be the difference between the heat of adsorption and the heat used for heating the gas from ambient to 30°C.

$$\dot{m}c_p\, DTt + DH = DH_a, \tag{3}$$

where DT is the temperature difference between ambient air temperature and adsorption temperature, DH – the exothermic peak area, DH_a – the heat of adsorption, $\dot{m}$ – the air mass flow rate, c_p – specific heat of the air (J/g K), t – the period of the exothermic peak. The heat capacity change of the gas stream was negligible compared to the heat of adsorption as understood from experimental runs without any sample. The heats of adsorption and solid moisture are shown in Table 2. The measured DH_a values were in the range 48–97 and 201–464 J/g for the tuff and zeolite 4A, respectively. The energy storage density of the natural zeolite (Bigadic – Turkey) was reported to be about 300–470 J/g zeolite by Ozkan and Ulku[8] for the regeneration temperature of 400°C. It was changed with the regeneration temperature of zeolite, for example to 100 J/g and 500 J/g zeolite for 40 and 175°C, respectively[7]. Lower values were found in the present study since the regeneration temperature was 175°C.

Table 2. Heat of adsorption and solid moisture of natural zeolite (tuff) and zeolite 4A

Sample type	Air relative humidity (%)	Change in solid moisture	DH_{peak} (J/g)	DH_a (J/g H_2O adsorbed)
Natural zeolite (tuff)	30	0.01	–48.48	–3635.08
	40	0.02	–62.6	–2794.64
	70	0.03	–66.34	–1750.39
	90	0.05	–97.79	–1814.28
Zeolite 4A	30	0.17	–464.54	–2640.93
	40	0.18	–201.88	–1104.83
	70	0.19	–277.79	–1396.63
	90	0.20	–275.33	–1348.33

The measured values of the heat of adsorption of the water vapour on the zeolitic tuff and zeolite 4A versus solid moisture are shown in Fig. 8. The regression coefficients for exponential curve fitting for zeolite 4A and tuff were found as 0.28 and 0.83, respectively. Heat of adsorption for zeolitic tuff in the 4.2 to 7.9 % moisture range was as follows:

$$DH_a = 9920.6X^{-0.8594} \tag{4}$$

and zeolite 4A in the 20.6 to 23.4% moisture range was as follows:

$$DH_a = 5\ ´\ 10^7 X^{-3.3613} \tag{5}$$

Ulku[7] found heat of adsorption for natural zeolite decreased from 3500 to 2600 J/g H_2O from 4 to 11.5% solid moisture. The lower heat of adsorption values was found in the present study compared with the foundings of other researchers Ulku[7], Ulku and Ozkan[8] and even below the limit of heat of condensation of water vapour 2445 J/g H_2O at 25°C (Ref. 16). This could be due to the following reasons.

1. Since solid temperature increased with the heat of adsorption, lower amount of H_2O than the equilibrium value at 30°C was adsorbed.

$$DT = DH_a X 1/C_p. \quad (6)$$

Adiabatic temperature rise was 48–97°C for natural zeolite and 142–316°C for zeolite 4A as found from equation (6) using solid moisture and DH_a values reported in Table 2 and measured specific heats.

At high relative humidities the surface temperature of dried sample increases more compared to low relative humidities due to higher adsorption capacities and higher driving force to mass transfer.

2. Since heat transfer coefficient of clinoptilolite was low (0.26 W/m K) (Ref. 11), the adsorbed heat was not transferred to metal cell and could not be detected by the calorimeter.

Thus, rather than a step change in air relative humidity, small incremental changes could eliminate this problem.

The method developed for determining heat of adsorption in this study allowed studying the entire humidity range of air at room temperature. Humidity control by mixing dry and wet air streams made possible to cover a range larger than equilibration with ice and water as done by other researchers[3].

CONCLUSIONS

Measurement of water vapour adsorption on natural zeolites and zeolite 4A was performed by a Calvet C-80 microcalorimetry. The amount of adsorbent used as adsorbent was higher than that of the DSC techniques (513–52 mg). Adsorption isotherms of zeolite samples were fitted to the Langmuir model with regression coefficients 0.93 and 0.94 for natural zeolites (tuff) and zeolite 4A, respectively. The monolayer capacities, X_m, were 9.68 and 26.35% H_2O for the tuff and zeolite 4A, respectively. Heat of adsorption values was found in the range 48–97 and 201–464 J/g for the tuff and zeolite 4A (1750–2835 J/g H_2O and 1104–2640 J/g H_2O) for zeolitic tuff and zeolite 4A, respectively. Heat of adsorption was shown to decrease with surface coverage for both samples. Specific heats of samples measured by microcalorimeter as 1.01 and 1.42 J/g K for zeolitic tuff and zeolite 4A, respectively.

A Seteram C-80 microcalorimeter was used as a flow microcalorimeter to determine the heat of adsorption versus solid moisture data. The sample regenaration was done *in situ*, preventing moisture adsorption during transfer of the sample. It was shown that natural zeolitic tuff could be substituted for zeolite 4A in water vapour adsorption columns and heat pumps making a compromise between lower adsorption capacity and lower heat of adsorption and cheaper cost of tuff than zeolite 4A. Larger volumes and masses required for the tuff than zeolite 4A should be compensated with its lower cost to have an economically feasible application of the tuff.

NOMENCLATURE

b – the Langmuir constant
CF – calibration factor
c_p – specific heat
$\dot{m}$ – air mass flow rate
p_w – partial pressure of water
RH – percent relative humidity at 30°C
t – period of the exothermic peak
X – solid moisture percent fitted to the Langmuir model
X_m – monolayer capacities fitted to the Langmuir model
DH – exothermic peak area
DH_a – adsorbed heat (J/g H_2O)
DH_f – heat of fusion
$(DH_m)_{meas.}$ – measured heat of melting
$(DH_m)_{real}$ – real heat of melting
DH_{peak} – measured peak area by microcalorimetry
DT – temperature difference between ambient air temperature and adsorption temperature
2q – angle of diffraction in measurement.

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