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SOLAR ENERGY STORAGE THROUGH WATER ADSORPTION–DESORPTION CYCLES IN ZEOLITIC TUFFS

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ABSTRACT

The process of thermal activation of an Italian natural zeolite, namely chabazitic tuff, is studied in the view of its possible use for solar energy storage.

An evaluation of the amount of heat storable through the dehydration of the zeolite is also given.

INTRODUCTION

Energy storage is fundamental to the technology of solar energy, due to its intermittent nature and because energy is often requested when solar availability is lowest.

Considering only low temperatures (< 300 °C), two main storage methods are commonly used: sensible heat storage, and the storage of heat associated with a phase change or solution process. Due to the problems usually concerned with the latter method, operational systems have so far relied more on the former which, despite the low energy density, requires only cheap materials and a simplicity of design. Energy storage methods based on adsorption processes have been proposed recently with promising perspectives. They present, in fact, higher energy densities, low cost, and simplicity of design for the material container and auxilliary systems, required for the delivery of energy to and from the storage unit, low cost and non-toxicity of materials, and minimum deterioration in performance or degradation of materials with repeated cycles [1–3].

Energy storage by adsorption is based on the principle that the adsorption of a gas by a solid is a spontaneous process in which the system entropy decreases due to the loss of freedom of molecules in the adsorbed phase.

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Adsorption is therefore accompanied by the release of heat of adsorption while the reverse process, desorption, is endothermic. In general, the utilization of the desorption–adsorption cycle as a means of low temperature heat storage, employing water vapour as adsorbate, initially involves a phase of activation during which water is desorbed from the adsorbent through solar energy heating. To extract heat, moist ambient air is driven through the hot adsorbent bed, which initially provides sensible heat. When the bed has cooled sufficiently, adsorption of the water vapour from the air stream releases the heat of adsorption; the result is a warm relatively dry, air supply. The sensible heat content of the bed depends essentially on the cycling temperature and normally represents only a small part of the total heat storage. Even if it is not used, the energy density compares favourably with phase change systems since heats of adsorption are of the same order of latent heats. The adsorbent bed may therefore be cooled to room temperature, without great loss in efficiency, to store energy indefinitely, provided water vapour is excluded. This gives a decided advantage over the other storage materials which require efficient thermal insulation.

Among adsorbent materials great attention is currently being paid to zeolites [4–7]. These products are framework silicates, characterized by crystalline structures with cavities and channels normally filled with water which can be reversibly and continuously removed by heating. Besides such a fundamental property, common to the other adsorbents, zeolites present the unique, and important, advantage of adsorbing water vapour, after activation, almost independently of environmental pressure. Other adsorbent materials present practically a direct proportionality between amounts of water adsorbed and water vapour pressure (relative humidity). Zeolites, however, rapidly reach saturation levels at pressures lower than the normal environmental humidity, after which the amounts of water adsorbed remain almost constant with the variation of the relative humidity, as can be seen from their water adsorption isotherms.

Between natural and synthetic zeolites, at least, the former appear at present to be the most promising for massive utilization in solar energy storage, because of their low cost. In this regard it must be emphasized that Italy, particularly the Central and Southern parts, possesses enormous, and easily mineable, deposits of natural zeolites such as chabazite and phillipsite [8]. The aim of this research is therefore to study the dehydration process of Italian natural zeolites, in view of their potential utilization in solar energy plants.

EXPERIMENTAL

Among Italian natural zeolites, locally called zeolitic tuffs, chabazite was chosen over phillipsite because of its higher water content and its faster water adsorption–desorption kinetics due to its more open structure [7].

The sample of chabazitic tuff under investigation came from Mercogliano (in the vicinity of Avellino) and contained about 65% chabazite; the remainder comprised sanidine, biotite, pyroxene and plagioclase, as well as unaltered vitreous material, pumices and slags. Its chemical composition, after oven-drying at 105 °C and successive equilibration over saturated $Ca(NO_3)_2$ solution at 20 °C for one week, was the following: SiO_2, 50.62; Al_2O_3, 16.05; Fe_2O_3, 3.75; FeO, 0.35; TiO_2, 0.46; MnO, 0.11; P_2O_5, 0.15; CaO, 4.29; MgO, 1.33; Na_2O, 2.55; K_2O, 7.02; H_2O, 13.60%. In order to achieve an enrichment of the zeolitic fraction of the tuff, the rock was ground for short periods, according to previously reported procedures [9], recovering only the finer powdered part by passing it through a 256 mesh sieve. This tuff fraction, richer in zeolite due to the greater friability of the zeolitic matrix [9], containing about 80% chabazite and showing a total water loss of 16.7%, was utilized for the dehydration experiments.

Isothermal water loss was measured via thermogravimetry (TG), using a Netzsch STA thermobalance (Model 429). Measurements were normally performed on the basis of 0.2-g samples, under constant nitrogen flow (flow rate, 150 ml min^{-1} at room temperature and pressure) with heating rates ranging from 1 to 100 °C min^{-1}. Such a high heating rate was employed in the preliminary part in order to rapidly reach the programmed temperature (a few min) and have a more correct indication of the desorption time of the sample at that temperature. It must be emphasized, on the other hand, that high heating rates are purely indicative and do not coincide with the actual heating rate of the sample.

To evaluate the influence of the cationic form of the zeolite on the amount of water desorbed, the chabazitic tuff was exchanged for K^+, Na^+ and Ca^{2+}. To this end, 5-g samples were added in Teflon containers to 100 ml of 1 M solution of each selected chloride. These containers were then rotated at 80 °C in an air thermostated oven and the solution was replaced several times every few hours. At the end of the treatment the exchanged tuff samples were recovered, washed, dried at 105 °C overnight and stored as specified above.

RESULTS AND DISCUSSION

Figure 1 reports the isothermal water loss of chabazitic tuff, in its original cationic form, as a function of the dehydration temperature. Data refer to measurements performed with a heating rate of 100 °C min^{-1} and show that advanced dehydration, near to the total water content, may be achieved at temperatures not higher than 250 °C, which are easily obtainable with solar concentrators.

Figure 2 and Table 1 summarize the results of water desorption experiments on cation exchanged tuff samples. Figure 2, in particular, reports, as

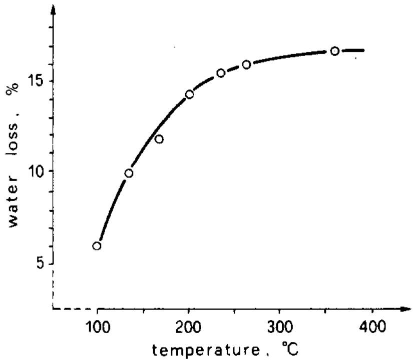

Fig. 1. Isothermal water loss for chabazitic tuff as a function of temperature. Heating rate, 100 °C min^{-1}.

Fig. 1, the trend of the isothermal water losses vs. temperature, with a heating rate of 100 °C min^{-1}, for the various exchanged forms; the superimposed dashed curve refers to the unexchanged sample (Fig. 1), reported here for comparison. In Table 1 the ultimate values of water adsorption are shown for cation exchanged and unexchanged samples of chabazitic tuff. It is evident that the cation exchange is not advantageous, since only in a few cases is the water amount desorbed, and therefore the storable energy, either at a given temperature or as final value, higher for the exchanged form than for the original sample. Even when this happens, the difference between the two values is too small in order for the exchange treatment to be used conveniently. Therefore, unless the use of a cation exchanged form presents advantages from a kinetic point of view, the original cationic form appears preferable.

Figure 3 refers to experiments performed to give a kinetic evaluation of the water desorption from the tuff. Since, at each temperature, water loss in the last desorption stages is very slow, the normal duration of a complete

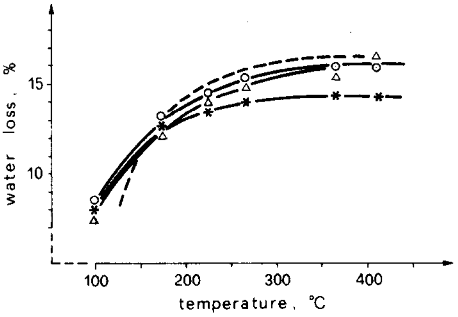

Fig. 2. Isothermal water loss as a function of temperature for Na (○), K (*) and Ca (△) exchanged forms of chabazitic tuff. The curve of Fig. 1 is reported for comparison (— — —). Heating rate, 100 °C min^{-1}.

TABLE 1

Water desorbed by exchanged forms of chabazitic tuff

Cation	Water desorbed (%)
no exchange	16.7
Na^+	16.2
K^+	14.2
Ca^{2+}	17.1

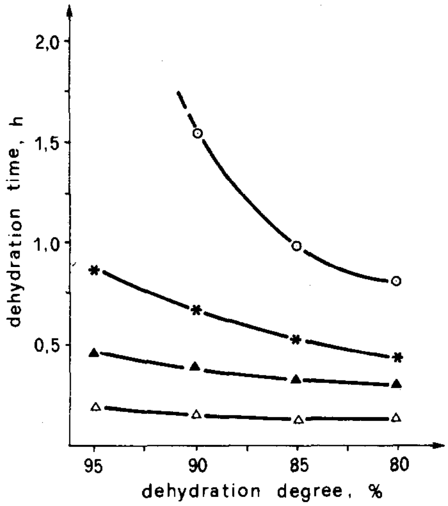

Fig. 3. Dehydration times of chabazitic tuff as a function of dehydration degree at 110 (○), 190 (*), 238 (▲) and 380 °C (△); total amounts of desorbed water are deducible from Fig. 1. Heating rate, 100 °C min^{-1}.

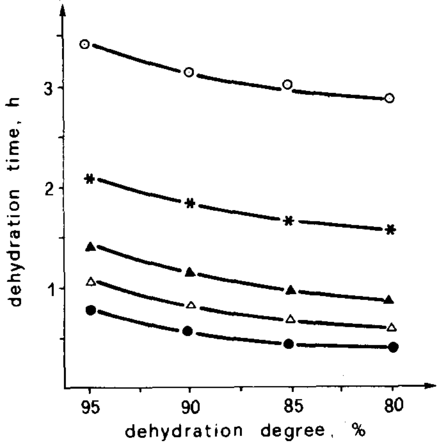

Fig. 4. Dehydration times of chabazitic tuff at 200 °C (total water loss, 14.6%), as a function of dehydration degree for the following heating rates: 1 (○), 2 (*), 5 (▲), 10 (△) and 100 °C min^{-1} (●).

experiment is rather long and poorly reproducible. It is, therefore, more convenient, on the basis of the total water content deducible from the curve of Fig. 1, to establish from the thermograms the time necessary to obtain a programmed partial dehydration. In Fig. 3, therefore, is reported the dehydration time of chabazitic tuff as a function of the dehydration degree for various temperatures. The heating rate is again 100 °C min^{-1}. It is evident that renouncing to desorb the "final" water from the tuff, the net dehydration time can become very short, of the order of less than 0.5 h, for temperatures higher than 200 °C. The actual dehydration times in real conditions depend, of course, not only on the final temperature, but also on the heating rate, which is variable throughout the course of the desorption. Nevertheless, a likely evaluation of such times can be made from the data of Fig. 4 which show the dehydration times at 200 °C as a function of the dehydration degree for various heating rates; the total amount of water desorbed from the chabazitic tuff at this temperature is 14.6%. It can be seen that, even considering low values of heating rates, an almost complete dehydration can be achieved in dehydration times of the order of $\leqslant 2$ h.

On the grounds of these results and the literature data, the amount of heat storable through the desorption process of chabazitic tuff can be evaluated with a fairly good approximation. The so-called isosteric heat of adsorption, q_{st}, can be initially calculated from a set of water vapour adsorption isotherms at various temperatures, both experimental or calculated as described elsewhere [7]. This parameter is a function of temperature and coverage (θ), i.e., the filling coefficient of the adsorbent, and is a differential quantity deducible, for every couple of the above isotherms, from the values, at constant coverage, of the equilibrium water vapour pressures in the presence of the adsorbent [7].

Some values of the isosteric heat of adsorption of water on chabazitic tuff, calculated accordingly, are reported in Table 2; q_{st} clearly depends much more on the coverage than on the temperature, suggesting that a zeolite is

TABLE 2

Isosteric heat of adsorption of water on chabazitic tuff

T (°C)	q_{st} (kcal mol^{-1} H_2O)			
	$\theta = 0.2$	0.4	0.6	0.8
80	16.87	15.36	14.12	12.60
100	16.80	15.29	14.05	12.53
120	16.73	15.22	13.98	12.47
140	16.68	15.17	13.93	12.42
160	16.63	15.12	13.88	12.36
180	16.58	15.08	13.83	12.31
200	16.54	15.05	13.79	12.27
220	16.50	15.02	13.75	12.24
240	16.47	15.00	13.72	12.20

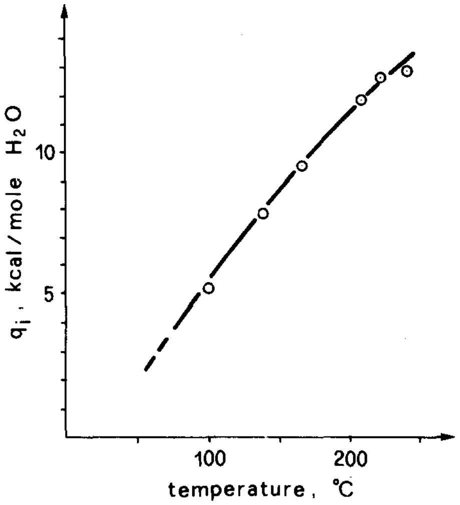

Fig. 5. Integral isothermal adsorption heats of water on chabazitic tuff as a function of the dehydration temperature.

more suitable for solar energy storage the higher its desorbable water content and the lower the dehydration temperature.

These q_{st} values allow, on the other hand, the evaluation, even with a certain approximation, of the total heat involved in the adsorption process. By plotting q_{st} against θ at a given temperature it is, in fact, possible to calculate through graphical integration, the isothermal integral heat of adsorption (q_i) which is, due to the very limited variation of q_{st} with temperature, quite near to the real heat of adsorption [7]. Assuming the values of isothermal water loss of chabazitic tuff previously reported (Fig. 1) to be quite close to the equilibrium coverages, q_i values for various dehydration temperatures have been calculated and appear in Fig. 5. The value of the total isothermal adsorption heat (q_t) obviously depends on the zeolite content of the tuff and can be easily obtained by multiplying q_i values by the

TABLE 3

Total isothermal adsorption heats for chabazitic tuff

T(°C)	q_t, kcal kg^{-1} tuff
80	36
100	49
120	61
140	73
160	85
180	97
200	109
220	116
240	121

number of moles of water contained in 1 kg of tuff. Some q_t values, in the range of interest of solar energy storage, are reported in Table 3.

CONCLUSIONS

The above reported results allow the confirmation of the promising perspectives of utilization of Italian natural zeolites in the storage of solar energy. Energy densities of chabazitic tuff systems are actually much higher than in systems based on sensible heat, and comparable with storage systems using latent heat. Zeolites also offer, apart from these methods, the advantage of the absence of corrosion problems and the possibility of long term storage without massive insulation.

A great deal of research, however, has still to be done in order to define the technical behaviour of zeolites in solar energy plants. Among others, the main problems are the choice of the most advantageous grain size of the tuff (compacted powder, tuff grains, tuff pellets, etc.), the thermal conductivity of the material, and the optimization of the techniques for extracting heat from the activated tuff beds.

Referring, finally, to the possible applications of zeolite-based storage systems, due to the low humidity levels of the warm air flow exiting from the activated zeolite beds during the phase of heat extraction, the most interesting perspectives appear at present in the field of industrial or agricultural drying processes.

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