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SOLAR ENERGY STORAGE BY NATURAL ZEOLITES. V. OPTIMIZATION OF THE THERMAL ACTIVATION PROCESS OF CHABAZITE TUFF.

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ABSTRACT

A research has been carried out, aiming to optimize the thermal activation of chabazite tuff. The thermogravimetric examination of the dehydration process has been carried out, as a function of several parameters, including tuff grain size (6-250 mesh), activation temperature (100-375 °C), heating rate (1-100 °C/min), obtaining indications on the best conditions of use. The ability of chabazite tuff to store thermal energy has been confirmed, pointing out that effective activations in static conditions are possible in few (1-4) hours at temperatures no higher than 200 °C.

INTRODUCTION

Several papers [1-7] have been published in the last few years on the possible use of chabazite tuff or self-bonded chabazite pellets for the storage of thermal energy, coming from the sun or from discontinuously running sources (e.g. industrial furnaces). It has been emphasized that the best performances in the process of heat captivation (storable heat is of the order of 100 Kcal/Kg tuff) are achieved by activation of tuff beds passed through by hot air streams and the best way for exploiting the stored energy is to produce in due time streams of warm and dry air, to be used for instance in drying of agricultural products. Thermal efficiency (up to about 0.30) of the dehydration/rehydration process depends on the zeolite content of the tuff but not significantly on its grain size distribution.

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In view to transfer the results of laboratory experiments to the plan of a pilot plant, this paper aims to complete the preliminary investigation, going deeper into the study of the thermal activation process of chabazite tuff.

EXPERIMENTAL

The sample of chabazite tuff comes from the quarry of San Mango sul Calore (AV). Its mineralogical and technical features have been reported elsewhere [8]. The material has been carefully ground and sieved, obtaining five grain size fractions (see Fig. 1). These have been washed by distilled water, dried and then treated for two hours at 350 °C, in order to remove definitively the non zeolitic water [9]. Water loss has been evaluated on 2 g samples by thermogravimetry, using a Netzsch STA mod. 449 thermobalance. Analyses have been carried out in dry air flow (15 ml/min), as a function of activation temperature (100-375 °C) and heating rate (1-100 °C/min).

Attrition tests have been performed on 2 g samples of each grain size fraction, utilizing a shaked bed operated by an air current (at constant air flow to average grain size ratio equal to 318.5 l $(mm\ h)^{-1}$) and allowing the fine powder generated by attrition to leave the top of the bed.

RESULTS AND DISCUSSION

Figure 1 reports the isothermal water loss of the various grain size fractions examined. It is to be noticed that all the samples lose at 375 °C more than 95% of the total water contents (data at 900 °C), while at least 80% water vapour is released at 200 °C. By the way, if these water amounts are considered completely of zeolitic origin, the data of Fig. 1 give also an indication of zeolite content of S. Mango chabazite, 20.88% [8], a rough evaluation of chabazite amount in the tuff grains gives values ranging between 60 and 66%. The kinetic trend of the isothermal water desorption is shown in Fig. 2 for the coarsest and finest grain size fractions. The curves a-c refer to partial dehydration degrees, from 85 (a), through 90 (b), to 95% (c). Activation kinetics appears practically independent of grain size distribution, which is an indication of the scaut resistance of

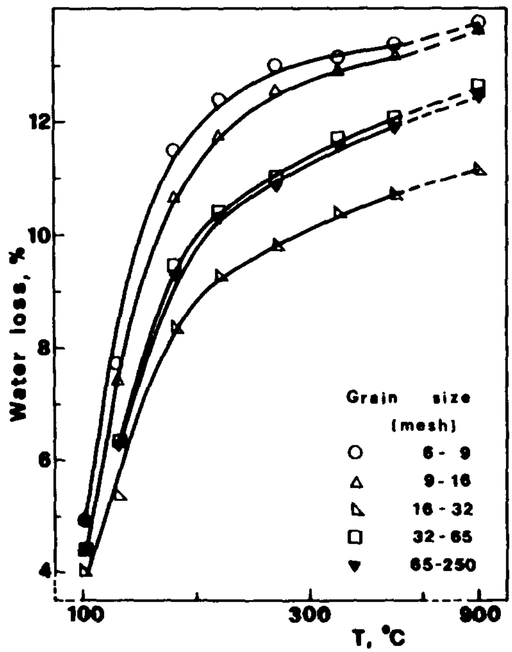

Fig. 1. Isothermal water loss of grain size fractions of chabazite tuff, as a function of the temperature at a heating rate of 100 °C/min.

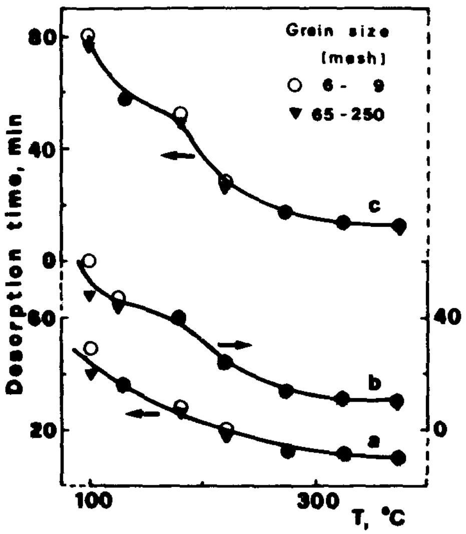

Fig. 2. Length of partial isothermal dehydration of chabazite tuff grains, as a function of the temperature, at a heating rate of 100°C/min Dehydration degree: a= 85%; b= 90%; c= 95%.

the material to intercrystalline compared to intracrystalline diffusion. The curves in Fig. 2 present a hump above 200 °C, which disappears at lower dehydration degrees (about 80%). This is evidently due to the presence in the zeolite framework of at least two different types of water sites with different values of bond energy, as it is also deducible from S. Mango chabazite DTA trace (Fig. 3). The temperature of 200 °C appears therefore the most suitable for activation in static conditions: it does not allow complete dehydration but involves high desorption kinetics. Figure 4 shows the time necessary for obtaining

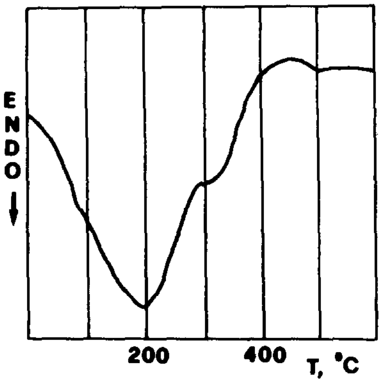

Fig. 3. DTA trace of San Mango sul Calore chabazite tuff. Weight of the sample: 0.200 g; heating rate: 10 °C/min; atmosphere: air

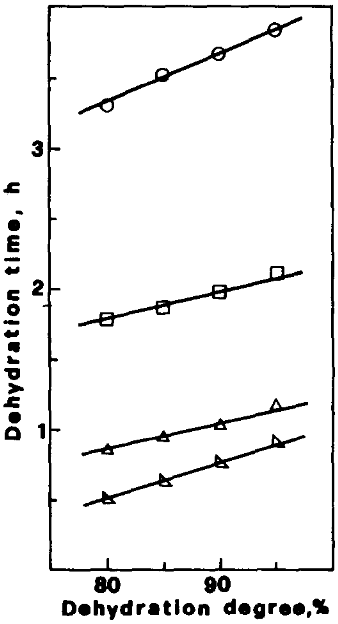

Fig. 4. Length of chabazite tuff grains dehydration at 200 °C as a function of dehydratation degree and heating rate (○ = 1 °C/min; □ = 2 °C/min; △ = 5 °C/min; ◺ = 10 °C/min).

dehydration degrees ranging between 80 and 95% at 200 °C as a function of heating rate. The values reported are the average of those obtained for the various grain size fractions. It may be seen that the first three points are on a straight line, the fourth one, referring at least in part to more strongly bound water, shifts from linearity. Anyway the dehydration is near completion in a few hours, between one and four, for heating rates ranging between 10 and 1 °C/min. It is to be noted that dehydration in dynamic conditions (tuff bed activation by hot and dry air streams) may be also more rapid [5].

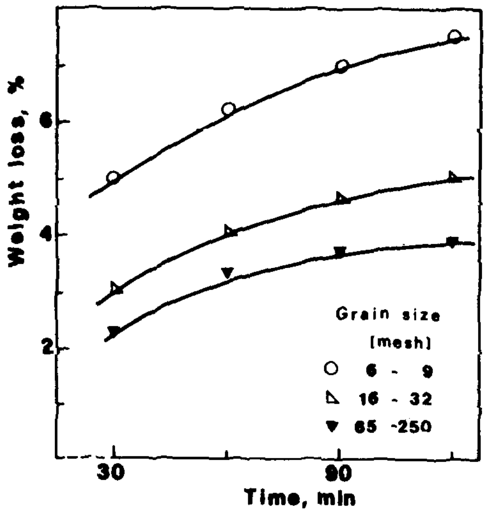

Fig. 5. Attrition tests: weight loss of grain size fractions of chabazite tuff, as a function of test length.

Figure 5 reports the data of attrition test, aiming to evaluate the friability of the various grain size fractions. The coarsest ones are more subject to erosion, but the material keeps unchanged its zeolite content (water content of the various fractions after the test shifts not more than 1% from the original value).

CONCLUSIONS

The results reported allow to draw the following conclusions:

- chabazite tuff confirms its versatility in storing thermal energy in a wide range of temperatures;
- effective activation in static conditions is possible in few (1-4) hours at 200 ^{o}C;
- still more rapid dehydrations are possible in dynamic conditions, provided an air stream is allowed to pass through the zeolite grains;
- tuff grain size does not affect greatly the velocity of the thermal energy storage;
- the erosion of the grains by friction does not reduce significantly their zeolite content.

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