

## THE RATES OF SOLAR ENERGY STORAGE AND RETRIEVAL IN A ZEOLITE-WATER SYSTEM

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**Abstract**—The salient features that determine the possible use of a water vapour-zeolite 13X system as a method of energy storage were investigated. Cycling studies over two months revealed no decrease in water capacity nor any structural deterioration. The rate at which water could be desorbed in a static situation was determined at various temperatures from 110 to 250°C. The adsorption isotherm and the heats of adsorption as a function of amount of adsorbed water were determined. The saturation capacity was 0.33 g H<sub>2</sub>O/g zeolite while the heat of adsorption declined from 90 to 50 kJ mol<sup>-1</sup>. The rate of heat development was found to be very high so that heat extraction from the store would not be a problem in any practical utilization of this system.

### INTRODUCTION

An earlier study[1] demonstrated the feasibility of a water vapour-zeolite adsorption system as a means of energy storage. The desirable characteristics of this system which lead to a high energy density are the high adsorptive capacity of zeolites for water vapour and the large heat of adsorption which is released in the adsorption process. The method of effecting energy storage and retrieval is simple in concept and involves a drying and wetting cycle analogous to a charging-discharging cycle of a battery. In the charging mode hot air is driven through a bed of zeolite particles of suitable size causing any adsorbed water to be expelled. This requires temperatures in the range 100–200°C depending on the degree of zeolite dryness required. In the discharge mode moist ambient air is driven through the bed, water vapour is adsorbed and the heat of adsorption is released. The bed temperature increases and the result is warm relatively dry air suitable for space heating.

While this method was initially viewed as a means of storing solar energy it is obvious that any source of waste heat or cheap off peak electrical power could be used to dry the zeolite.

The superior energy density of this system in comparison to phase change and sensible heat methods was based upon the published equilibrium properties of water vapour adsorption on various zeolites. In this communication we wish to report on those factors which would directly affect its practical feasibility. First, any system undergoing repeated cycling may show a deterioration in efficiency. To determine whether this applies to zeolites we have carried out wetting drying cycles over a two month period to monitor any loss in adsorptive capacity. Second we have determined the adsorptive capacity under ideal conditions and the heat of adsorption as a function of the amount of adsorbed water.

Third, we have determined the rate of adsorption and the concomitant release of heat. Any practical realization of zeolites as an energy storage medium is critically dependent on whether the stored energy can be released at rates consistent with demand.

### EXPERIMENTAL

#### *Cycling studies and dehydration rates*

Small zeolite samples ( $\approx 10$  g) were placed in 100 ml beakers and oven dried at 300°C for 24 hr to obtain the dry weight. After saturating the zeolite with water vapour they were placed in ovens at 110, 150, 200 and 250°C for 24 hr. The beakers were then placed in shallow pans containing water, covered with aluminum foil and allowed to adsorb water vapour for 24 hr. The heating and adsorption cycle were then repeated. Commercially available Linde zeolites 4A, 5A and 13X in both bead (1/16" dia.) and powder forms were used.

Concurrent with cycling studies, dehydration rates were determined on bead zeolites saturated with water in order to obtain information on the rate at which the system can be charged. After saturation, zeolite samples were placed in ovens and weighed every hour.

#### *Adsorption properties and rate of heat development*

A schematic of the adsorption vacuum line and the calorimeter-adsorption cell is shown in Fig. 1. Prior to its installation on the vacuum line the cell was weighed, filled with 13X beads, heated to 300°C for 24 hr and reweighed to find the dry weight of zeolite. Because of the large water capacity of zeolites, a large gas volume was required for gas delivery to the adsorbent. A 21. and 51. bulb were used. The exact volumes were calibrated with water while pertinent line volumes were calibrated using helium and standard gas burette techniques. The ultimate pressure was less than  $1 \times 10^{-6}$  torr. Low pressures are required in the vacuum jacket around the cell to minimize any heat conduction losses during calorimetric measurements. During the adsorption process the

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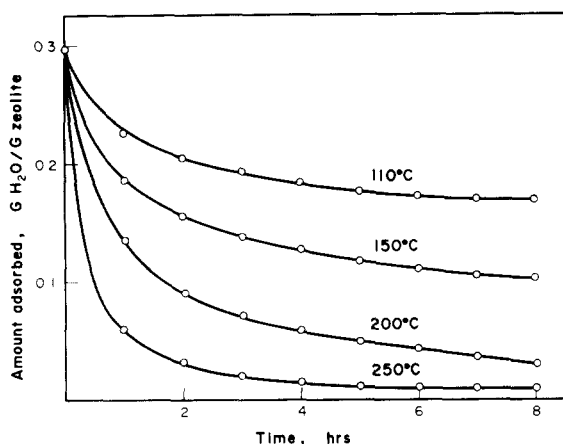


Fig. 3. Dehydration rates at various temperatures.

ment thereafter. While temperatures in excess of 200°C are required to reduce water content to <2 per cent these results indicate that it may be more economical to use lower temperatures in the range 110–150°C to dry the zeolite. While this would reduce the energy density to 43 and 66 per cent of the maximum the less stringent temperature requirement would make the system more practicable. Dehydration tests in the dynamic case where drying is effected by a hot air flow have shown that the rate of water loss and the final amount desorbed is significantly greater than in the static case. An air stream at 110°C dries the zeolite to a water content of 13 per cent in 4 hr. The energy density would then be 57 per cent of the maximum.

#### Adsorption isotherms, heat of adsorption and rate of heat development

The room temperature adsorption isotherm shown in Fig. 4 is an approximate step function with a maximum

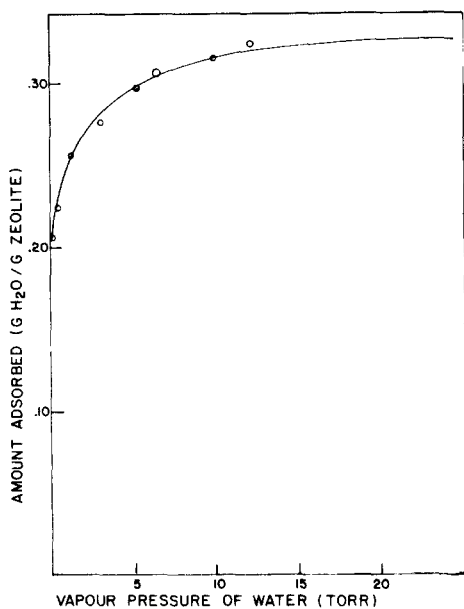


Fig. 4. Adsorption isotherm at 25°C.

capacity of 33 per cent water by weight. The most notable feature of the isotherm is that almost 75 per cent of the maximum capacity is reached at equilibrium pressures of less than 1 torr (at 25°C the vapour pressure of water is 23.8 torr indicating that most of the water is adsorbed rapidly. It is just this characteristic which distinguishes zeolites as a superior adsorbent for energy storage. Others such as silica gel may have a higher capacity but their isotherms only show a gradual increase with equilibrium pressure.

The variation of the heat of adsorption with the amount adsorbed is seen in Fig. 5. The value decreases gradually from 88 to 66 kJ mole of adsorbed water over the range 0–25 per cent water content. Beyond this range heat values were difficult to obtain because of the slower rate of adsorption and the intrinsic cell heat loss but it is likely that it decreases to approx. 50 kJ at saturation [2].

The main concern of this research is the speed with which water is adsorbed and the rate at which heat is developed. Figure 6 gives the decrease in pressure with time when 7.45 l. of water vapour at 23°C and 22 torr (0.00887 moles of water) is exposed to 7.35 g of zeolite with various amounts of pre-adsorbed water. Up to a water content of 21 per cent the rate of adsorption is extremely rapid with the pressure dropping to less than 2 torr in 2 min. As the pre-adsorbed amount approaches the saturation value the rate then declines gradually.

The rate of heat developed is consistent with the rapid adsorption. Figure 7 gives the initial rate of heat produced per gram of zeolite as a function of the pre-adsorbed water content. These values corresponding specifically to the case when 7.35 g of zeolite are exposed to a fixed water dosage of 0.0089 moles should be viewed in the context of the total heat stored per gram of dry zeolite calculated previously [1] to be 1.3 kJ. As the results indicate, heat is developed initially at the rate of 0.07 kJ min<sup>-1</sup> g<sup>-1</sup> (i.e. 5.5 per cent of the total stored energy is released in the first minute) when the zeolite is completely dry. As the water content increases the rate is reduced to 0.01 kJ min<sup>-1</sup> g<sup>-1</sup> near saturation but by this

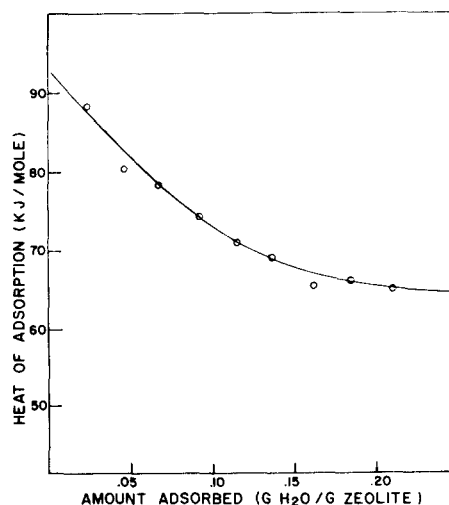


Fig. 5. Heat of adsorption as a function of amount of adsorbed water vapour.

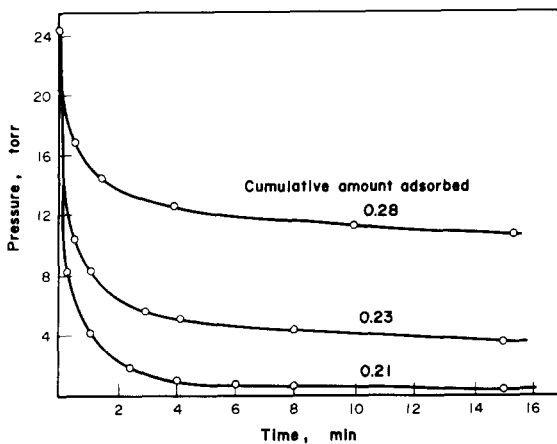


Fig. 6. Pressure decrease as a function of time for various amounts adsorbed.

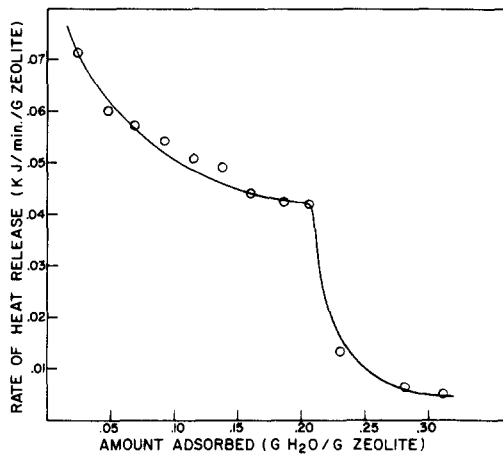


Fig. 7. Rate of heat development as a function of amount adsorbed.

time about 90 per cent of the stored energy has already been retrieved. Perhaps a better indication of the rapidity of heat retrieval is the percentage of the total available heat per adsorption dose released within 5 min as a function of water content. Up to a water content of 0.2 g water/g zeolite this is almost 100 per cent while near saturation only 20 per cent is recovered in 5 min. Despite the decline, however, the rate is sufficient to raise the zeolite temperature by 10–15°C which is still suitable for heating purposes.

It is evident from the preceding data that under the conditions of the experiment virtually all of the stored energy may be developed at rates which are sufficient for utilization. Calculations based on the mid adsorption range indicate that 1000 kg zeolite could generate approximately 50,000 kJ ( $\approx$  50,000 BTU) in one minute a rate which is far in excess of heating requirements. These figures would obviously be strongly modified in any actual working storage where vacuum conditions may not be utilized and heat losses may be substantial. Nevertheless it would appear that the rate of heat retrieval is not the area where problems associated with a working system are expected. At the present time a prototype zeolite storage system is under investigation to determine the parameters that will maximize the storage efficiency.

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#### REFERENCES

1. R. Gopal, B. Hollebone, C. H. Langford and R. Shigeishi, Solar energy storage using chemical potential changes associated with drying of zeolites. *Solar Energy* **23**, 489 (1979).
2. V. K. Chuikina, A. V. Kiselev, L. V. Mineyeva and C. G. Muttik, Heats of adsorption of water vapour on  $N_aX$  and  $KN_aX$  zeolites at different temperatures. *J. C. S. Faraday I*, **72**, 1345 (1976).
3. D. W. Breck, *Zeolite Molecular Sieves*, p. 442. Wiley, London (1974).