

# SOLAR ENERGY APPLICATION OF NATURAL ZEOLITES\*

D. I. TCHERNEV

*Lincoln Laboratory, Massachusetts Institute of Technology,  
Lexington, Massachusetts 02173, U.S.A.*

**Abstract** – The utilization of solar energy for cooling is usually achieved by means of sorption-refrigeration cycles. However, the conventional cycles using ammonia-water or lithium bromide-water solutions are inefficient because of the low solution temperatures obtainable with solar radiation and the high condenser temperatures required by air-cooled condensers. Zeolites provide a unique opportunity for a solid-gas adsorption cooling system because of their extremely nonlinear adsorption isotherms. We have demonstrated the feasibility of using a zeolite system to provide domestic hot water and space heating with overall efficiencies above 75% and space cooling with an overall efficiency above 50%. The system uses natural chabazite or clinoptilolite as the solid adsorber and water vapor as the working fluid. The operation of the system is described and the experimental results are discussed. Preliminary estimates indicate that such a system will be economically competitive.

## INTRODUCTION

There are many different ways to obtain cooling from solar energy. For example, one can utilize photovoltaic solar cells to convert the solar energy to electricity and then use conventional refrigerators. Such a system, in addition to being expensive, will have a small overall efficiency of less than 15%. Another method is to convert the energy from the sun into mechanical form by means of one of the numerous cycles available and then to use the mechanical energy to drive the compressor in refrigeration equipment. However, the Carnot efficiency of all such cycles is low because of the low temperatures obtainable from the sun without extensive concentration and complicated sun-following techniques.

The simplest and potentially most efficient method therefore utilizes the well-known sorption-refrigeration cycle. Faraday was the first to discover that some gases, like ammonia, are sorbed by solids or liquids at low temperature and desorbed at high temperature. Numerous solid-gas sorption-refrigeration systems utilizing alkali-metal chlorides and ammonia gas have

been constructed, mostly in the 1920s and 1930s in Europe. In the United States the majority of systems have utilized instead the variation with temperature of the solubility of a gas in a liquid, initially ammonia in water and later water vapor in lithium bromide. Many of the solid-gas and liquid-gas systems have recently been revived for the purpose of using solar energy for cooling.

In sorption-refrigeration cycles the liquid or solid sorbent is heated and desorbs the working gas. The partial pressure of the gas thereby increases, and it can be liquefied in a condenser, rejecting heat to the outside. The liquefied gas is evaporated at lower temperature and partial pressure, while absorbing heat from the volume to be cooled. After the depleted sorbent is cooled down, it resorbs the evaporated gas at lower partial pressures. Thus, in each complete cycle heat is withdrawn by the evaporator from the refrigerated volume and rejected by the condenser to the outside world. Solid sorbents have to be cycled in time while liquid sorbents can be pumped through a heater and cooler, thereby providing a continuous cooling process.

Such sorption systems are used extensively for commercial air conditioning and refrigeration whenever an inexpensive supply of heat (usually steam) is available. They can achieve an overall efficiency (also called coefficient of performance) of 70–80% if the source of heat is at about 250–300°F and the condenser is water-cooled to below 85°F. Solar collectors, however, usually provide hot water at temperatures of less than 190°F. Furthermore, an air-cooled condenser is necessary for residential applications, and such a condenser can reach 120°F on days when the air temperature is 100°F. Under such conditions the efficiency of conventional sorption systems drops to below 30%. Since solar collectors are only 50% efficient at such operating temperatures, the overall efficiencies would be on the order of 10 to 15%.

\* This work was supported by NSF-RANN.

### OPERATING PRINCIPLE OF THE ZEOLITE SYSTEM

Zeolites provide a unique solution to the above problems of solar cooling because of their unusual sorption properties. Zeolites are capable of adsorbing large quantities of a variety of refrigerant gases, ranging from water vapor and ammonia to carbon oxides and freons. Interestingly enough, for most of these gases the amount sorbed is about the same — 30 wt.%. Since the heat of vaporization of water is the largest of any common refrigerant and about 10 times larger than that of the freons, the zeolite-water vapor combination can provide the most efficient system and requires the smallest quantity of zeolite for its operation. Zeolites also have the unique property, which is of critical importance for solar applications, that their adsorption isotherms have an extremely *nonlinear* pressure dependence.

In contrast with zeolites, other sorbents have almost *linear* pressure isotherms. For example, Fig. 1 shows a family of adsorption isotherms for water vapor on silica gel; these are similar to those for most solid-gas and liquid-gas systems. It is seen that the quantity of adsorbed water vapor is a monotonic, almost linear function of partial pressure. For this reason in the refrigeration cycle, from sorption at low temperature and low partial pressure to desorption at high temperature and high partial pressure, there is only a small change in the amount of adsorbed gas. This accounts for the low efficiency of solar cooling with conventional sorbents. Actually, under the extremely unfavorable conditions of low desorption temperature

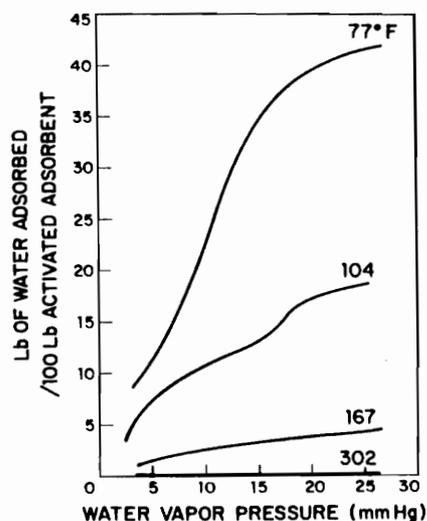


Fig. 1. Adsorption isotherms for water vapor on silica gel, showing quantity of water adsorbed as a function of the partial pressure of water vapor.

available from the sun and high condenser pressure for air-cooled condensers, the efficiency can even go to zero. This is also the case for the lithium bromide-water and ammonia-water systems.

The contrasting behavior of zeolites is shown in Fig. 2, which gives typical isotherms for the sorption of water vapor on a zeolite. The extreme nonlinearity of the amount adsorbed as a function of partial pressure is obvious. The isotherms saturate at low partial pressure, after which the amount adsorbed is almost independent of pressure. Therefore, when the zeolite is at ambient temperature it can adsorb large quantities of water vapor

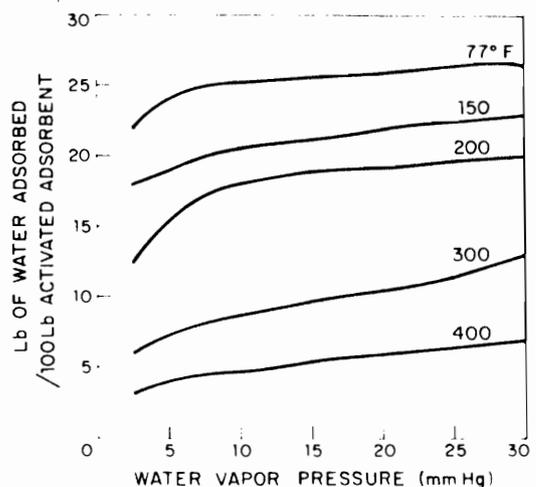


Fig. 2. Adsorption isotherms for water vapor on a zeolite.

even at low partial pressures. On the other hand, when the zeolite is heated it desorbs most of the water vapor even at high partial pressures, corresponding to high condenser temperature. Therefore, the difference in adsorbed gas between the high- and low-temperature states is large and depends only slightly on condenser pressure. This makes it possible to achieve high efficiencies under conditions typical of solar applications. Thus, the shape of the adsorption isotherms is critical for the superiority of the zeolite system over conventional sorption-refrigeration cycles.

To describe the situation in another way, one can compare the thermal activation of the different processes involved. The solubility of ammonia in water, the solubility of water vapor in lithium bromide, and the adsorption of water vapor on silica gel or activated alumina all depend exponentially on  $\Delta H/RT$ , where  $\Delta H$  is the heat of solution or adsorption and  $T$  is the absolute temperature (i.e. they obey the Arrhenius equation). Adsorption on zeolites, on the other hand, has been shown by Dubinin (1971) to depend

exponentially on at least the second, and as high as the fifth, power of  $\Delta H/RT$ . It is this extreme nonlinearity of thermal activation that makes zeolites so well suited for cooling.

Figure 3 illustrates the principle of operation of a zeolite solar-cooling system. The zeolite is sealed in an airtight container that is irradiated by the sun. During the day cycle, shown on the left side of Fig. 3, the zeolite and its container are heated to a maximum temperature of 250°F. At about 100°F water vapor starts desorbing from the zeolite, and its partial pressure begins to rise. When the pressure reaches the value determined by the condenser temperature, for example 1 psia for 100°F, the vapor begins to liquefy, heat is rejected to the outside, and the liquid water is stored in a storage tank. During the night cycle, on the right side of Fig. 3, the zeolite is cooled by convection cooling to ambient temperature and is ready to adsorb water vapor even at low partial pressures. Liquid water from the storage tank is introduced into the evaporator, where it absorbs heat from the space to be cooled and is converted into water vapor. If the partial pressure can be maintained at 0.1 psia, the water in the evaporator will boil at 35°F. The function of the zeolite is to adsorb the water vapor produced by the evaporator, maintaining the partial pressure below 0.1 psia and rejecting the heat of adsorption to the atmosphere. At the end of the night cycle the zeolite is loaded with all the water it will adsorb at 0.1 psia and is ready for the beginning of a new day cycle.

A zeolite system, like any refrigeration system, has to be free of air. Therefore the zeolite is placed in hermetically sealed metal panels. These panels, which are painted black for maximum solar absorption, are connected through ordinary plumbing to the condenser, water-storage tank, and evaporator. After the zeolite is

charged with water vapor, the whole system is outgassed, evacuated, and sealed off.

In the operation of the system in Fig. 3, cooling is produced during the night. Although this is quite satisfactory for many applications, such as the production of ice and the refrigeration of food, in the air conditioning of buildings the demand for cooling occurs mostly during the day. For this reason it is necessary to provide some type of storage, a feature typical of all solar systems.

One storage method is shown in Fig. 4. In this system cooling is produced during the day by operating the evaporator, and the water vapor is then held in a buffer storage until evening, when the zeolite is cool enough to be recharged. The buffer storage in principle could be just an empty tank with sufficient volume to keep the water partial pressure below 0.1 psia until the zeolite can begin adsorption. For a system of large cooling capacity,

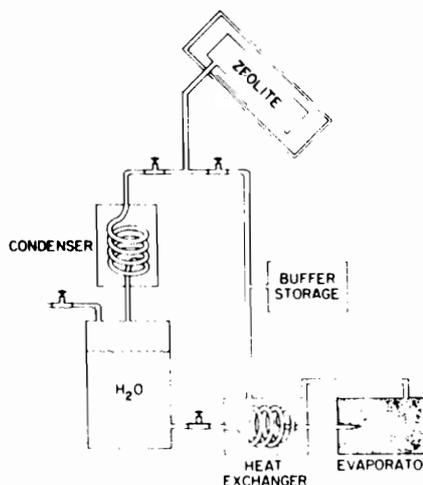


Fig. 4. Schematic diagram of zeolite system with buffer storage for water vapor.

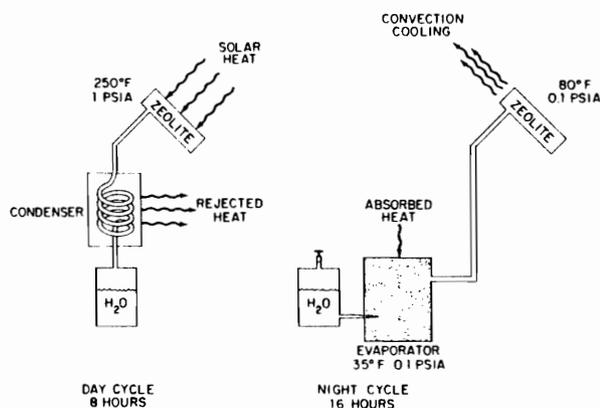


Fig. 3. Schematic diagram illustrating day and night cycles for zeolite-water system.

however, the size required for such an empty tank would be impractical. In order to reduce its size, the tank can be filled with a sorbent, such as silica gel, whose affinity for water vapor is less than the zeolite's. During the day, because of the temperature difference between the two sorbents, the water vapor is adsorbed by the silica gel, but at night, when the zeolite cools down, the vapor is transferred from the storage tank to the zeolite.

Another method for providing buffer storage is especially suitable for complete systems utilizing solar energy for both heating and cooling. One such system is shown in Fig. 5. Here the condenser and evaporator are combined into a single unit that is cooled by an external water loop. During the day water vapor desorbed from the solar-heated zeolite is condensed in this unit, and the

liquid water is stored below the condenser in the usual condensate storage tank until evening. The heat of condensation is rejected to the external water loop. This heat can be used for providing domestic hot water and during the winter season for space heating as well. During the heating season hot water is stored during the day to provide heat during the night, as in any conventional solar system. Whenever there is a demand for heat, hot water from the storage tank is circulated through a coil located in the air ducts of the forced air-system, and the heated air is distributed throughout the building. If too much heat is liberated in the condenser, as for example in the spring and summer, the excess can be rejected to the outside by an air-cooled coil.

During the night, water from the condensate storage tank is circulated back into the condenser-evaporator unit, where it evaporates from the same surfaces on which it originally condensed. The vapor is then adsorbed on the cool zeolite. Since evaporation takes place at night, the system does not require buffer storage for water vapor. The external water loop provides the necessary heat of vaporization, producing chilled water for use in air conditioning. The chilled water can be stored during the summer season in the same storage tank used for hot water during the heating season. The changeover from one season to the other is achieved by simple valving.

### EXPERIMENTAL RESULTS

In order to demonstrate the efficiency of zeolite systems for solar heating and cooling, we have constructed a number of 1- and 2-ft<sup>2</sup> test panels from various metals, including brass, copper, aluminium, and tin-plated steel. (We expect panels up to 16 ft<sup>2</sup> in area to be used in full-scale systems.) For condensation and evaporation pressures of 1 and 0.1 psia, respectively, for most zeolites the differential water loading is about 10% by weight between ambient temperature and 250°F, which is about the maximum temperature attainable with present flat-plate solar collectors. Since the average daily amount of incident solar energy is sufficient to cause the desorption of about 1 lb of water per square foot, the panels were designed to have a zeolite capacity of 10 lb/ft<sup>2</sup>, requiring a depth of 2½ inches. The upper surface of each panel is painted black, and a single pipe is provided at the side wall to permit the water vapor to enter and leave. Each panel was leak-tested prior to use.

Some initial tests were conducted with various synthetic zeolites, but the efficiencies obtained were quite low. The maximum theoretical efficiency for cooling with a zeolite is roughly equal to the heat of

vaporization of water – about 1000 BTU/lb – divided by the heat of adsorption of water on the zeolite. Since synthetic zeolites used for drying gases have heats of adsorption of about 1800 BTU/lb of water, their maximum theoretical efficiency is only about 55%. On the other hand, natural zeolites such as mordenite, with heats of adsorption of only 1200 BTU/lb of water, have maximum theoretical efficiencies of about 80%.

Most of our tests were performed with two natural zeolites obtained from Letcher and Associates of Lancaster, California: Zeosorb 3.5 A, a clinoptilolite from Horseshoe Dam, Arizona, and Zeosorb 5.0 A, a chabazite/erionite from Bowie, Arizona. Figure 6 shows

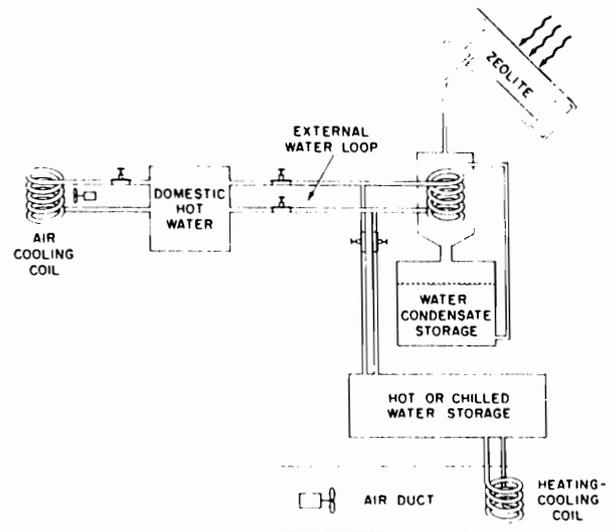


Fig. 5. Schematic diagram of zeolite combined heating/cooling system.

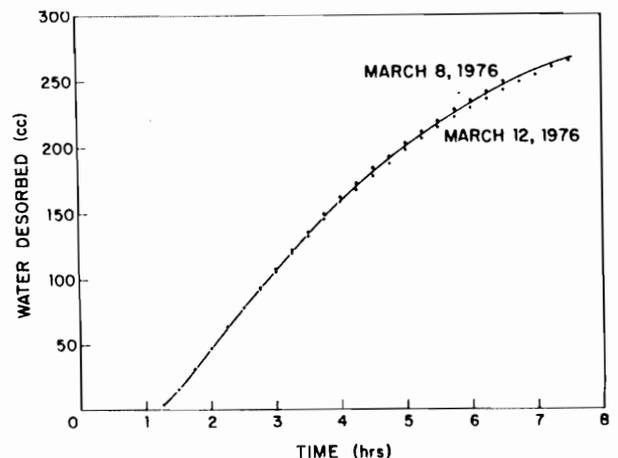


Fig. 6. Amount of water desorbed from panel containing 8 lb of zeolite for input power density of 1 kW/m<sup>2</sup>.

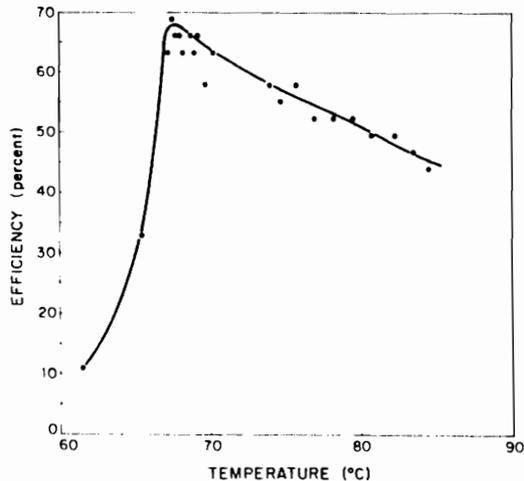


Fig. 7. Heating efficiency as a function of panel temperature for Zeosorb 5.0 A with input power density of  $1 \text{ kW/m}^2$ .

the weight of water desorbed (and condensed) from a  $1\text{-ft}^2$  aluminum panel containing about 8 lb of Zeosorb 5.0 A as a function of time for an initial zeolite temperature of  $70^\circ\text{F}$  ( $20^\circ\text{C}$ ), a condenser temperature of  $120^\circ\text{F}$  ( $50^\circ\text{C}$ ), and a simulated solar input of  $1 \text{ kW/m}^2$  (or  $320 \text{ BTU/ft}^2\text{-hr}$ ). The experimental points are from two runs made 4 days apart. It is seen that in  $7\frac{1}{2}$  hours over 8% by weight of water is desorbed and condensed.

Figure 7 shows the heating efficiency for Zeosorb 5.0 A as a function of panel temperature for a simulated solar input of  $1 \text{ kW/m}^2$  and a condenser temperature of  $140^\circ\text{F}$  ( $60^\circ\text{C}$ ). The measured engineering efficiency, defined as the ratio of the heat of condensation to the radiant energy incident on the panel, is 68% for a panel temperature of  $160^\circ\text{F}$ . In these experiments the zeolite is loaded with water at a vapor pressure of 15 psia, since the evaporator can be bypassed during the heating season by pumping liquid water from the condensate storage tank directly into the zeolite panels.

In the cooling experiments the zeolite is loaded at room temperature with water vapor at a partial pressure of 0.1 psia, corresponding to an evaporator temperature of  $35^\circ\text{F}$ . Figure 8 shows the efficiency of Zeosorb 5.0 A as a function of panel temperature for a simulated solar input of  $1 \text{ kW/m}^2$  and a condenser temperature of  $120^\circ\text{F}$  ( $50^\circ\text{C}$ ). The value of 44% obtained when the panel is heated to  $160^\circ\text{F}$  is two to three times larger than the efficiencies possible with present lithium bromide-water systems under the same conditions.

Outdoor tests of cooling and heating with solar energy were conducted in November and February on the roof of our laboratory in Boston. Figures 9 and 10 show the heating efficiencies obtained with Zeosorb 3.5 A and 5.0 A, respectively, as a function of panel temperature for a condenser temperature of  $140^\circ\text{F}$ . The

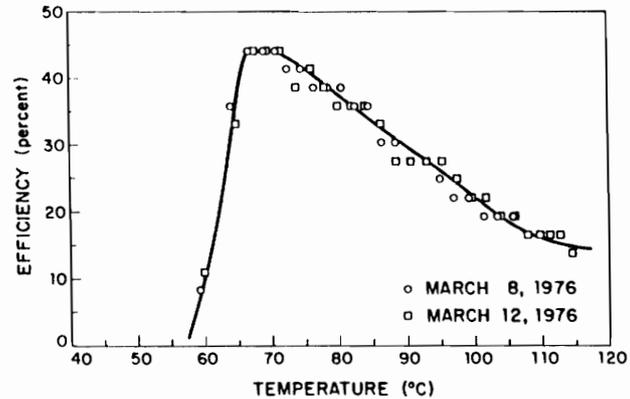


Fig. 8. Cooling efficiency for Zeosorb 5.0 A with input power density of  $1 \text{ kW/m}^2$ .

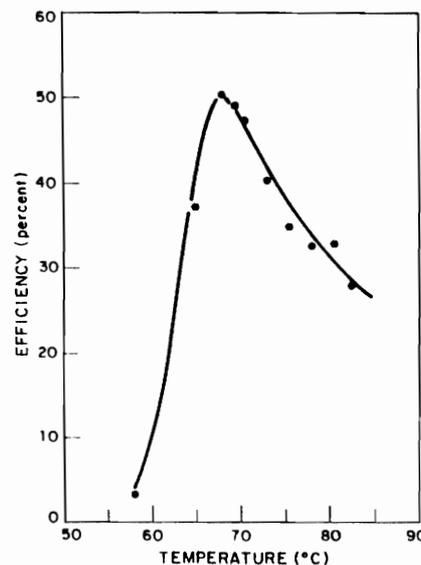


Fig. 9. Heating efficiency for Zeosorb 3.5 A heated by the sun.

overall heating efficiency of 70% obtained with Zeosorb 5.0 A in February, without selective absorbing coatings for the panels, is better than the values so far reported for conventional flat-plate collectors.

Finally, in Figs. 11 and 12 the cooling efficiencies obtained with solar energy are plotted as a function of panel temperature for Zeosorb 3.5 A and 5.0 A, respectively, for a condenser temperature of  $120^\circ\text{F}$ . Again the chabazite-rich 5.0 A shows superior performance, achieving an overall engineering efficiency of 42%, including all losses. Even higher efficiencies would be obtained for lower condenser temperatures.

For tests on a larger scale, a 1-square-yard system has been constructed from nine panels of  $1 \text{ ft}^2$  each. The system is insulated with 2-inch polyurethane foam and

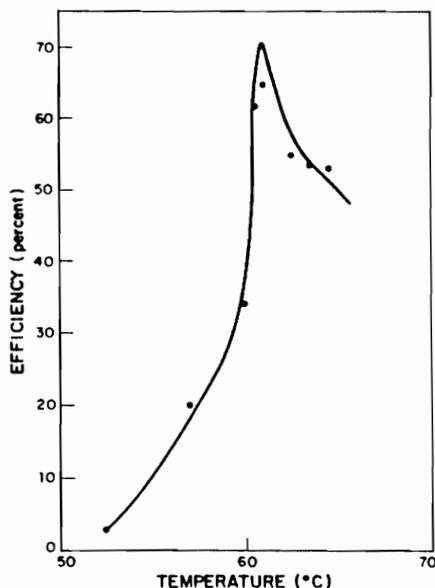


Fig. 10. Heating efficiency for Zeosorb 5.0 A heated by the sun.

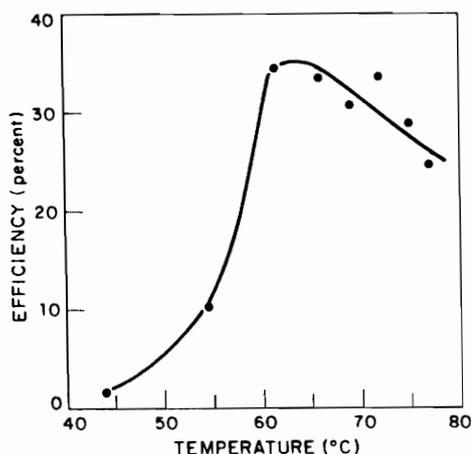


Fig. 11. Cooling efficiency for Zeosorb 3.5 A heated by the sun.

has double-layer glazing. A view of the partially assembled system is shown on Fig. 13. With a solar input of 20,000 BTU/day it produces 9000 BTU/day cooling. The only moving part is the fan used to blow the cold air out of the evaporator. The system has been operated for one summer season without any difficulties, and we expect operating lifetimes of over 20 years for full-scale systems.

### CONCLUSIONS

We have demonstrated that natural zeolites can be used successfully for solar heating and cooling. The

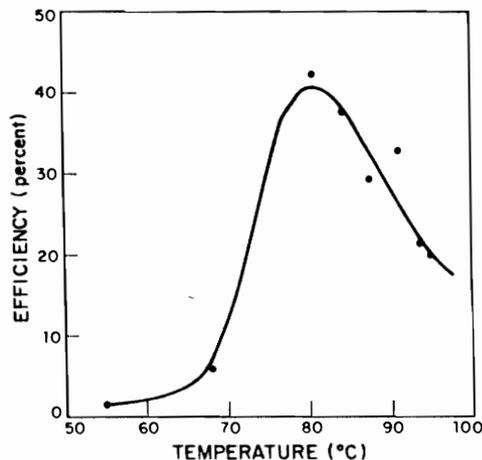


Fig. 12. Cooling efficiency for Zeosorb 5.0 A heated by the sun.

efficiencies already obtained are at least as good as those of any solar systems now available. They can be increased further by using zeolites that have smaller heats of adsorption, such as mordenite, particularly if their adsorption isotherms more closely approach a step-function.

It will require about 1 ton of zeolite, distributed over 200 ft<sup>2</sup>, to produce 1 ton of air conditioning. For a typical house with a 3.5-ton air conditioner, less than half of the roof area will have to be covered with zeolite panels. We estimate that in large-scale production these panels will cost \$1 to \$2 more per square foot than the conventional flat-plate collectors used for solar heating. However, with the addition of a condenser-evaporator unit costing only a few hundred dollars a zeolite system will provide cooling as well as heat and hot water. Because of this additional capability, the year-round reduction in energy costs will permit the repayment of the initial investment on the zeolite system in only 10 to 12 years, rather than the 25 to 30 years typically projected for solar-heated homes. We believe that with a small additional development effort, economically feasible zeolite systems could be available in only a few years.

### ACKNOWLEDGMENTS

The author is grateful to W. J. LaFleur, D. F. Kolesar, and R. E. Fahey for their help in the construction and testing of the zeolite system.

### REFERENCE

- Dubin, M. M. and Astakhov, V. A. (1971) Description of adsorption equilibria of vapors on zeolites over wide ranges of temperature and pressure: In *Molecular Sieve Zeolites-II*, American Chemical Society, Washington, D.C., pp. 69-85.

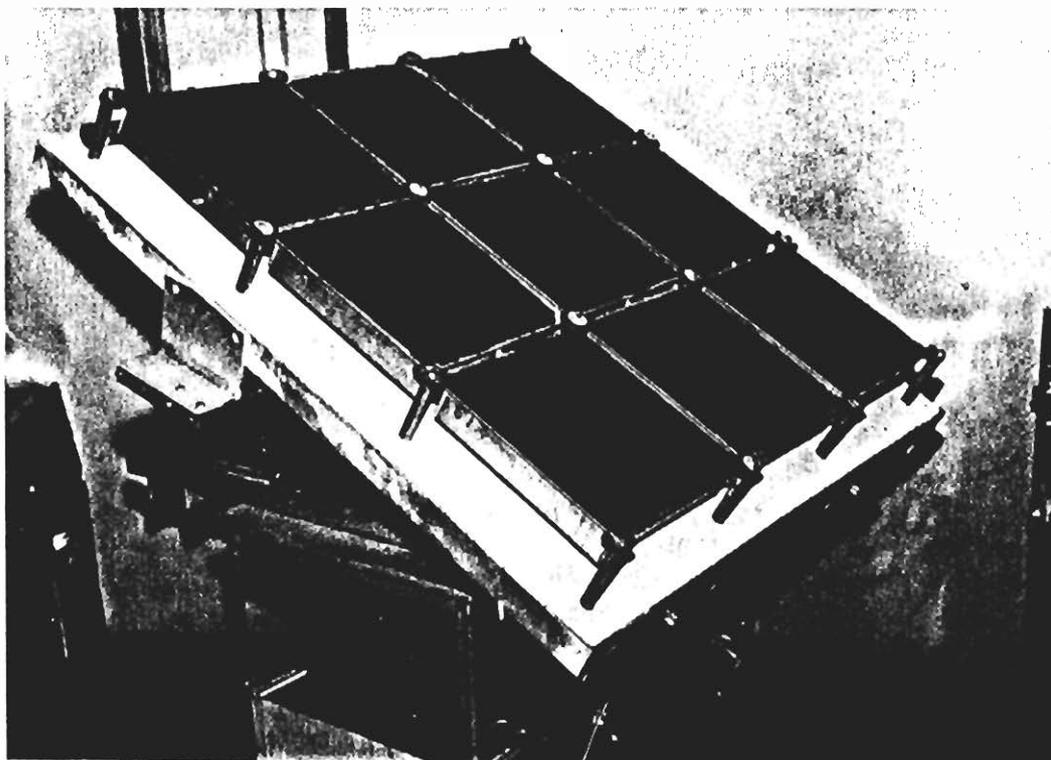


Fig. 13. Square-yard zeolite system, consisting of nine panels each 1 foot square.