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THERMAL ANALYSIS OF ADSORBENTS IN HEAT TRANSFER SYSTEMS *

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ABSTRACT

Natural zeolites and synthetic high surface area metal oxides have been investigated as adsorbents for solar-powered refrigeration systems as well as off-peak thermal storage devices. In this laboratory we have used a Du Pont 1090 thermal analyzer to determine both adsorptive capacity and adsorption isobars with water as the heat transfer agent. For one sample methanol was also investigated. Based on the shape of the isobars, performance of adsorbents as part of cooling or heating systems can be predicted. A natural zeolite was compared with two alumina and a porous carbon sample at different dew points and temperatures between ambient and 200 ° C.

The instrumental arrangement included a constant temperature bath and a thermogravimetric analyzer modified to allow the use of water vapor saturated gases.

INTRODUCTION

Adsorptive systems with water/ammonia have been used for refrigeration ever since this industry developed. However, only recently have high surface area solids, such as natural zeolites, been investigated as adsorbents for water in heat transfer or storage devices [1–4]. Several patents, for instance, describe solar refrigerators using the day/night cycles to affect cooling [5,6]. Figure 1 represents the operating principle of such a device. The main components are a bed of a solid adsorbent (A), a condenser (B) and an evaporator (C) in a closed system under low pressure. During the day, solar

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* Dedicated to Wes Wendlandt with best wishes for his 60th birthday and as an expression of gratitude for his many contributions to the field of thermal analysis as a teacher, author, editor, organizer and friend. Since the publication deals with climactic situations characteristic of Professor Wendlandt's area of residence, we feel that it is particularly appropriate for this anniversary issue of "his Journal".

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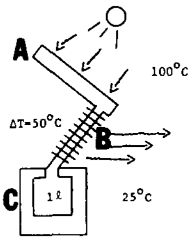

SIMPLIFIED ADIABATIC MODEL

Heat of vapor. ~ 500cal
Mass transfer 1g

RESERVOIR: 1.day 1000g at 25° + 1g at 50° ~ 25cal
→ 1001g at 25.025°

1.night 1001g at 25.025 -1g ~ 500cal
→ 1000g at 24.525°

Thus cooling effect ~
0.5°/gH_2O transferred/ℓ reservoir/cycle

Fig. 1. Operating principle of a solar refrigerator with 1 l reservoir capacity, 1 g/cycle coolant transfer and 50 °C condenser temperature.

radiation heats a bed of water-laden adsorbent, such as a zeolite, under reduced pressure which causes desorption and a pressure increase. The resulting water vapor is condensed at (B), the heat of condensation radiated to the environment and the liquid water collected in a reservoir (C). During the night as the bed cools it re-adsorbs the lost water which is supplied by evaporation from the reservoir, causing its temperature to drop while the heat of adsorption is also radiated to the environment. Assuming an amount of 1 l of water in the reservoir at 25 °C, and 1 g of water evaporated per cycle and returned at 50 °C, the cooling effect would amount to 0.5 °C per cycle. After a few cycles the liquid water is sufficiently cooled to maintain refrigeration. The critical aspects for this operation are an efficient heat transfer, especially for the release of the unwanted heats of condensation and adsorption, and a maximum transport of the heat transfer agent (water in this case) between the highest and lowest temperatures attained during a complete cycle. These factors will not only affect the economy of operation but also determine the construction costs of the device. While described as a solar refrigerator, this principle can also be used as an air conditioning unit or a heater, and solar energy may be replaced by any other form of low-grade heat.

To be practical for solar refrigeration, an adsorbent should have a high capacity for water, especially at room temperature and a 5 °C dew point, and it should allow for a maximum material transport between ambient temperature and about 130 °C to satisfy the ideal conditions for one full cycle. Adsorption isobars for different partial pressures should lie close together and the heat of adsorption should be as low as possible [7].

EXPERIMENTAL

Materials

Zeolite. The zeolite sample was supplied by Zeopower, Inc. and was a natural mineral (Chabazite/Erionite) mined in the Bowie, AZ area [1]. For the experiments it was ground to about 200 mesh. An X-ray powder diffraction pattern is shown in Fig. 2.

Alumina A. The first of the two alumina samples was prepared by hydrolysis of a proprietary aluminophosphate organo-hydrogel [8].

Alumina B. The second alumina sample was prepared by hydrolysis of aluminum nitrate in aqueous ammonia, according to ref. 9.

Carbon. This experimental material was supplied by The Dow Chemical Co. [8] and obtained by controlled pyrolysis of a sample of poly(vinylidene)chloride.

Instrumentation

Total capacity

Initially, the range of water adsorption between ambient temperature and 250 °C was determined as weight loss by TGA, using a Du Pont 951 thermogravimetric analyzer.

The next experiment was designed to determine maximum loading capacities within the important range for this application [6]. A 100-ml round-bottom flask was filled with 50 ml of distilled water and placed in a Neslab

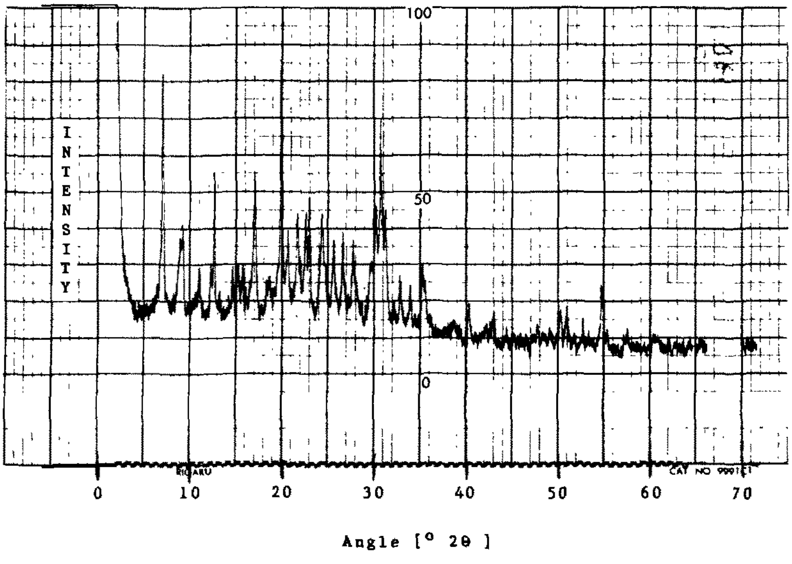

Fig. 2. X-ray diffraction pattern of natural zeolite.

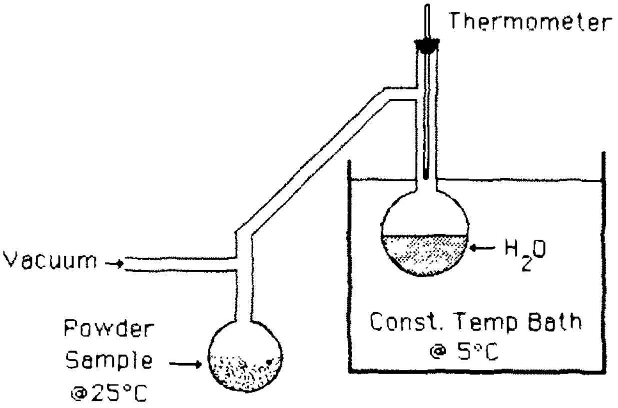

Fig. 3. Setup for initial screening of adsorption capacity.

constant temperature bath kept at 5 °C. About 1 g of each test sample was placed in a 25-ml round-bottom flask and connected to the water reservoir through a short transfer line (see Fig. 3). The system was evacuated to 25 torr and kept overnight, with the samples being held at room temperature. The saturated adsorbents were quickly sealed and subsequently analyzed by isothermal thermogravimetry (TG) at 100 °C. An example is shown in Fig. 4.

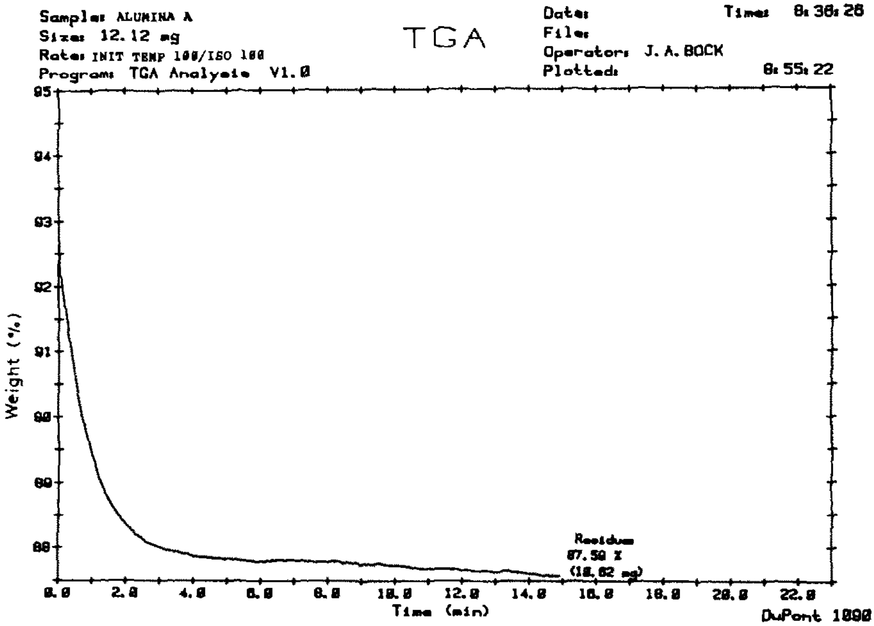

Fig. 4. Isothermal TG of alumina A.

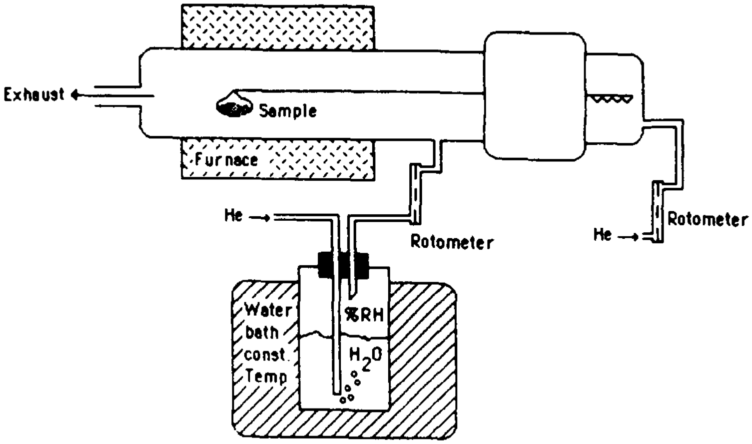

Fig. 5. TGA setup for measuring isobars.

TABLE 1

Natural zeolite

Sample temp. (°C)	Adsorbed water (%)		
	Dew point 5°C	Dew point 15°C	Dew point 25°C
200	3.41	4.44	6.13
175	4.57	5.80	7.75
150	6.13	7.75	9.98
125	8.34	10.24	12.55
100	11.11	12.84	14.81
70	14.38	15.85	17.64
40	17.63	18.91	21.03

TABLE 2

Alumina A

Sample temp. (°C)	Adsorbed water (%)		
	Dew point 5°C	Dew point 15°C	Dew point 25°C
200	3.63	4.00	3.81
175	3.93	4.42	4.61
150	4.30	4.97	5.05
125	4.95	5.43	6.27
100	5.54	6.47	7.26
70	7.10	8.66	10.01
40	10.23	12.70	16.93

TABLE 3

Alumina B

Sample temp. (°C)	Adsorbed water (%)		
	Dew point 5°C	Dew point 15°C	Dew point 25°C
200	1.05	1.33	1.53
175	1.27	1.63	1.78
150	1.63	2.01	2.23
125	2.16	2.60	2.89
100	2.95	3.49	4.17
70	3.67	5.66	6.97
40	8.87	12.73	19.31

TABLE 4

Carbon

Sample temp. (°C)	Adsorbed water (%)		
	Dew point 5°C	Dew point 15°C	Dew point 25°C
185	0.07	0.07	0.10
159	0.13	0.13	0.13
132	0.22	0.19	0.19
106	0.29	0.28	0.32
84	0.42	0.46	0.39
63	0.94	0.80	0.92
52	1.17	–	–
41	1.22	2.30	9.64
31	3.00	16.50	39.73
28	–	34.69	40.88

TABLE 5

Carbon

Sample temp. (°C)	Adsorbed MeOH (%)		
	Dew point 5°C	Dew point 10°C	Dew point 15°C
210	0.62	1.35	1.60
184	0.79	1.56	1.79
158	1.18	1.88	2.30
132	1.69	2.60	3.29
105	3.19	4.53	5.78
84	7.09	–	11.16
63	18.53	22.57	3.76
52	22.48	29.01	–
41	31.40	33.14	–
31	34.71	35.74	–

TABLE 6

Carbon

Sample temp. (°C)	Adsorbed MeOH (%) [a]	Sample temp. (°C)	Adsorbed MeOH (%) [a]
213	0.14	87	2.71
187	0.36	65	6.91
161	0.51	44	20.32
135	0.74	33	27.89
108	1.50	27	30.57

[a] Dew point, −10 °C.

Adsorption isobars

To obtain complete adsorption isobars for different dew points, a Du Pont 1090 thermal analyzer with a 951 thermal balance was modified as shown in Fig. 5. A stream of helium was saturated with water vapor at the temperatures shown in Tables 1–6. To avoid condensation on the balance itself, it was necessary to flush the balance chamber with dry helium as indicated in Fig. 5. The resulting dilution caused a slight drop in the partial water pressure over the sample as compared with that given by the temperature of the thermostated water bath.

Surface area

The surface areas of all samples were determined by a single point nitrogen adsorption using the BET method and a Quantachrome instrument.

RESULTS

After initial screens for maximum loading characteristics, four samples were chosen for a more detailed study.

Table 7 shows the total amount of water adsorbed at room temperature and a dew point of 5 °C. It appears that the loading capacity of similar adsorbents is related, at least to a first approximation, to their surface areas.

TABLE 7

Physical properties

Sample	Total water capacity [a]	Surface area (m^2 g^{-1})
Natural zeolite	7.59	339
Alumina A	14.12	328
Alumina B	~14.3 [b]	424
Carbon	~15.0 [b]	950

[a] Grams of water adsorbed per 100 g of dry sample.

[b] Extrapolated from isobars.

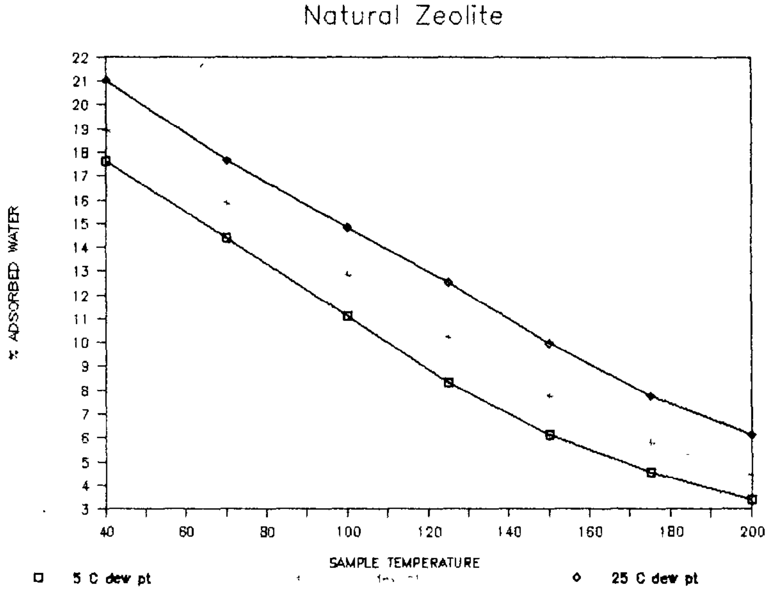

Fig. 6. Isobars for natural zeolite for three dew points.

On the other hand, a comparison of ad- and desorption patterns between 100 and 250 °C had shown differences even between similar materials and especially between dissimilar samples. Therefore complete isobars were recorded for three dew points. Two of the adsorption data in Table 7 were taken from these isobars. There was good agreement between both methods.

The isobars for all four samples are shown in Figs. 6–9. As mentioned above, the actual water partial pressure is lower by about 10% than that corresponding to the water bath temperature. However, since all data were obtained under identical conditions, the comparison of the four samples is valid.

Equilibrium weights were recorded for increasing and decreasing temperatures. A hysteresis effect was observed and the plotted data represent the averaged values between heating and cooling cycles. Measurements at dew points above room temperature were obviously unreliable due to insufficient insulation for the setup used and are not reported.

Natural zeolite (Fig. 6) shows almost linear water adsorption as a function of temperature, which makes its performance dependent only on the temperature difference during a cycle.

On the other hand, high surface area alumina performed better than the natural zeolite at low temperatures and low partial pressures (Fig. 7).

The second alumina sample is similar to the first. Here also, the slopes are steepest at the low temperature range (Fig. 8).

Finally, porous carbon (Fig. 9) not only has the highest total capacity for

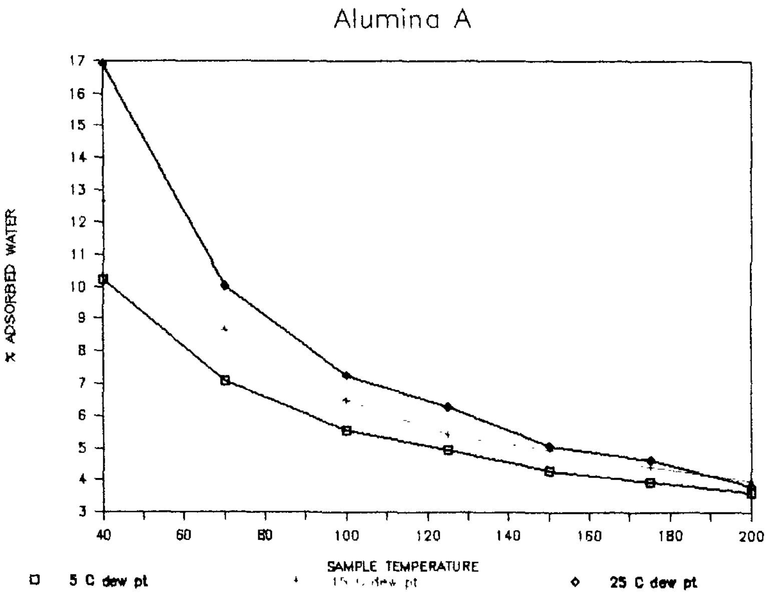

Fig. 7. Isobars for alumina A for three dew points.

water, it also shows the steepest slope for its isobars which occurs at temperatures below 60 ° C.

From the isobars a set of isosteres, i.e. lines of constant loading, can be constructed. Figure 10 represents a set of isosteres as grams of water per

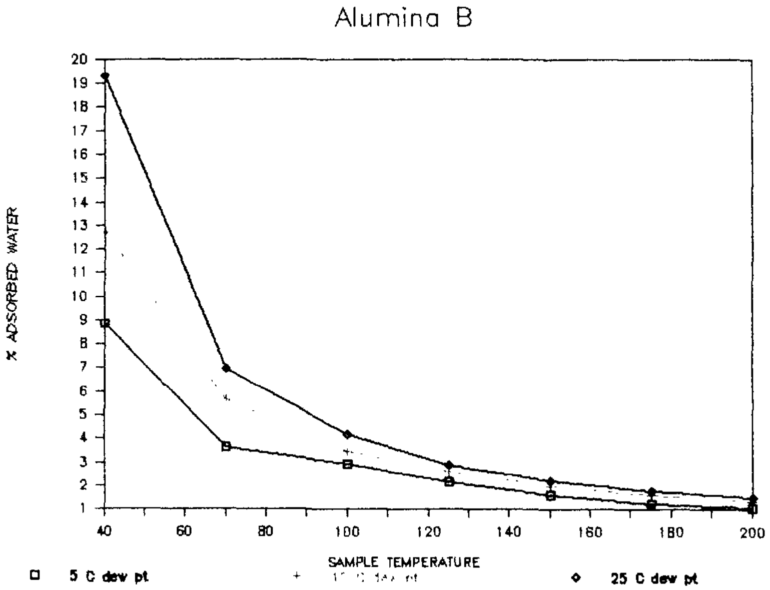

Fig. 8. Isobars for alumina B for three dew points.

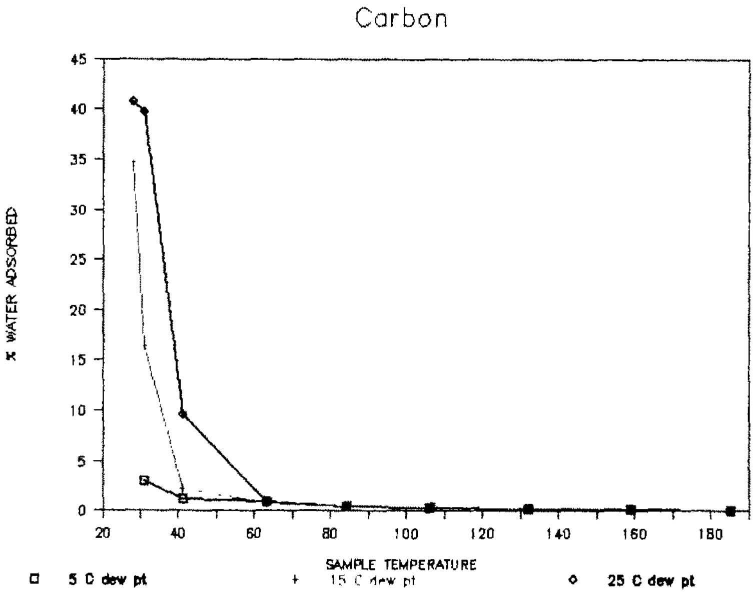

Fig. 9. Isobars for porous carbon for three dew points.

kilogram of zeolite reported in ref. 2. At point A the reservoir and the collector both are at their lowest temperature, while at point C both are at their highest. From the cycle ABCD the amount of water transported (BC) and thus the efficiency of the system can be directly determined. In addition, according to the Clausius–Clapeyron equation,

$$\ln(p_1/p_2) = (dH/R)(1/T_2 - 1/T_1)$$

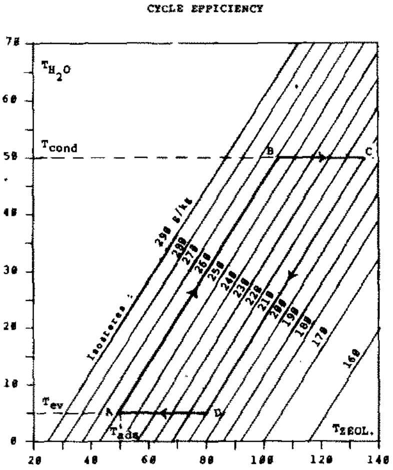

Fig. 10. Isosteric representation of ad/desorption cycle.

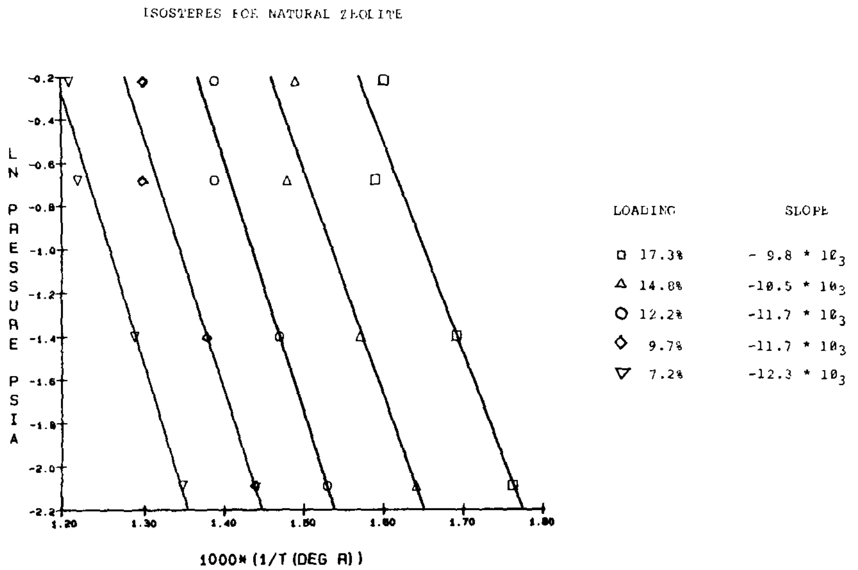

Fig. 11. Isosteres for natural zeolite.

or

$$-R(\ln p_2 - \ln p_1)/(1/T_2 - 1/T_1) = \mathrm{d}H \text{ adsorption}$$

the slope of these isosteres is a measure of the heat of adsorption and thus

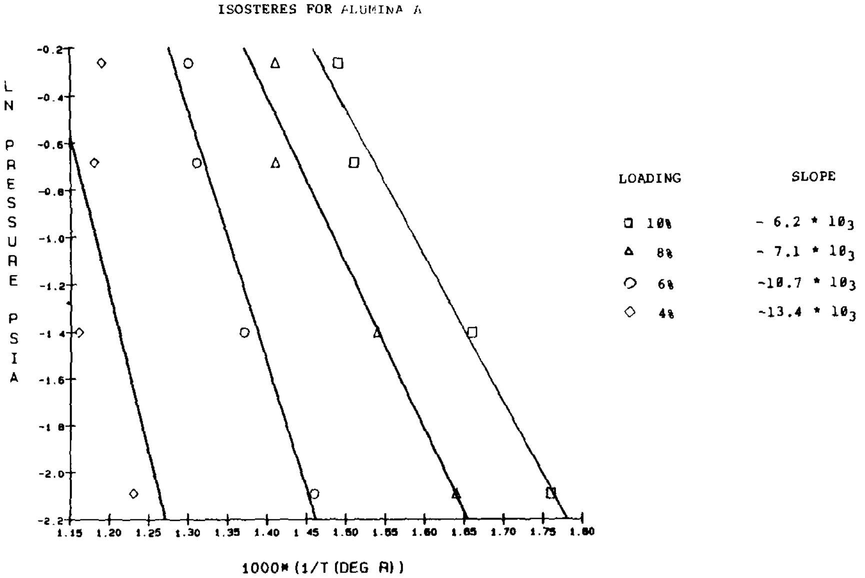

Fig. 12. Isosteres for alumina A.

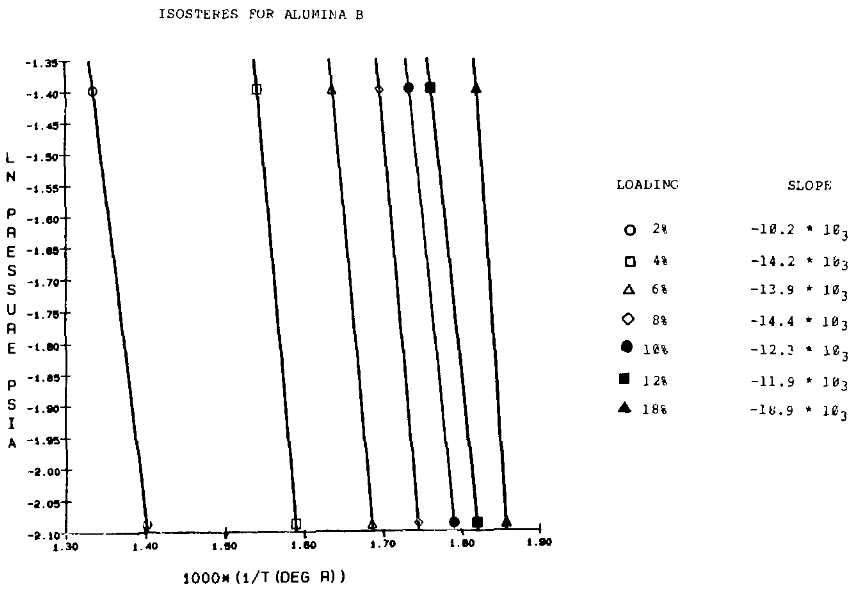

Fig. 13. Isosteres for alumina B.

supplies information about the amount of heat to be radiated from the adsorbent bed during the cooling cycle and the amount of energy necessary for the desorption (regeneration) process. Hence, it should be as low as

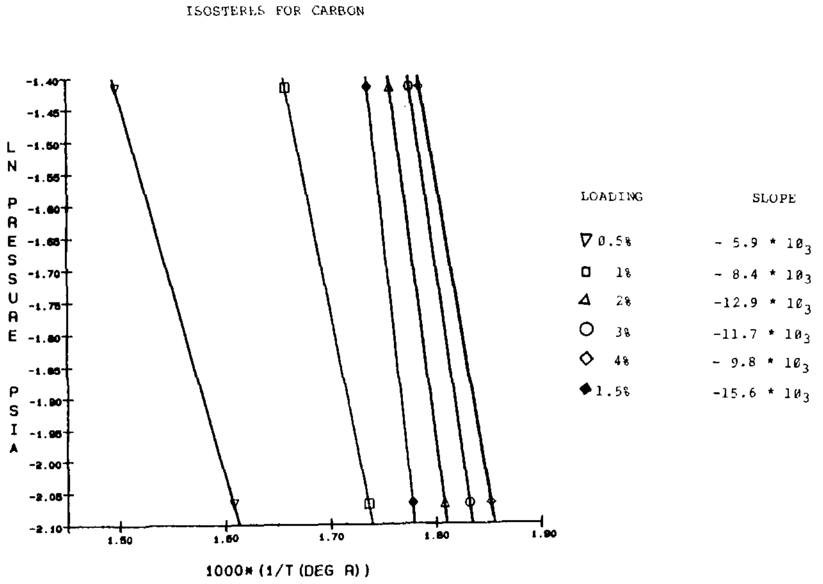

Fig. 14. Isosteres for porous carbon.

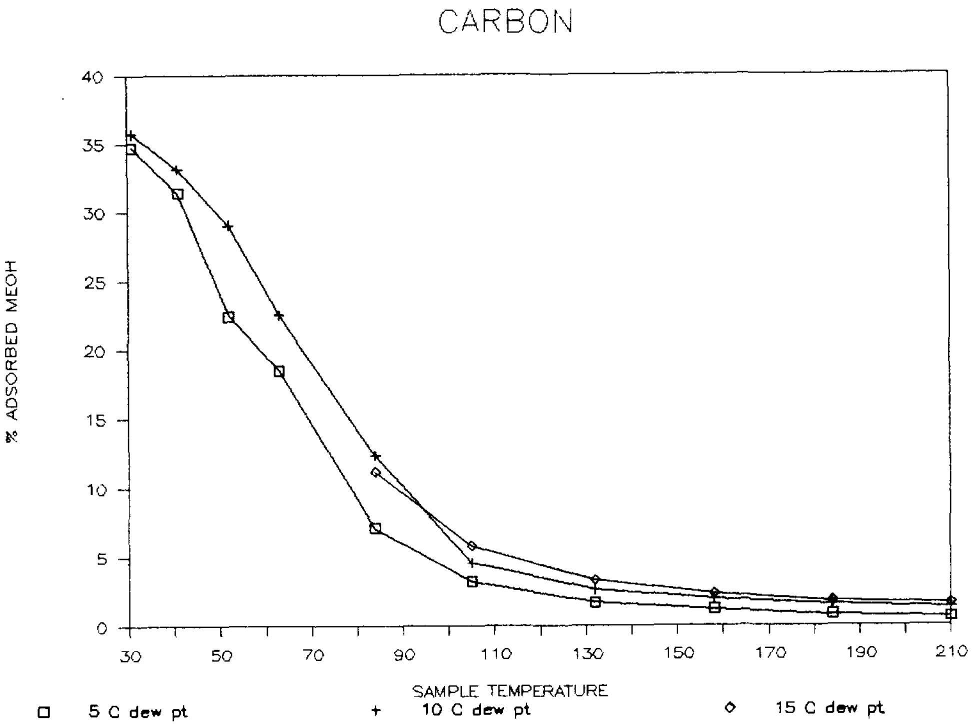

Fig. 15. Isobars for porous carbon and methanol for three dew points.

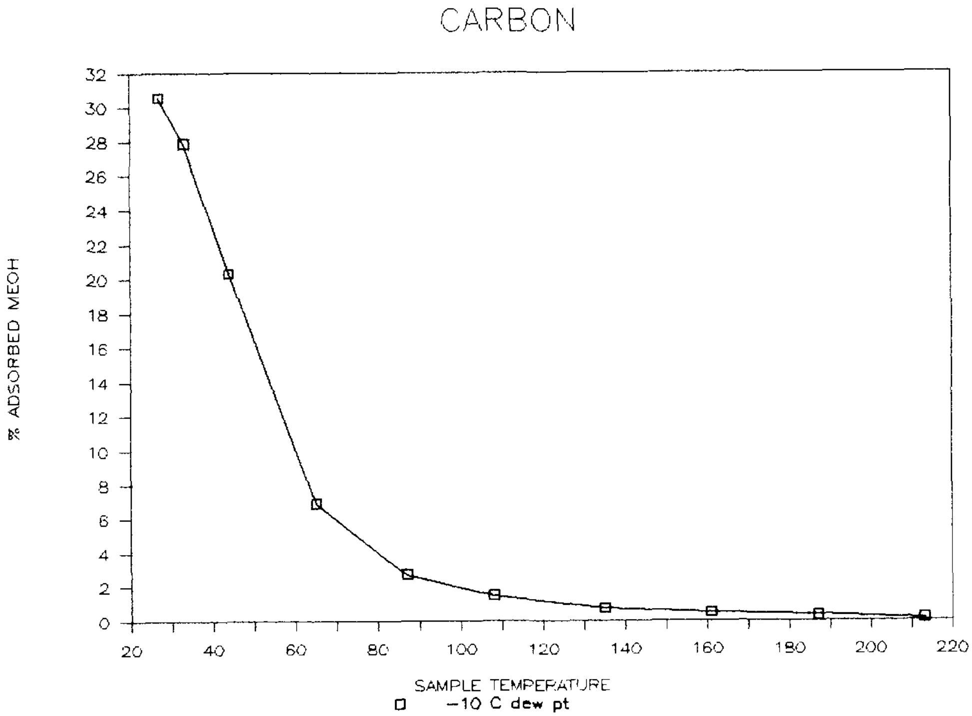

Fig. 16. Isobars for porous carbon and methanol at −10°C.

possible for a refrigeration system, or alternatively, provisions should be made for its recovery in a heating cycle. To construct isosteres, which are linear, only two points are necessary; however, any additional measurements are useful to evaluate the experimental results. This is obvious from Figs. 11–14. Deviations from linearity are caused by insufficient insulation of the equipment as evidenced by the higher temperature measurements.

Because of the strong temperature dependence of the adsorption of water on carbon, the experiment was repeated with methanol, chosen for its chemical similarity to water, but with a lower freezing point. As expected, the adsorption dependence was extended to lower temperatures, as demonstrated by the isobars in Figs. 15 and 16.

CONCLUSIONS

It has been shown that thermogravimetry is a convenient tool to evaluate adsorptive properties of porous materials, as well as performance characteristics for a chosen or given set of conditions.

Natural zeolite appears to be an economical adsorbent for refrigeration systems using low-grade thermal energy. While synthetic materials have shown higher adsorptive capacities, their utilization is limited to a lower temperature range, where refrigeration is not necessarily a serious problem. On the other hand, in warmer temperature zones, dissipation of unwanted heat may present an engineering problem.

Use of methanol as a heat transfer system with a high-capacity neutral adsorbent such as carbon, showed promise for operation as a freezer system.

ACKNOWLEDGMENT

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REFERENCES

1 D.I. Tchernev, in L.B. Sand and F.A. Mumpton (Eds.), Natural Zeolites: Occurrence, Properties, Use, Pergamon Press, Oxford, 1976.
2 J.J. Guilleminot, F. Meunier and B. Mischler, Rev. Phys. Appl., 15 (1980) 441.
3 D.I. Tchernev, Integrated Solar Zeolite Collector for Heating and Cooling, Proc. 1981 Annu. Meet., Int. Solar Energy Soc., Univ. of Delaware, Newark, DE 19711.
4 E.F. Lindsley, Pop. Sci., (1984) 64.
5 D.I. Tchernev, Sorption System for Low-Grade (Solar) Heat Utilization, USP 4034569, 12 July 1977.

6 D.I. Tchernev, Sorption System for Low-Grade (Solar) Heat Utilization, USP 4138850, 13 Feb. 1979.
7 D.T. Tchernev, private communication, 1984.
8 Private communication, The Dow Chemical Company, 1985.
9 T. Kotaigawa, M. Yamamoto, M. Utiyama, H. Hattori and K. Tanabe, Appl. Catal., 1 (1981) 186.