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Development of Zeolite-Water Heat Pump System

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Models of the heat-pump system were developed so far in three stages: 1) the two smallest glass-models having the zeolite amount of 350g, 2) the metallic experimental model with 3-4kg of zeolite and 3) the exhibition model having two zeolite beds filled with 10kg of zeolite in each. Repeated operations of them clarified several characters of the heat pump including problems to be solved and gave valuable suggestions for the development. The system should be a vacuum instrument keeping ideal water-vapor system inside. This guarantees the heat-pump to work well according to thermal natures of both zeolitic water and water.
Key words: Zeolite, Heat pump, Water, Entropy, Energy save

1. INTRODUCTION

Zeolite-water heat pump system has been proposed by Tchernev(1978, 1980)[1,2]. Although the system had been attractive enough for energy save, it has been under investigation level until now. An adiabatic water vapor hydration calorimeter developed by ourselves [3,4,5] had been used to evaluate the hydration heat of Na-A-type zeolite (hereafter, Na-A) synthesized by using waste solution from the Bayer process [3]. Kasai et al.(1994)[3] and Mizota et al. (1995)[4] found that Mg-exchanged A-type zeolite has large heat exchange ability of almost twice of that of natural zeolites such as clinoptilolite and mordenite.

The integral molar hydration enthalpy, ΔH_h, of Na-A dehydrated at 373K attained about -64kJmol^{-1} and the heat exchange capacity, Q, about 490kJkg^{-1}[4]. The Q, is defined as total hydration energy of a dehydrated absorbent at a dehydration temperature, T_d, being normalized to 1kg of the fully hydrated absorbent [4].

2. EXPERIMENTAL

2.1 Mg-exchanged A zeolites as absorbents

Mg-exchanged A zeolites prepared until now are listed in Table I for Mg-exchanged percent, T_d, W_h, W_d, ΔH_h, and Q. The Mg89-A zeolite(Table I) has been obtained [5]. The abbreviation, Mg89-A, represents 89%-exchange of Na^+ in Na-A with Mg^{2+}. The Mg-richest A-zeolite shows the maximum heat exchange capacity of 1MJkg^{-1}, if it is dehydrated at 473K. Mg53-A as-synthesized powder was used at the early stage, but later solidified zeolite has been used to prevent dispersion.

Table I Results of hydration calorimetry of Mg-exchanged A zeolites. Mg% means charge exchange % of A type zeolite with Mg^{2+}. T_d: dehydration temp., W_d and W_h: dehydration and hydration percent, respectively.

Mg %	T_d/K	W_d/%	W_h/%	$-\Delta H_h$ /kJmol^{-1}	Q /kJkg^{-1}	Mg %	T_d/K	W_d/%	W_h/%	$-\Delta H_h$ /kJmol^{-1}	Q /kJkg^{-1}
38	333	7.97	8.05	64.8	287	68	333	7.19	7.31	66.2	264
	353	12.38	11.70	63.9	440		353	11.92	11.15	65.2	432
	373	18.34	16.27	65.6	668		373	17.57	15.42	65.7	642
	393	18.98	17.73	64.4	679		393	19.62	17.70	65.4	713
	413	19.18	18.07	66.4	707		413	20.62	18.40	67.0	767
	433	19.55	17.58	66.0	717						
53	333	7.23	6.90	64.9	260	89	333	7.62	5.70	63.7	270
	353	11.89	9.09	64.6	427						
	373	16.51	14.27	65.4	601		373	15.23	12.08	65.9	557
	393	19.07	16.85	66.1	700						
	413	19.95	17.72	65.5	727						
	433	20.79	17.86	66.7	738		433	22.29	18.18	67.3	835
	453	22.30	18.63	65.6	813						
	473	22.92	19.32	65.4	833		473	24.84	20.76	72.4	999

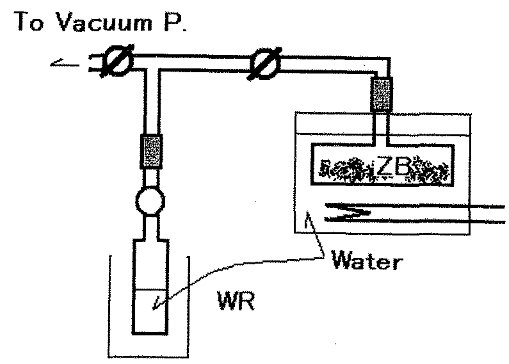

Fig. 1 The first stage zeolite heat pump. Zeolite is heated in hot water. ZB: Zeolite bed, WR: Water reservoir

2.2 Development of Zeolite Heat Pump

The first stage heat pump (Fig. 1) including two models are characterized by a small zeolite bed made of glass tubes and contains 350g of Mg53-A zeolite. These are small for energy exchange capability but still have enough values to show an experimental and/or educational functions. The most delicate point of concern is connecting glass-tubes [6] to keep vacuum. We can observe directly water-freezing or drying of flowers and plants in the glass tube of 3cm in diameter[7]. The second type was improved only to give wide evaporation area by adding a rotation mechanism to the water reservoir. These models attained the lowest temperature of 255K, when the zeolite bed was dehydrated at 373K and afterwards the water reservoir was placed in a vacuum jar[7].

The third type (Fig. 2) in the second stage was made of metal (mainly stainless steel) reserving 3 to 4kg of zeolite in the bed, is made by modifying a heat exchanger of a small car-air-conditioning system. The aluminum fin is removed to insert zeolite pellets in-between of heat-exchange-plates (Fig. 3) in which the silicone oil is flowing. The heat pump has the heat exchange ability of about 1MJ at the dehydration temperature of 433K. Results of repeated operations were shown in figure 5. This proved the repeatability of the heat pump operation.

The forth type of the heat pump (Fig. 4) operated successfully in the three exhibitions held two times in Yamaguchi Prefecture and one in Kitakyushu City on 2001. The system has two beds with 10kg of pelletized zeolite for each to enable continuous operation. The central freezer is made of transparent glass to show freezing at real time, and is equipped with heat exchange pipes inside that serve cooled air-blowing. The total heat exchange ability is over 15MJ and cooling output 500W for 6h., when it is dehydrated at 433-453K.

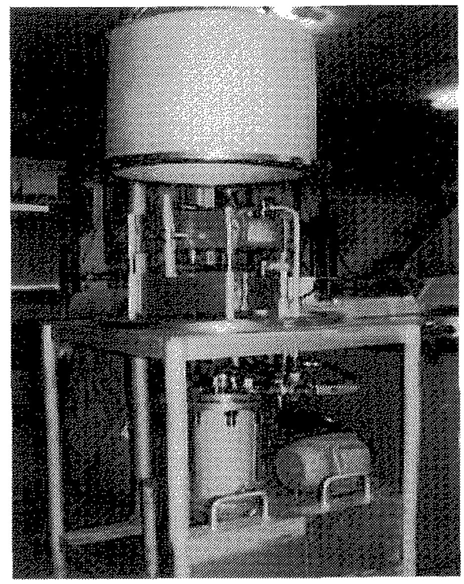

Fig. 2 The third type zeolite heat pump

3. RESULTS AND DISCUSSION

3.1 Repeated operation of the heat pump

Results of operations of the third type heat pump are shown in figure 5, in which the first four cycles show results changing dehydration temperatures and successive five cycles at the same temperature of around 430K. The latter clarified almost perfect cycle recovering hydration/dehydration amounts, each of which is equal to those obtained from TG-data at the heating rate of $3Kmin^{-1}$.

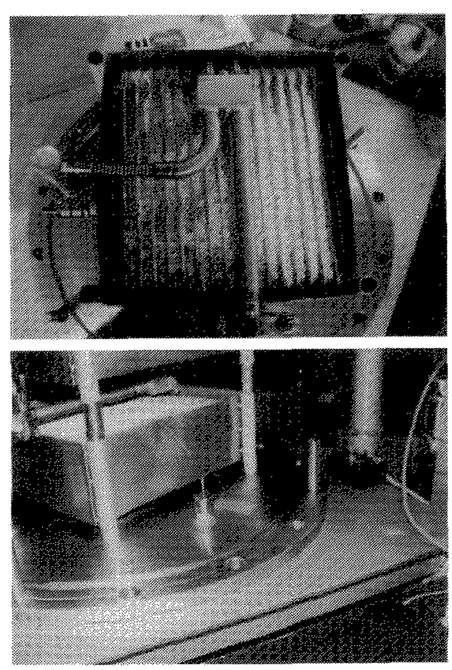

Fig. 3 The zeolite bed of the third type heat pump filled with zeolite pellet (upper) and the side view of the zeolite bed (lower).

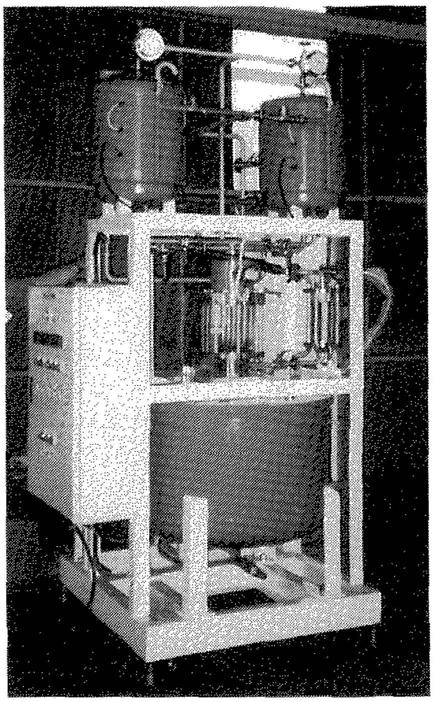

Fig. 4 The fourth type zeolite heat pump with two zeolite beds, 10kg zeolite in each of them.

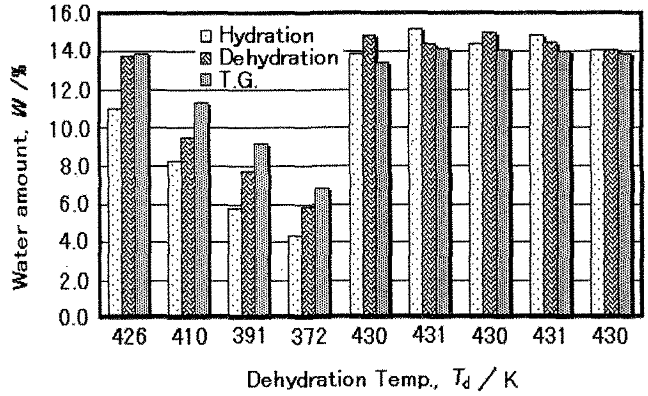

Fig. 5 Hydration and dehydration amounts obtained from repeated operation of the third type heat pump relative to dehydration amount measured from TG of the same zeolite sample at the heating rate of $3Kmin^{-1}$. The left four bars indicate dependency on change of dehydration temperatures. The right five show repeated results at the same dehydration temperature.

3.2 Importance of Carnot efficiency in relation to zeolitic water

H_2O, an energy carrier of the system, takes three states such as vapor, water or zeolitic water as an independent phase. The maximum efficiency of any engine is defined as the Carnot efficiency, as follows,

$$\eta_c = 1 - \frac{T_l}{T_h} \quad (1),$$

where, T_h is the temperature of the heat source to the engine and T_l is that of the waste heat from it. Almost all engines so far developed have been equipped to increase the efficiency by increasing T_h, because the waste heat temperature is restricted to above ambient temperatures on the earth surface. The more general expression of the Carnot efficiency, equation (1), can be written as

$$\eta_c = 1 - \frac{q_l}{q_h} \quad (2),$$

where q_l and q_h are energy amounts absorbed from the higher temperature heat source and exposed to the lower temperature heat source, respectively. The equation (2) is rewritten to the following equation (3) taking respective entropies of the carrier as S_l and S_h.

$$\eta_c = 1 - \frac{S_l \cdot T_l}{S_h \cdot T_h} \quad (3).$$

The efficiency is also apparent to increase with decreasing T_l. This is analogous to decreasing S_l in the form of equation (3). The small entropy value of zeolitic water and entropy relations among vapor, water, ice and zeolitic water are shown in figure 6[9].

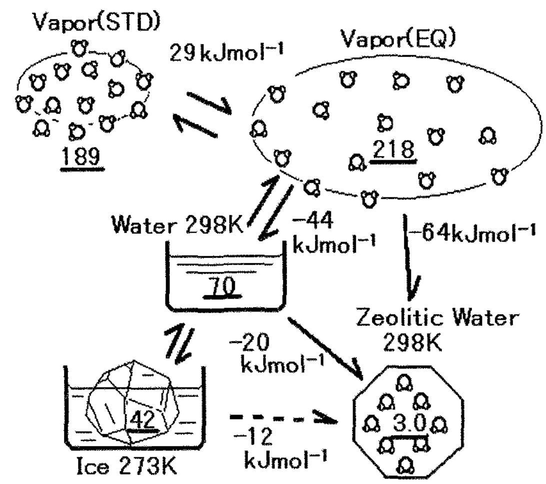

Fig.6 Phase-change enthalpies and entropy values (underscored numerals in $JK^{-1}mol^{-1}$ unit) for vapor, water, ice and zeolitic water[9]. STD: standard state (298K, 100kPa) EQ: equilibrated with water at 298K.

The space for the zeolitic water can be regenerated easily and repeatedly by only heating up to dehydration temperatures.

3.3 Importance of vacuum

Both dehydration and hydration processes were however intermitted at the early stage, although the monitored temperatures and pressures were normal. The vapor pressure is then around that of water, about 3.3kPa at room temperatures. Minute amount of air, if existed, may be pushed aside by water vapor to accumulate and finally fill up the condenser to interrupt the dehydration. In the case of hydration process, the vapor pressure of the zeolite bed become very low to aspirate vapor from water surface above which the vapor pressure is below 610Pa at 273K. Small amount of air may easily fill up inside of the zeolite bed. Model calculations concerning internal volumes of a real heat pump gave such interruption by remaining air of only 0.01 molar percent of total water vapor[11].

The joint and the valve systems have heavy importance for continuous operations, because vacuum level of most parts in production lines in conventional chemical industries are generally 600-700Pa. Thus, the most commercial valves are useless for the zeolite heat pump system.

Zeolite heat pump is however a system operating at near dew point of vapor, especially at the dehydration stage. Condensation may thus occur any time and everywhere inside. The low pressure of the system means small pressure difference as the driving force of vapor. When the condensed water fills the pipe-line of the system by only about 30cm of water-head difference, the pressure difference corresponds to 4kPa. Valves with wide opening are thus necessary for the system. It will be more serious that the workers have not recognized the importance of these facts.

3.4 Energy transport in the zeolite heat pump

The zeolite-water heat pump system may also be doubtful for the amount of treating energy due to the low pressure. The velocity, V (ms^{-1}), of water-vapor molecule at room temperature will be correlated energetically in one direction:

$$\frac{1}{2}mV^2 = \frac{1}{3}RT \qquad (4),$$

where m stands for molecular weight of H_2O, R the gas constant. The equation gives V=303ms^{-1} at 298K. Setting the vapor pressure of 3.3kPa and the 10cm in pipe-diameter, the flow rate of water vapor molecules is obtained to be 3.2mol·s^{-1} along the pipe. As one mole of water molecule conveys energy of 44kJmol^{-1} as the condensation energy. The pipe has the ability as an energy guide of 140kW.

3.5 Arrangement concordant with the gravity

The zeolite bed must be at the top height of the system (Fig. 4). The dew appeared in the inner surface should drop down to the water reservoir. The active use of gravity gradient is effective especially for the small system.

Perfect hydrophobicity will be the most desirable nature of the inside of pipe line, because no dew adhesion occurs there. In the condenser the perfect hydrophilicity is favored ideally for the easy heat exchange on the surface.

4. CONCLUSION

Zeolite water heat pump system should really be considered as an pure water-vapor-zeolitic water system. For this purpose, suitable valve and joint-parts should be developed having wide opening and the better vacuum character than those for conventional chemical instruments. The energy reserve amount has attained 1MJkg^{-1} for Mg89-A, 1kg of which will make ice of 1.4kg [10]. This means that the zeolite system has ability in weight bases by 1.4-times larger than that of ice system. This will contribute much to the energy save in the near future.

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