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Hydration enthalpies of synthetic Na-A, cation-exchanged-A and some natural zeolites for evaluating as heat exchange absorbents ☆

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Abstract

Hydration enthalpies of synthetic A-type and some natural zeolites have been measured by an adiabatic gas-absorption calorimeter to evaluate zeolite as a heat exchange absorbent for a solar-powered system. The Mg-exchanged A-zeolite is a suitable absorbent, if it is dehydrated at 100°C. The total hydration heat is the highest (531 kJ kg^{-1}) of the A-type zeolites treated in the present work and is twice that of natural mordenite or clinoptilolite. An empirical equation is proposed to simulate the relation between differential enthalpies and hydration amounts.

Keywords: Enthalpy; Heat exchange; Hydration; Zeolite

1. Introduction

In 1980, Tchernev [1, 2] made ice using a solar refrigeration system with a water–zeolite pair for the heat exchange. He concluded that natural zeolites such as chabazite and clinoptilolite were more suitable for the absorbent than synthetic zeolites, because the instantaneous efficiency, defined as $\Delta H_w/\Delta H_z$, (evaporation enthalpy of water)/(evaporation enthalpy of zeolitic water), was large for these natural zeolites which have smaller absolute values of hydration enthalpy than those of synthetic zeolites. The efficiency is only a measure at an operating instance of a heat exchange system, and is insufficient for the actual evaluation of absorbents, because the total energy exchanged

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☆ Dedicated to Hiroshi Suga on the Occasion of his 65th Birthday.

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depends on the amount of water hydrated or dehydrated at the operating temperature. Contrary to Tchernev's conclusion, the hydration enthalpies of natural zeolite are not always smaller than those of synthetic zeolites, as seen in data compiled by Carey and Navrotsky who showed that the dehydration enthalpies of zeolites fall in the range between 56 and 85 kJ mol^{-1} [3].

Hydration enthalpy values and discrepancies among differential enthalpy data for water absorption to outgassed zeolites were discussed extensively by Barrer and Cram [4]. Although it is natural from a scientific point-of-view that many workers have sought to determine the initial hydration enthalpy of completely dehydrated zeolites [4], we have concentrated on the partial dehydration at around 100°C in order to evaluate the solar-powered system which will be operated mainly below 100°C. The hydration enthalpies of the synthetic Na-A, cation-exchanged A, and some natural zeolites outgassed at relatively low temperature, 80–120°C, have been measured to identify suitable zeolites to use as the heat exchange absorbent.

2. Experimental

2.1. Sample preparation

The Na-A zeolite was synthesized in a conventional autoclave at 105°C by reacting sodium silicate reagent with sodium–aluminum solution which is a by-product of the Bayer process, the main method of alumina production from bauxite, so as to make use of waste materials [5]. Cation-exchanged varieties of A-type zeolites were prepared by reacting Na-A zeolite with various cation-solutions [6]. Mordenite from Kromogawa, Iwate Prefecture, Japan, and mordenite and clinoptilolite from Indonesia were also used for comparison. The chemical compositions are listed in Table 1.

2.2. Calorimetry

The amount of sample was about 0.4 g in the first stage of the calorimetric experiment, but was later decreased to 0.25 g because a smaller amount is preferable for

Table 1

Oxide ratios and total charge of exchangeable cations C_{ex} for Na-A zeolite and the cation-exchanged A-type zeolites. Water contents were determined by ignition at 800°C: $x = 2$ for Na, K, Ag; $x = 1$ for Ca

Sample	Oxide molar ratio (0 = 8)					C_{ex}
	M_xO	Na_2O	Al_2O_3	SiO_2	H_2O	
Na-A	0	1.03	1.00	2.00	4.45	2.06
K-ex-A	0.83	0.15	0.99	1.93	2.11	1.81
Ag-ex-A	1.09	0.00	1.09	2.54	4.25	2.02
Mg-ex-A	0.49	0.48	1.00	1.99	5.33	1.94
Ca-ex-A	0.82	0.22	1.01	2.01	1.98	2.08

homogeneous absorption and proved sufficient in maintaining the precision of the measurement. The sample was placed in a glass flask which was evacuated and heated for dehydration at various temperatures for 1 h. The flask, with a greaseless valve and a vacuum joint, is detachable from the calorimeter for direct weighing before and after the hydration treatment to determine the amount of hydration [5]. The central part of the calorimeter is composed of a calibration heater, a thermistor thermometer, the sample flask and an agitator. These are immersed in 0.4 dm^3 of water in a vacuum jar. The temperature was measured by a thermistor thermometer of precision ± 0.1 mK and calibrated by means of a quartz thermometer, Tokyo Denpa Kiki Co., Ltd., Model DMT-610, of accuracy $\pm$ 10 mK. All the data, including resistivity and voltage values for the heat supply, were acquired by a micro-computer system through a digital multimeter (Yokogawa 7561 (6.5 digits)). No special temperature control was implemented for the system, except for conventional room temperature control at around 25°C. Water vapor was introduced through a glass tube to the sample from a water reservoir and the temperature elevation by hydration was measured. The heat value was calculated based on the linear relation between temperature elevation and the electric power supplied. Each step height, the temperature increment, was determined by the conventional method of interpolating the aperture between lower and higher steps [6].

3. Results and discussion

3.1. Dehydration temperature and hydration heat

Hydration enthalpies ΔH_h were measured for Na-, Ag-, Mg- and Ca-exchanged A-zeolites, and natural zeolites (Tables 2–4). Six independent measurements gave $64 \pm 1.7\,\mathrm{kJ\,mol^{-1}}$ for the hydration enthalpy of Na-A-zeolite dehydrated at 100°C. Five of them are listed in Table 4 (65.6, 64.7, 62.9, 64.4 and 64.2 $\mathrm{kJ\,mol^{-1}}$ at a hydration level of over 6.15 $\mathrm{mmol\,g^{-1}}$), and another in Table 2 (63.0 $\mathrm{kJ\,mol^{-1}}$), for Na-A dehydrated at 100°C and hydrated to nearly full hydration level. Although the reproducibility is considered to be in this range for the present experiment, the precision is worse at the low hydration level below 2.0 $\mathrm{mmol\,g^{-1}}$ for Na-A, as seen in Table 2.

It is convenient to use the total heat of hydration Q to evaluate a zeolite absorbent

$$Q = -\Delta H_\mathrm{h} \Delta m_\mathrm{h} \tag{1}$$

where ΔH_h and Δm_h denote respectively the hydration enthalpy and the amount of water hydrated per kilogram of zeolite. Q values for various zeolites are shown in Table 2 with the dehydration temperature t_d and dehydration/hydration percent.

The hydration enthalpy of the zeolite will then be a measure of vapor pressure. The relation between hydration enthalpy and vapor pressure is derived from the well-known Clausius–Clapeyron equation

$$\ln P = \frac{\Delta H_\mathrm{h}}{RT} + \mathrm{const.} \quad \text{or} \quad P = \exp(-|\Delta H_\mathrm{h}|/RT + \mathrm{const.}) \tag{2}$$

Table 2
Dehydration and hydration amounts ($W_{\mathrm{dehy.}}$ and $W_{\mathrm{hydr.}}$), hydration enthalpy (ΔH_{h}) and total heat of hydration (Q) for zeolites dehydrated at various temperatures (t_{d})

Sample	t_{d}/°C	$W_{\mathrm{dehy.}}$/%	$W_{\mathrm{hydr.}}$/%	$-\Delta H_{\mathrm{h}}$/kJ mol^{-1}	Q/kJ kg^{-1}
Na-A	40	4.54	3.89	60.2	130
	60	10.08	8.75	64.2	311
	80	14.39	11.97	65.1	435
	100	13.71	13.95	63.0	487
	120	17.77	13.56	64.5	486
	150	18.18	12.61	64.7	453
Mg-ex-A	40	4.93	5.42	60.6	182
	60	8.81	6.10	53.7	215
	80	15.60	7.24	67.2	270
	90	15.37	11.96	63.9	424
	100	16.83	14.71	65.1	531
	120	16.03	12.06	67.1	449
Ca-ex-A	40	4.31	3.64	56.6	114
	60	6.59	5.65	60.3	189
	80	7.94	6.95	63.0	243
	100	9.25	9.41	66.2	346
	120	14.02	11.32	70.8	444
	130	15.46	12.62	70.1	491
	140	17.49	13.70	69.7	530
	150	17.64	14.88	70.1	577
Mordenite					
Chikalong	100	10.04	6.31	63.4	222
Koromogawa	100	nd	7.17	58.4	233
	120	nd	7.64	59.9	254
Na-ex-m	120	nd	5.65	62.7	197
Ca-ex-m	120	nd	5.96	63.2	209
Ag-ex-m	100	nd	6.59	55.4	203
	120	nd	6.87	59.0	225
Clinoptilolite					
Bogor	100	10.51	5.82	61.1	197

nd: not determined.

where ΔH_{h} is the hydration enthalpy which is negative. As the $P - |\Delta H_{\mathrm{h}}|$ curve shows negative inclination at a constant temperature, a larger absolute value of the hydration enthalpy gives a lower vapor pressure for zeolite absorbents. Although a large hydration enthalpy of an absorbent decreases the value of the instantaneous efficiency, a lower vapor pressure is preferable for a heat exchange system.

The Q value shows an increase with dehydration temperatures (t_{d}) (Table 2, Fig. 1). A downward bending is, however, seen for Na-A at 100–120°C and also for Mg-ex-A at 100°C, which indicates a decrease in hydration amount due to the collapse or deformation of voids in the zeolites at the higher dehydration temperature. The

Table 3
Hydration heat ($-q$), amount of water hydrated (Δm_h) and hydration enthalpies (ΔH_h) for mordenite from Koromogawa (Raw-m) and the cation-exchanged mordenites (Na-ex-m, Ca-ex-m and Ag-ex-m) dehydrated at 120°C for 1 h in vacuum

Sample	Δm_h/mmol g^{-1}	$-q$/J g^{-1}	$-\Delta H_h$/kJ mol^{-1}
Raw-m	2.88	186	64.8
	3.24	202	62.2
	3.93	236	59.9
	4.27	251	58.9
Na-ex-m	2.74	174	63.3
	3.10	194	62.7
	3.55	216	61.0
	3.57	218	61.0
Ca-ex-m	2.85	186	65.5
	3.32	210	63.2
	4.13	254	61.4
	4.28	262	61.1
Ag-ex-m	2.55	157	62.5
	2.93	183	61.6
	3.51	210	59.0
	3.89	223	57.3

Q values for Mg-ex-A increase steeply from 80 to 100°C and the value of 531 kJ kg^{-1} (Table 2) is the maximum for all those dehydrated below 100°C (Fig. 1). In the dehydration at 80°C, Na-A is preferable, whereas Ca-ex-A becomes useful at higher temperatures above 140°C (Fig. 1). Natural zeolites, mordenite and clinoptilolite, show small Q values (Table 2) at dehydration temperatures of both 100 and 120°C, and should be dehydrated at higher temperatures to obtain large Q values.

3.2. *Hydration enthalpy*

Dubinin derived a theoretical equation for the differential heat of adsorption, q' [7]

$$q' = \Delta H_{wv} + A - \alpha R T^2 \left(\frac{\partial \ln p_g/p}{\partial \ln m}\right)_T \tag{3}$$

where ΔH_{wv} is the latent heat of condensation, A the differential molar work of adsorption, α the thermal coefficient of expansion of the adsorbed substance at a constant value of A, p_g the saturated vapor pressure of the gas, p the equilibrium pressure, and m the amount of adsorbed gas. The equation gives the differential

Table 4
Hydration heat ($-q$), amount of water hydrated (Δm_h) and hydration enthalpies ($-\Delta H$) for Na-A zeolite and the Ag-exchanged-A zeolite, dehydrated at 80°C and 100°C for 1 h in vacuum

Sample (dehy.temp.)	Δm_h/mmol g^{-1}	$-q$/J g^{-1}	$-\Delta H_h$/kJ mol^{-1}
Na-A	0.78	46	59
(100°C)	1.3	73	56
	1.6	97	61
	2.0	150	75
	6.15	404	65.6
	7.55	488	64.7
	7.75	488	62.9
	8.22	529	64.4
	8.49	545	64.2
(80°C)	4.72	310	65.5
	6.50	421	64.8
	6.65	433	65.1
	7.50	480	63.9
	8.12	518	63.9
Ag-ex-A	4.87	311	63.9
(100°C)	5.63	356	63.2
	6.02	378	62.8
	6.28	393	62.5
(80°C)	4.52	288	63.7
	5.38	338	62.8
	5.61	352	62.7
	5.71	364	62.6

enthalpy using a set of experimental data from the adsorption isotherm. Dubinin compared the differential enthalpies of adsorption of benzene to active carbon from calculated and experimental results, the maximum discrepancy being ± 5%. The Clausius–Clapeyron method has been widely used to obtain enthalpies for gas absorption with an accuracy of, for example, ± 0.5 kJ mol^{-1} for xenon absorption in Ag-exchanged Y-zeolite [8]. These two methods are, however, not so easy to apply for a water vapor system, because strong interactions between water molecules and the inside-wall materials of the equipment lead to unstable measurement of the vapor pressure at ambient temperature.

Barrer and Gibbons tried to determine the initial hydration enthalpies theoretically in terms of isolated cation–water interactions, and stated that they obtained reasonable values comparable to the differential enthalpies of zeolites determined from their experiments [4, 9]. Discrepancies among differential enthalpies have bee discussed by Dubinin and others (discussions in Ref. [41]). The enthalpies change stepwise or non-linearly according to the hydration state in the zeolite as shown by Dubinin who measured them using a Tian–Calvet-type calorimeter.

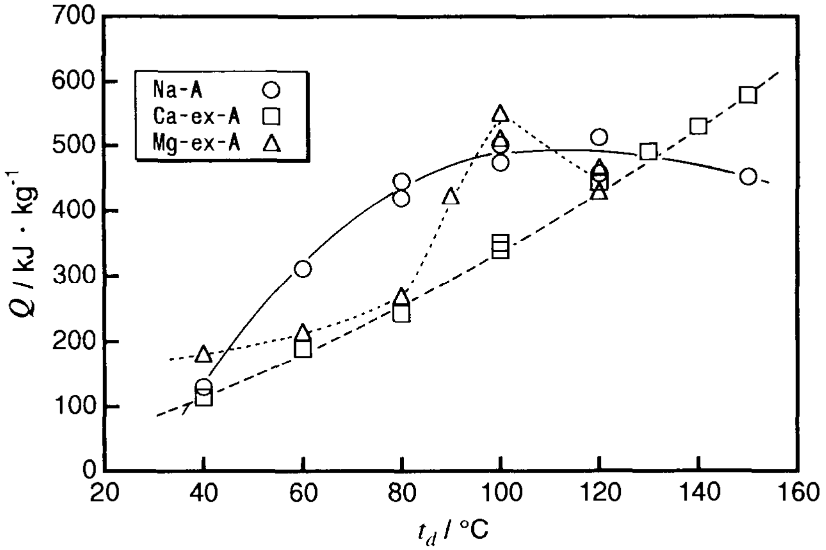

Fig. 1. Relations between total heat of hydration Q and the dehydration temperature t_d for A-type zeolites.

Although we tried several times to determine the initial enthalpy or the differential enthalpy by increasing the sample amount to the 1 g level, the results were insufficient for analysis, because each amount of water hydrated in a stepwise manner was too small to give heat values of good precision. As the integrated hydration enthalpy can be determined with considerable accuracy, we can use these values for the evaluation. Hydration heats q of Na-A were measured successfully in a relatively narrow Δm_h range near full hydration (Tables 3 and 4) with some additional data, which were not always sufficient in quality, near the initial hydration, $\Delta m_h \sim 0$ (Table 4). Values of differential enthalpy are greatly influenced by framework deformation of zeolite as well as by displacement of exchangeable cations through the dehydration process. The initial hydration enthalpy should, therefore, be verified for a sample dehydrated below the temperture causing irreversible changes of the structure.

The following empirical equation is given for the differential of q, expressing the differential enthalpy as $q'(\Delta m) = \Delta H_d$, so as to simulate the $-q$–Δm relations plotted in Fig. 2

$$-\left(\frac{\partial q(\Delta m)}{\partial \Delta m}\right) = -q'(\Delta m) = a + b\exp[-c\Delta m] \tag{4}$$

where a, b and c are constants, and c is positive. Eq. (4) shows the relation that $-\Delta H_d$ decreases exponentially with increasing hydration in the zeolite voids. The initial differential enthalpy ΔH_{di} is then defined at $\Delta m = 0$

$$-\Delta H_{di} = -q'(0) = a + b \tag{5}$$

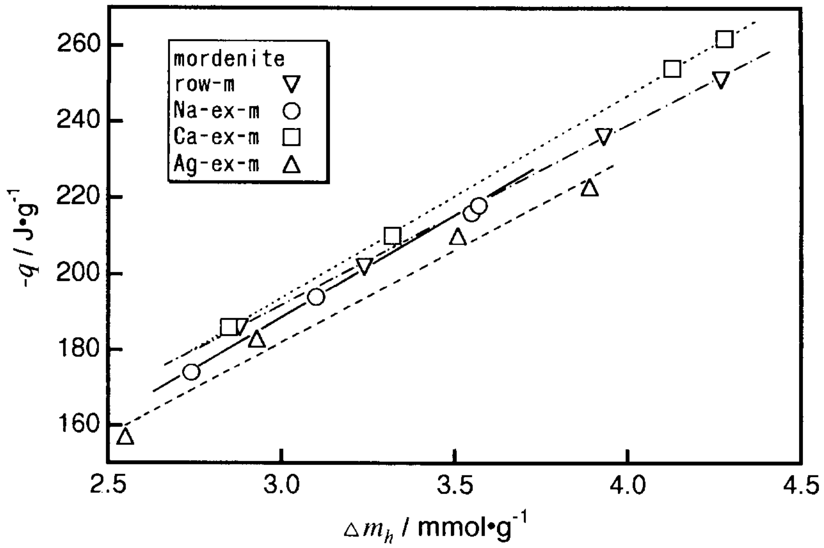

Fig. 2. Plots of experimental values for heat of hydration q vs. hydration amount Δm_h for mordenite samples dehydrated at 120°C for 1 h.

At full hydration, the differential enthalpy will be equal to the condensation enthalpy, ΔH_{wv}, to liquid water

$$-\Delta H_{wv} = -\lim_{\Delta m \to \infty} q'(\Delta m) = a \tag{6}$$

Experimental $-q$–Δm plots for mordenite samples (Fig. 2), for example, show linear relations in the relatively high hydrated state

$$-q(\Delta m) = h + s\Delta m \tag{7}$$

where h and s are constants. The differential, $-q'(\Delta m_m) = s$, should be defined at the center, Δm_m, of the region. Using the s value, we obtain from Eq. (4)

$$c = -\frac{1}{\Delta m_m}\ln\left(-\frac{(s-a)}{b}\right) \tag{8}$$

Integrating Eq. (4), we finally obtain the integrated heat of hydration

$$-q(\Delta m) = a\Delta m - \frac{b}{c}[\exp(-c\Delta m) - 1] \tag{9}$$

The non-linear least-squares calculation for Eq. (9) gives an optimum ΔH_{di} by fixing both the values of $a = -45\,\mathrm{kJ\,mol^{-1}}$ $(= \Delta H_{wv})$ and the experimentally determined slope s. Calculated examples are shown in Fig. 3 and parameters fitted by the

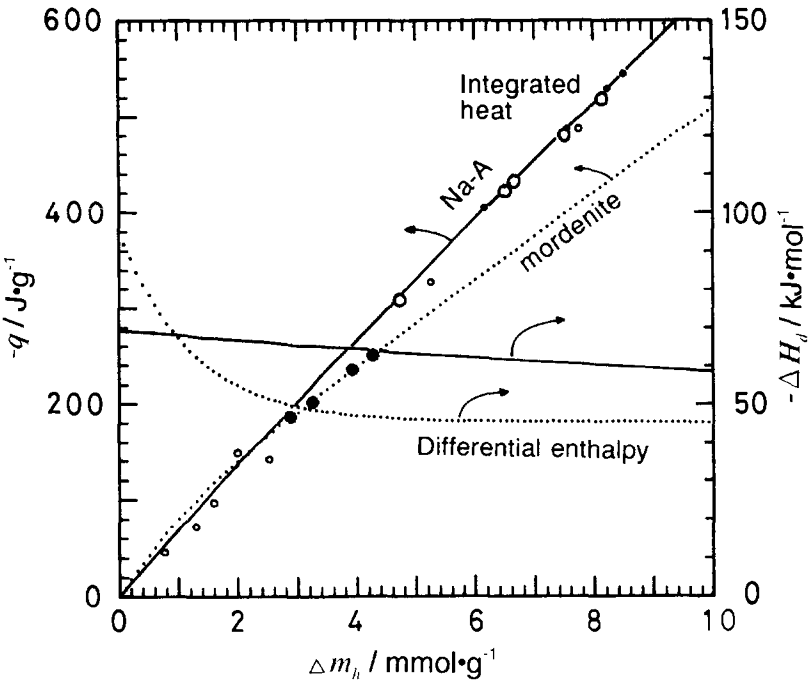

Fig. 3. Curve fittings of heat of hydrations q vs. hydration amounts Δm_h and the calculated differential enthalpy ΔH_d curves for zeolites. Lines are obtained using Eqs. (4) and (9) for ΔH_d and q, respectively.

Table 5

Constants obtained from the curve fitting of experimental data from hydration calorimetry for zeolites using Eq. (9); $-\Delta H_{di}$ is the initial hydration enthalpy; $-\Delta H_{wv}(=a)$ is fixed at 45 kJ mol^{-1}; $-\Delta H_{wf}$ is defined as the value at full hydration, Δm_f; t_d is the dehydration temperature; and c and s are defined in Eqs. (7) and (8)

Sample	t_d/°C	c	s/kJ mol^{-1}	$-\Delta H_{di}(=a+b)$ /kJ mol^{-1}	$-\Delta H_{wf}$ /kJ mol^{-1}
A-type Zeol.					
Na-A	100	0.0603	60.7	69.6	60.0
	80	0.0578	61.3	68.8	59.9
Ag-ex-A	100	0.119	57.8	69.9	56.9
	80	0.114	58.6	69.3	57.7
Mordenite from Koromogawa					
Raw-m	120	0.837	47.5	96.1	46.4
Na-ex-m	120	0.452	52.7	77.3	51.2
Ca-ex-m	120	0.417	52.8	79.4	50.7
Ag-ex-m	120	1.03	46.9	97.0	45.9

least-squares calculation are listed in Table 4. The data from Na-A in the low-Δm_h region are plotted in Fig. 3 and are valuable with reference to the whole profile of the curve, but were omitted from the least-squares calculation due to insufficient precison. Despite the simple assumption above, the equation simulates well the data obtained from experiments.

The differential enthalpies of hydration calculated for Na-A by Eq. (4) are rather flat and give low ΔH_{di} values of around 70 kJ mol^{-1}, whereas those of Koromogawa mordenite are increased steeply to $\Delta m_h = 0$ and give high values of from 80 to 97 kJ mol^{-1} (Table 5 and Fig. 3).

The largest Δm_h value of the individual hydration data was very close to the almost full hydration amount (Δm_f) for the zeolite; thus $q'(\Delta m_f) = \Delta H_{wf}$. The $-\Delta H_{wf}$ value is large for Na-A, 57–60 kJ mol^{-1}, whereas it is rather close to the vapor condensation enthalpy to free water for mordenite, 46–51 kJ mol^{-1} (Table 5). The small $-\Delta H_{wf}$ values may indicate that the large cavities in mordenite composed of 12-membered rings allow looser accumulation of water molecules than those in the smaller cavities of A-type zeolites composed of 8-rings. The larger absolute values of the differential enthalpy of hydration for A-type zeolites in the relatively high hydration state indicate that this type may be effective for use as a heat exchanger for a low-temperature heat source, as in a solar system. Eq. (4) gives a smoothed average of the differential enthalpies of a zeolite from dehydration to full hydration (Fig. 3). Fig. 3 includes plots for Na-A dehydrated at both 100 and 80°C. These are simulated with the same curve, despite the difference in the dehydration temperature of 20 K.

4. Conclusions

To evaluate the solar heat exchange absorbents of zeolites, the total heat of absorption Q (kJ kg^{-1}) is valuable. Mg-exchanged A-zeolite has the largest Q value of all the A-type zeolites tested, namely 531 kJ kg^{-1}, which is more than twice those of natural zeolites, when it is dehydrated at 100°C which is close to the operating temperature of the solar system. Ca-exchanged-A and natural zeolites will be effective when the system is used at higher dehydration temperatures. A proposed empirical equation is useful to simulate relations between the hydration heat and the amount of hydrated water, even if only a few data sets are obtained for the heat of hydration and the amount of water hydrated.

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