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Thermochimica Acta 370 (2001) 57–63

thermochimica acta

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Na-montmorillonite clay as thermal energy storage material

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Received 16 June 2000; accepted 5 December 2000

Abstract

Sodium montmorillonite (Na-M) was investigated as an energy storage material. The study was conducted through the adsorption isotherms, infrared (IR) spectroscopic and differential thermal analysis (DTA). The clay systems were subjected to different preheating temperature, 125, 160, and 200°C, before subjecting the clay to the adsorption process carried out. The adsorptive capacities of Na-M ranged between 0.12 and 0.48 g H_2O/g of dry clay, depending on the preheating conditions of the clay. The stored energy of Na-M 781 cal/g when the clay preheated to 200°C, at which the clay has lost all the water molecules that could be evaporated, and become, therefore, able to adsorb the maximum amount of water vapor allowed. Na-M, when appropriately set, could be considered as an energy storage material. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Montmorillonite; Clay; Energy storage; Hydration–dehydration; Water vapor adsorption

1. Introduction

Bentonites are naturally occurring minerals. Their high heat of adsorption and ability to hydrate and dehydrate while maintaining structural stability has been found to be useful in various heat storage. The initial entry of water into nearly anhydrous clay is strongly exothermic. Also, the water is firmly held in the coordination sphere of the cation and in contact with the surface oxygen. After one or two water layers have been introduced, further expansion is probably driven by osmotic forces, i.e. the presence of water dilutes the concentration of the interlayer ionic solution. In terms of entropy changes, this expansion increases the entropy of the interlayer cation by allowing it greater freedom of movement. The hygroscopic property of bentonite coupled with rapid, intense exothermic reaction when taken from dehydrated to hydrated form (heat of adsorption), makes bentonite effective in the storage of solar and waste heat energy. The size and the ion charge of the exchangeable cation is considered as one on the important parameter, which affect on the adsorption capacity of the bentonite [1–5].

The most practical method to hydrate clay surfaces is by using water vapor. This vapor is a result or could be produced throughout many industrial activities, solar energy, or by any sources of waste heat energy. The experiments are designed in a manner analogous to what is actually happen in nature.

In previous work, the authors investigate the behavior of calcium saturated montmorillonites during the adsorption–desorption reactions, to evaluate their performance for thermal energy storage [6].

The present work aimed to investigate one of the monovalent saturated montmorillonite,

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PII: S0040-6031(00)00769-3

Na-montmorillonite (Na-M), as material for thermal energy storage. This study will conduct through the adsorption isotherms, IR spectroscopy and DTA, which will show the effect of the charge of cation on the adsorption capacity of the clay.

2. Experimental

2.1. Materials

The investigation was carried out with montmorillonite clay supplied by the International Company for Mining and Investment, Egypt. The chemical and mineralogical composition of this clay was reported by one of the authors elsewhere [7].

Sodium-clay was prepared by saturating the colloidal fraction of Egyptian montmorillonite with normal NaCl solution. This treatment was repeated five times. Then the clay fraction was obtained by allowing larger fractions to settle out of a suspension. The clay was washed with distilled water and separated in a high-speed centrifuge until the equilibrium solution was free of chlorides.

2.2. Methods

Approximately 2.5 g of adsorbent was weighed out into an 800 ml beaker alongside a 30 ml beaker half filled with water. The larger beaker was covered with aluminum foil and the water vapor uptake was determined by weighing the clay at different time periods.

The adsorbent was first saturated with water vapor and then dried at 125, 160, and 200°C for 24 h in a controlled oven. After the drying process has taken place, further adsorption was carried out. This system could be used as a simulation to solar energy at different conditions and various types of solar collectors.

The IR spectra of clay samples were obtained using a Perkin-Elmer 1420 IR spectrophotometer having a frequency range of 4000–600 cm^{-1}. Solid samples were analyzed using a potassium bromide disk.

Thermal analysis was performed with a Shimadzu DT-30 under the following conditions: weight of sample 9 mg; heating rate 10°C/min; sensitivity ±25 μV and chart speed 5 mm/min.

3. Results and discussion

Fig. 1 shows the adsorption isotherm of water vapor, at room temperature as a function of time under equilibrium conditions, for air-drying saturated Na-M, as well as the adsorption isotherms of the same material, when it was preheated at different temperature; 125, 160, and 200°C, for 24 h, in a controlled oven. The adsorptive capacity of the clay was calculated and expressed as the maximum amount of water adsorbed on certain amount of clay (g H_2O/g of dry clay). The adsorptive capacity of air dried Na-M is 0.12 g H_2O/g of dry clay after 190 h (saturation time). This value was increased to reach 0.48 g H_2O/g of dry clay after 113 h (saturation time) when the sample was preheated at 200°C, as indicated in Table 1. The total amount of water in montmorillonite represents the sum of the initial water content and the water vapor adsorbed amount. Thus, as the preheating temperature increases; the initial clay water content decreased leaving more pore sites larger than the critical slit wide of condensations. These pores will be ready to adsorb more water vapor. This leads to increases the water absorption (Table 1).

The amount of water adsorbed, 0.12 g H_2O/g of dry clay, as indicated by water vapor sorption isotherms, suggested that one-layer of hydrates formed as the preheating temperature was the room temperature. Also, the shape of the isotherms (Fig. 1) indicates that the difference between energy of interaction between the first monolayer of water molecules adsorbed and the active surfaces is not significant with that of the energy of condensation of the subsequent layers, as approved by other investigators [8].

The water vapor adsorption isotherms of the Egyptian clays was found to be similar to those reported on the other similar type of montmorillonite clays [9].

Table 1
The average amount of water adsorbed on Na-M at a different preheating temperature

Preheating temperature (°C)	Maximum adsorptive capacity (g H_2O/g of clay)	Saturation time (h)
Air dried	0.12	190
125	0.29	122
160	0.39	119
200	0.48	113

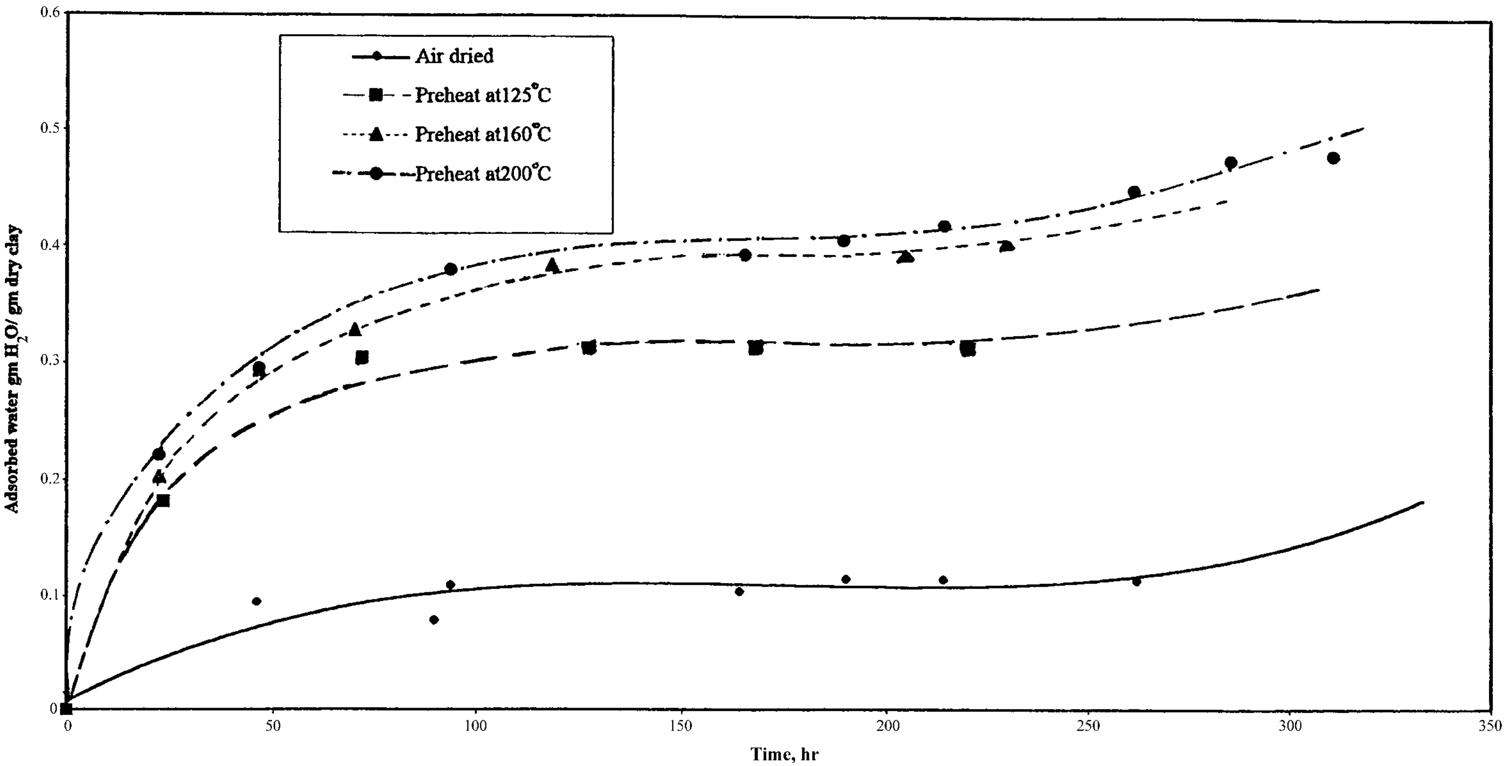

Fig. 1. The adsorption isotherms of water vapor on Na-M clay with different preheating temperature.

But, because of the irregular shapes of the isotherms, each isotherm can be assigned to certain type of known isotherm depending on the preheating temperature. This is also due to the complex mechanism of water adsorption. In general, the sorption of water by montmorillonite is governed by the size and charge of saturating cation, by the value and the localization of layer charge of the adjacent silicate sheets and surface characteristics [10]. In the previous works [6] for air-dried clay presented, the Ca-isotherm is concave to the time axis while, now, Na-M curve is upward concave. Examining these shapes according to the BET theory [11,12] indicates that in the Ca-M system the energy of interaction between the first mono-layer of water molecules adsorbed and the active surfaces is greater than the energy of condensation of the subsequent layers. In Na-M, the difference between these two energy terms is not significant, indicating that the hydration forces in Na-M are less than those in Ca-M. The same behavior recognized by another author [13]. From the adsorption isotherms, Na-M is believed to form two to three layers hydrate while Ca-M form a three to four layers hydrate. The proposed model in which the pattern of water molecules associated with the exchangeable cations is close to the configuration of hexagonal ice like structure. For the one-layer hydrate of montmorillonite saturated with divalent cations, the same structure may not exist because of the strong solvation energy of the exchangeable cations. In the case of Na^+, the water molecules may be organized in a manner consistent with the hydration shell of the cation and the nearby presence of parallel silicate layers. At high water vapor adsorption, multi layers hydrate state will be formed (amount of adsorption 0.12–0.48 g H_2O/g of clay). A mono-layer state can be formed at the level of 0.11 g H_2O/g of clay, as the surface area of this clay is 790 m^2/g. Two different cases are distinguished: (a) cations such as Ca^{2+} with high energy of hydration leading to a predominant two-layers hydration state; (b) cation such as Na^+ with lower hydration energy produces one-layer hydration state. Thus, the shape of the isotherms is influenced by the nature of the exchangeable cation. Also the rehydration properties of montmorillonite are strongly dependent on the size of the interlayer cations. For example, the lack of electrostatic attraction between the interlayer clay surfaces when sodium ions are between such surfaces, the amount of water adsorbed on the clay-oxygen surfaces through hydrogen bonding is much more than in the case of calcium as exchangeable ions. This variation of adsorptive capacity explains the importance of the interlayer cation, and its charge density.

An estimation of the polarizing power of the cations was calculated by dividing the charge of the cations by the radius of hexa-coordinated metals. This approximate polarizing power for Ca^{2+} and Na^+ are 1.75 and 0.86 C/Å, respectively. Therefore, the energy of cation solvation in the case of Ca-M is being higher compared to Na-M. This explains why Ca-M adsorption capacity increases slightly comparing with Na-M, under the same equilibrium conditions.

The adsorption isotherm indicated that the free energy change in the Ca-system is larger than in Na-system at the low water content up to 0.22 g H_2O/g of dry clay. This amount of water corresponding to two layers of adsorbed water. Above 0.25 g H_2O/g of dry clay, the free energy change of the adsorbed water in both Na- and Ca-M system is similar. This indicate that, as water content increases, the adsorbed has properties similar to those of bulk water, and the influence of the clay surface does not extend beyond a few molecular layers of adsorbed water. The amount of water vapor adsorbed on rehydration processes suggested that a two-layer hydrate state seem to be formed for all montmorillonites corresponding to an amount of adsorbed water higher than 0.25 g H_2O/g of dry clay [14]. As a results, the size as well as the charge of the saturating cation govern the adsorption–desorption phenomenon of water vapor on homoionic montmorillonite and the amount of water adsorbed.

The IR spectra of dry Na-M as wells as hydrated forms are shown in Fig. 2 from 4000 to 600 cm^{-1}. Spectral hydration features in montmorillonite have been attributed to structural OH in the octahedral layer, water adsorbed on grain surfaces and water adsorbed or bounded in the interlayer regions. The character of these interlayer water molecules is greatly dependent on the moisture level of the interlayer cations. The band assignments of the fundamental vibrations are summarized in Table 2. A weak band at about 3630 cm^{-1} is due to lattice hydroxyls OH stretching mode, which arises from the vibration of firmly bounded H_2O. Also strong broad band at 3430 cm^{-1} can be attributed to the H–O–H stretching

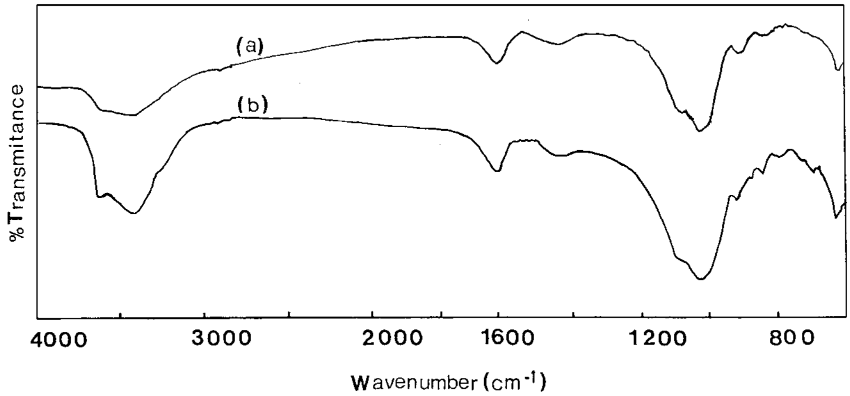

Fig. 2. The IR spectra of Na-M: (a) dried sample at 105°C and (b) hydrated sample.

vibration of H_2O readily lost upon heating. This band reflects the free H_2O adsorbed onto the structure and/or inter-laminar water OH stretch. The band near 1630 cm^{-1} is due to the water of crystallization bending vibration. The strong band near 1115 cm^{-1} is due to Si–O bending vibration. The Si–O–Si stretching vibration appears near 1045 cm^{-1} as a strong band. The 920 and 850 cm^{-1} band is due to Al–OH and. Mg–Al–OH, respectively. The weak band nears 800 cm^{-1} is attributed to the vibrations of quartz.

Similar structural interpretations and band assignments are made for the previous studied systems, Ca-M [6]. It was found that, there are a shift to higher frequencies compared to Na-M especially the band at 3430 and 1630 cm^{-1}. This may be assigned to two factors. The first is the polarizing power of the interlayer cations as mentioned before. This trend is consistent in general to the vibrational energies of the water bending vibrations. The stronger the polarizing power of the cation, the more the cation hinders the bending vibration. Thus, the peak positions in case of Ca-M has a higher frequencies comparing to Na-M. The symmetric stretching modes involve motion along the H-bonding axis and in the direction of the cation–oxygen bonds which implies that H-bonding and bonding with the interlayer cation should influences these vibrations. The second factor is due to hydration, which it is higher in case of Ca-M than for Na-M. The moisture content has been shown to influence H_2O bending vibration near 1630 cm^{-1}. Based on the increasing polarizing power from Na to Ca, the 3430 cm^{-1} band energies are expected to decrease from Na to Ca. This is observed for the 3430 cm^{-1} band vibration energies of the samples containing higher moisture contents. However, this absorption under dry conditions for the Na sample has shifted to a lower energy than those for the Ca samples.

Table 2
The band assignments for water and structural OH in Na-M

Wavenumber (cm^{-1})	Vibration
3630 (s)	H–O–H stretch
3430 (s, b)	H–O–H stretch
1630 (m)	H–O–H bend
1115 (s)	Si–O bend
1045 (s)	Si–O–Si stretch
920 (m)	Al–OH
850 (m)	Mg–Al–OH
800 (w)	Quartz

Other workers [9,15] had observed a shift in the vibration from 1640 to 1630 cm^{-1} in films of Na-M as the water content was decreased from 7 to 2 H_2O molecules per Na^+ cation. Our results are agree with these studies, where there are shift to lower vibrational energy in the band from 1630 to 1625 cm^{-1} in Na-M upon heating the sample to105°C as shown in Fig. 2. In contrast, the band at 3430 cm^{-1} is shifted to higher frequencies under dehydration to 3440 cm^{-1} compared to the air-dried ones. This implies that H-bonding in H_2O of the montmorillonite systems increases with increasing water content and that H-bonding is reduced in the interlayer H_2O of dehydrated montmorillonite. Therefore, the frequency of OH stretching vibrations decreases with the strength of hydrogen bonding. Also the intensity of the H_2O stretching vibrations increases with increasing H-bonding.

When hydrated montmorillonite are subjected to forced drying by heating to higher temperatures; 125, 160, and 200°C, there is a marked variation both in their retention of water and in their ability to rehydration when re-exposed to moisture, as mentioned above. The relative amount of the adsorbed water vapor to the clay surface can be elucidated through the IR spectroscopy data. By assuming that the absorption of radiant energy by water and the clay obeys the Beer–Lambert equation. The ratio of absorbance, log I_0/I, of the stretching vibration band at $3430\,\mathrm{cm}^{-1}$ to the bending vibration band at $1045\,\mathrm{cm}^{-1}$ can be taken as an indication of the water content or moisture content adsorbed on clay surface. This ratio was increased as the preheating temperature increased as indicated in Table 3.

The results of IR indicate the same trend of increasing the water content in the following order $Ca^+ > Na^+$. This is comparable to the adsorption isotherm trend observed for Na^-, and Ca-M, where the amount of water adsorbed by a given montmorillonite varies with the type of interlayer cation and the relative humidity.

The DTA curves, shown in Fig. 3, exhibit one low-temperature strongly endothermic peak up to 100°C, corresponding to the desorption of physically adsorbed water. This form, which is held by less strong attraction, is found on the surface of the clay in defect sites of broken bonds at the silicate surfaces. It is usually presented in small quantities, which are proportional to the surface area of the clay. Since all clay have roughly the same outer crystalline surface area, the amounts of adsorbed water are similar from one species to another, as indicated earlier in IR analysis. This peak of Na-M is distinguished as a double peak with a shoulder when the clay preheated at higher temperature. This shoulder means that the release of water at the external surface and inter-laminar water not bonded to exchangeable cations proceeds at lower temperatures [16]. Semi-quantitative analysis can be applied assuming that the area under the low temperature endothermic peaks is proportional to the amount of adsorbed water on the clay surface, which could be

Table 3
The relative absorbance of the various type of adsorbed water to each molecule of clay at different preheating temperature

Preheating temperature (°C)	H_2O molecule/Si–O–Si molecule
Air dried	0.20
125	0.22
160	0.33
200	0.60
Dried at 105°C[a]	0.44

[a] Dried sample without rehydratio.

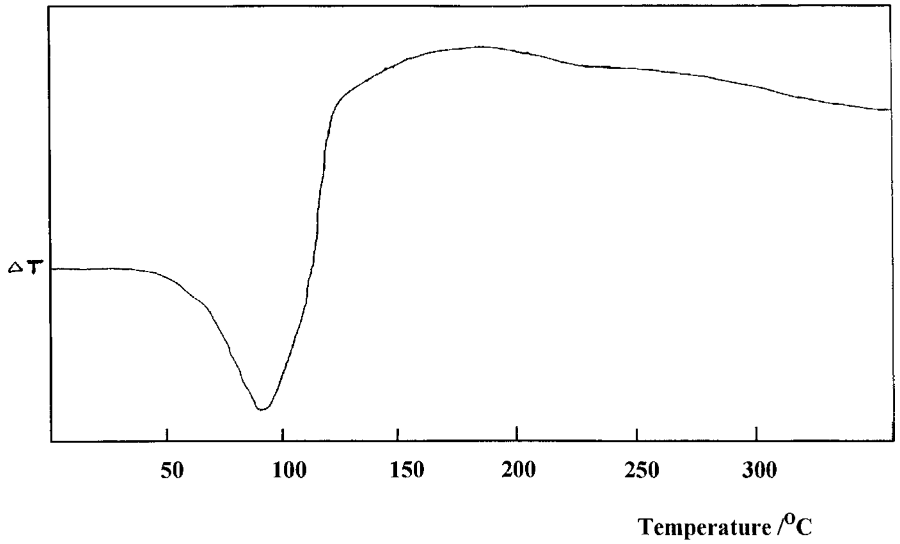

Fig. 3. DTA curve for Na-M.

Table 4
Summery of DTA data

Preheating temperature (°C)	First peak (°C)	Peak area (cm^2)	Energy storage (cal/g)
125	95	22.0	679
160	95	22.2	685
200	95	25.3	781

liberated from the surface. The storage energies of all the studied systems, could be obtained depending on this assumption, were represented in Table 4 for Na-M at different preheating temperatures. Na-M can storage energy up to 781 cal/g when the clay preheated to 200°C, at which the clay can loss all the water molecules, and become ready to adsorb the maximum allowed amount of water vapor.

As indicated in the previous systems [6,17], the sequence of temperatures of water loss for the different cations is as follows; Na $< 200°C$, and Ca $< 230–250°C$. Therefore, during the preheating the clay lost a certain type of the previously adsorbed water depending on the preheating temperature and the amount of re-adsorbed water act as a function of drying temperature. The amount of the water vapor uptake on Ca-M is less than that on Na-M at different preheating temperature. This unexpected behavior can be attributed to the free energy of the two cations, which decreased as the water content increased for both Na- and Ca-M. Due to the lower hydration energy of Na comparing to Ca ions. The preheating treatment removes all the hydrated water around the Na ions while in Ca-M, the surface retained some of these hydrated water molecules as first hydration shells.

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