ELSEVIER

Thermochimica Acta 363 (2000) 47–54

thermochimica acta

www.elsevier.com/locate/tca

Ca-montmorillonite clay as thermal energy storage material

Olfat M. Sadek*, Wafaa K. Mekhamer

Department of Materials Science, Institute of Graduate Studies and Research, Alexandria University,
163 Horreya Avenue, P.O. Box 832, Alexandria, Shatby 21526, Egypt

Received 28 February 2000; accepted 3 July 2000

Abstract

Ca-montmorillonite clay (Ca-M), is one of the materials, which can perform reversible direct hydration/dehydration process. The feasibility of using Ca-M as a thermal energy storage material was investigated. The adsorption isotherms, differential thermal analysis (DTA) and infrared (IR) spectroscopy data were studied. The adsorptive capacity of Ca-M was calculated and expressed as the maximum amount of water adsorbed on certain amount of clay. The results showed a reasonable adsorptive capacity for Ca-M, which amounted to 0.31 g H_2O/g of dry clay, as pre-hydration temperature reached 250°C. The energy storage capacity was calculated as a function of the net adsorbed amount of water on the clay surface. The maximum heat storage capacity obtained for dry clay was 487 cal/g. Thus, Ca-M can be considered as an efficient energy storage material compared to the other materials used. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Montmorillonite clay; Solar energy storage; Thermal energy storage

1. Introduction

An efficient and reliable energy storage system allows the collection and storage of solar energy while it is plentiful, and uses it up when it is not, i.e. when the energy is unavailable. Solar heating of buildings and food drying, takes advantage of the accumulation and storage of solar energy during sunny days to provide heating during nights and cloudy days. Many workers have developed systems where solar energy is stored thermally in the form of sensible heat, latent heat and heat associated with chemical reactions. The most simple and common way to store thermal energy is in the form of sensible heat of water or rocks. This, however, has two main disadvantages: (a) the low energy density and (b) the insulation requirements. The stored energy can be lost in a short period of time when the temperature difference between surroundings and systems is large [1–5]. To overcome such problem, thermal energy can be stored for infinite period of time with no insulation in the form of chemical potential. This may involve a reversible chemical reaction, adsorption, and/or a direct hydration process. In the case where thermal energy is stored via adsorption, the adsorbent material must have high surface area. The most commonly investigated systems which involve water vapor as adsorbate, are zeolites and silica gel [6–8].

Another promising material for these systems are clays; which are chemically inert, resistant to deterioration and are commercially available in large quantities. Montmorillonite clay satisfies one of the main requirements for energy storage, which is the ability to absorb large quantities of water, 7–10 times of its volume. Also, clays operate in a reversible hydration–dehydration mode. They are highly porous

---

* Corresponding author.

PII: S0040-6031(00)00598-0

materials whose surface area ranges between 3×10^5 and 7×10^5 m^2/kg [6].

The clay minerals Bentonite are mainly composed of Montmorillonite (smectite), together with some other clay and inorganic minerals. Structurally, montmorillonite mineral is 2:1 phyllosilicate in which the negative layer charges, produced from the isomorphous substitution, are electrically balanced by the equal charge of exchangeable cations located primarily between its silicate layers [9,10].

It is well known that an exothermic reaction occurs when montmorillonite clays are in contact with water or water vapor. This is due to the water molecules penetration between the unit layers through hydrogen bonds between water molecules and the hydroxyl group on clay structure and also the hydration of the exchangeable cations. Such 'interlayer swelling', or (intra-) crystalline swelling of montmorillonite, depends on the type of clay and the type of cation. A rather stable configuration of the hydrated clay is obtained, corresponding to the presence of one to four monomolecular layers of water between the unit layers. When the interlayer cations in montmorillonite become hydrated, large hydration energy is evolved [11,12].

The choice of an efficient adsorbent depends on the magnitude of the heat of adsorption. The amount of water adsorbed and the corresponding basal spacing are governed by both the size and the charge of the saturating cation, as well as the value and localization or distribution of the charge of the adjacent silicate sheets that the exchangeable cations neutralize [13].

The aim of this work is to investigate the adsorption–desorption phenomenon as a way of thermal energy storage, using Ca-montmorillonite clay under variable moisture conditions. The adsorption behavior of water molecules on the clay surface will be analyzed through the adsorption isotherm, infrared spectroscopy and differential thermal analysis techniques.

2. Experimental

2.1. Materials

Egyptian Bentonite clay, supplied by the International Company for Mining and Investment, was used in this study. The chemical and mineralogical composition of this clay has been previously reported by one of the authors elsewhere [14].

2.2. Methods

2.2.1. Clay preparation

For conventional homoionic saturated clay surface, a sample of clay (10 g) was suspended in distilled water (1000 cm^3). The suspension was homogenized by vigorous stirring. A solution of metal ion (Ca^{2+} in 0.1 molar aqueous solution in a chlorinated form) was slowly added to the suspension with continuos stirring (24 h). The slurry was centrifuged. The homogenization step, followed by centrifugation, was repeated four times. The solid material, which was separated finally, was washed by chloride-free water and dried.

2.2.2. Water adsorption on clay

The adsorbent, Ca-M (approximately 5 g), was weighed out into a beaker (800 cm^3) with a suspended 30 cm^3 beaker half filled with water attached to it. The two coincided beakers were covered with aluminum foil and the water uptake was determined by weighing the larger beaker containing the clay at different periods [6]. This system was used to determine the adsorption isotherm curve under static equilibrium.

2.2.3. Pre-heating of clay material

The adsorbent was first saturated with water vapor and then dried at 125, 160, 200, 240, and 500°C for 24 h in a temperature controlled oven. After the drying process, further adsorption was carried out, and the clay was resaturated with water again. This system could be used as a simulation of various types of solar collectors, collecting solar energy at different conditions.

2.3. Infrared analysis

The solid clay samples were pressed with potassium bromide to form a disk. The infrared spectra of clay samples were recorded using a Perkin-Elmer 1420 Infrared Spectrophotometer through a frequency range of 4000–600 cm^{-1} (2.5–16 μm).

2.4. Differential thermal analysis

Thermal analysis was performed using a Shimadzu DT-30 instrument under the following conditions:

weight of sample 9 mg; heating rate 10°C/min; sensitivity ±25 μv; chart speed 5 mm/min.

3. Results and discussion

The behavior of the adsorbed water vapor on Bentonite has been studied to find out the factors, which may determine the water adsorption capacity.

Fig. 1 represents the adsorption isotherm of water vapor at room temperature as a function of time, under equilibrium conditions. The produced adsorptive capacity of the clay is expressed as the maximum amount of water adsorbed on certain amount of clay (g H_2O/g dry clay). Table 1 shows the average amount of water adsorbed on the homoionic Ca-montmorillonites (Ca-M), at different pre-heating temperatures. For comparative reasons, the adsorptive capacity after 118 h was taken, as reference point, as this is the time when the air-dried samples have reached saturation. It is evident that the adsorbed water vapor increases by increasing the time of adsorption. The adsorptive capacity of air-dried Ca-M when reached saturation is 0.13 g H_2O/g dry clay, which corresponds to about 7.0 mmol H_2O/g of dry clay. This result is in good agreement with values reported by previous workers [13,15,16]. Also, the shape of the water vapor adsorption isotherm of the used clay is similar to those clays taken from other sources represented by other investigators [10,17–19].

It is important to investigate and measure the net amount of water adsorbed when the absorbent is preheated at various temperatures. The adsorption isotherms of Ca-M with different pre-heating temperatures are represented in Fig. 1. The maximum adsorptive capacity of the clay which was preheated at 125, 160, and 200°C is nearly the same, which equals to 0.25 g H_2O/g dry clay, but still higher than that for air dried samples. The adsorptive capacity increases to 0.31 g H_2O/g dry clay as prehydration temperature reaches 250°C. Also, it was found that, the saturation time has been reduced and the adsorptive capacity of Ca-M after 118 h, saturation time of air dried sample, has increased as the pre-heating temperature was increased.

When the pre-heating temperature reached 500°C, the clay looses its ability for rehydration; due to breakdown of the clay structures. The increase in the adsorptive capacity of the clay with the increasing the pre-heating temperatures could be attributed mainly to two reasons: (i) the loss of the water retention in or on the clay structure during heating which will increase the clay ability to rehydration, and (ii) the increase in clay surface area after drying. These in general might be due to the nature of water molecular energy of adsorption which can be classified into three categories: (a) physisorbed water molecules, which occupy interstitial pores, i.e. interlamellar spaces water. This water has been eliminated by heating to 80–90°C; (b) water molecules coordinated directly to the exchangeable metal cations, i.e. hydrated water, and leave the structure at 100–250°C; (c) finally, the water of crystallization, which is found within clay structure. This water is firmly bonded to the structure as hydroxyl groups, and needs temperature of 500°C or above to be freed. Therefore, during the pre-heating of the clay, certain type of the previously adsorbed water will be lost depending on the pre-heating temperature, and the clay becomes partially dehydrated. The amount of readsorbed water depends on the drying temperature. At 250°C, Ca-M looses all the water adsorbed on the surface and around the cation, but at a temperature below 250°C it loses only the surface water. Therefore, on

Table 1
The average amount of water adsorbed on the clay at a different pre-heating temperature

Pre-heating temperature (°C)	Max. adsorptive capacity at saturation time (g H_2O/g of clay)	Saturation time (h)	Adsorptive capacity after 118 h (g H_2O/g of clay)
Air dried	0.13	118	0.13
125	0.25	216	0.18
160	0.25	166	0.21
200	0.25	145	0.24
250	0.31	143	0.29

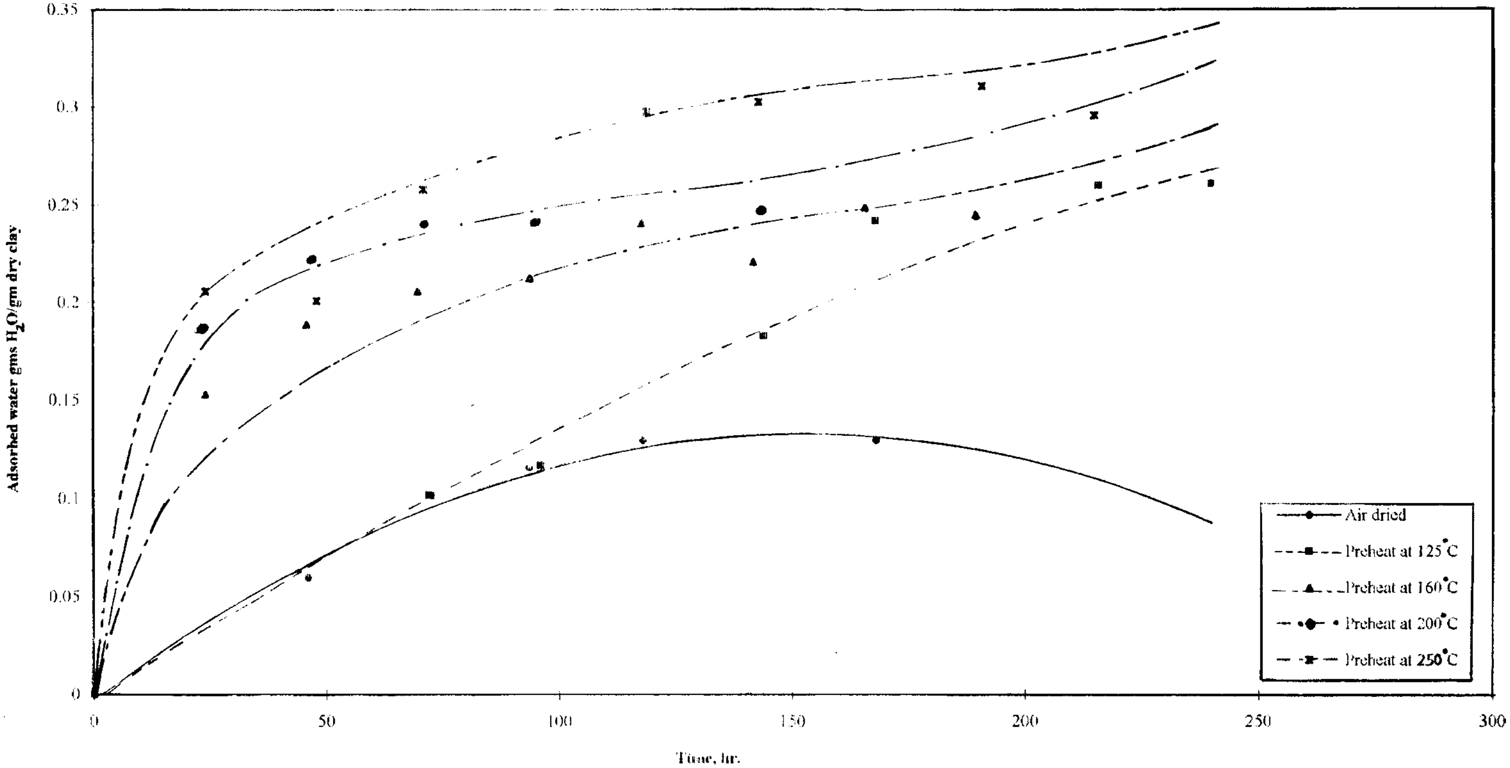

Fig. 1. The adsorption isotherms of water vapor on Ca-montmorillonite clay with different preheating conditions.

rehydration, after pre-heating at 250°C, Ca-M can adsorb more water due to the presence of a vacant site around the cation. If the amount of the adsorbed water exceeds 0.25 g H_2O/g dry clay, a two-layer hydrate state seems to be formed for Ca-M. Although these isotherms have irregular shapes, which is dependent on the pre-heating temperature that affects the structure of the adsorbing clay, each isotherm can be assigned to certain known type. This is also due to the complex mechanism of water adsorption. In general, for air-dried sample, the adsorption isotherm of Ca-M is concave to the time axis. This could be explained by the BET theory [13,15,17] which indicates that the energy of interaction of the Ca-M system between the first mono-layer of the adsorbed water molecules and the active surfaces is greater than the energy of condensation of the subsequent layers. In the case of Ca^{2+}, 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 concentration of a water vapor (amount of adsorption 0.23–0.25 g H_2O/g of dry clay), a two-layer hydrate state will be formed for all divalent cations on montmorillonite. A one-layer state may be formed on Ca-M. Therefore, the adsorption isotherms show a different behavior depending on the pre-heating temperatures.

According to the previous studies [12,13], the C-spacing of Ca-M is about 14 Å. This vacant volume is able to accommodate the maximum amount of water adsorption obtained in this study. This emphasizes the presence of two molecules of water at the montmorillonite surface.

The IR spectroscopic analysis was used to confirm the adsorption behavior of water vapor on clay that was suggested using the adsorption isotherm. Spectral hydration features in montmorillonite have been attributed to structural OH in the octahedral layer, water adsorbed on clay 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 cation. The infrared spectra of Ca-M hydrated with water vapor as well as the dried sample at 105°C are shown in Fig. 2 along the range 4000–600 cm^{-1} (2.5–16 μm).

Water exhibits three vibrational modes: a symmetric stretch, an asymmetric stretch and an H–O–H bend [20]. A weak band at about 3660 cm^{-1}, is assigned to lattice hydroxyls OH stretching mode which arise from the vibration of firmly bound H_2O. Also a strong broad band which has appeared at 3450 cm^{-1} can be attributed to the H–O–H stretching vibration of H_2O. This band which was lost upon heating, readily reflects the free H_2O adsorbed onto the structure and/or inter-laminar water OH stretch. The band near 1600 cm^{-1} is due to the water of crystallization bending vibration. The strong band near 1100 cm^{-1} is assigned to the Si–O bending vibration, while the Si–O–Si stretching vibration has appeared near 1040 cm^{-1} as a strong band. The 920 and 850 cm^{-1} bands were attributed to Al–OH and Mg–Al–OH groups, respectively. The band

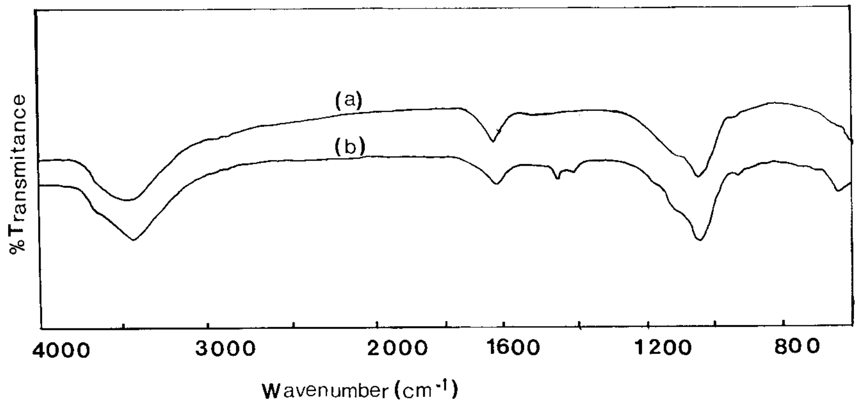

Fig. 2. The infrared spectra of Ca-M: (a) dried sample at 105°C, and (b) hydrated sample.

near 800 cm^{-1} is due to the skeletal vibrations of quartz.

The symmetric stretching modes involve motion along the H-bond axis and in the direction of the cation–oxygen bond which implies that the existing H-bonding and bonding with the interlayer cation should influence these vibrations.

The moisture content has been shown to influence H_2O bending vibration near 1640 cm^{-1}. However, many investigators [20,21] have observed spectral absorptions centered near 1625 cm^{-1} which was attributed for thin films of dry hectorite; a similar class to montmorillonite. The indicated wavenumber of 0% relative humidity hectorite showed a shift to a higher wavenumber, near 1635 cm^{-1}, for the same material with relative humidity up to 50%. A similar effect was noted in our study where a shift towards lower vibrational energy from 1640 to 1630 cm^{-1}, in Fig. 2, in the band of Ca-M has appeared upon heating the sample to 105°C. In contrast, the 3450 cm^{-1} IR band of the air-dried Ca-M is shifted to higher wavenumber, 3470 cm^{-1}, when the sample was subjected to dehydration. This implies that H-bonding in H_2O of the montmorillonite systems increases as the water content of the dehydrated montmorillonite increased.

The results indicated that 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.

These results indicate the presence of at least two kinds of interlayer water in montmorillonite: water that is readily removable through drying or heating up to 105°C, and water is held more firmly. The firmly bound water molecules are thought to form the inner hydration sphere of the interlayer cations (water bound directly to cations), while the readily removable water consists of outer sphere water molecules bonded through hydrogen bonds to each other in the inter layer region. The water molecules bound to the interlayer surface in montmorillonite have been predicted to have higher H–O–H stretching vibration than bulk water, but it is not uniformly accepted that these ‘surface’ bounded water molecules have significantly different H–O–H stretching vibration than other highly H-bonded interlayer water molecules.

The relative amount of the adsorbed water vapor to the clay surface can be elucidated through the IR spectroscopy data by applying Beer–Lambert equation [22,23], to the relative absorbance of the symmetric H–O–H stretch, appeared at 3450 cm^{-1}, to that for the stretching vibration of Si–O–Si, appeared at 1040 cm^{-1}. From the analysis of the IR data, this ratio was found to be equal to 0.69 for air-dried sample, and equal to 0.63 for dried one at 105°C. These values are attributed to absorption of various kinds of OH stretch of bound H_2O molecules, inner sphere and surface-bounded, and H_2O molecules in outer solvation shells.

The water loss upon heating of the clay has been by the thermal analysis data. The temperatures at which such changes occur are typical for various types of clay. Heating of clay, at a regular rate, causes the weight loss depending upon the retention of water inside or on the surface of the clay structures [9,24,25]. The DTA curves, shown in Fig. 3, exhibit a low-temperature strong endothermic peak at 100°C for the Ca-M, corresponding to the desorption of physically adsorbed water. This type of water has a very high kinetic energy. Such adsorbed water, which is held by less strong attraction, is found on the surface of the clay in defected sites of the silicate structure. The physically adsorbed water is usually present in small quantities, which is proportional to the surface area of the clay. There is another very weak endothermic peak, around 230°C, attributed to the expulsion of water supposedly bound to Ca cation and exhibit a very low kinetic energy. External water is bonded less strongly than interlayer water located around the cations, and it is, therefore, liberated at lower temperature. Semi-quantitative analysis can be applied assuming that the area under the low temperature endothermic peaks is proportional to the amount of adsorbed water which could be liberated from the surface of the clay [26].

The integral enthalpy of montmorillonite-water system could be calculated semi-quantitatively by using DTA results where the energy change of the whole system (clay, exchangeable cation, and the adsorbed water) is reached via this the calorimetric methods [27]. The adsorption isotherm at two different temperatures were not used as this method gives the enthalpy change of the water phase only.

The results show that the amount of the water released from the wet clay is increased with the increasing of the pre-heating temperature, as presented in Table 2. These results were confirmed with

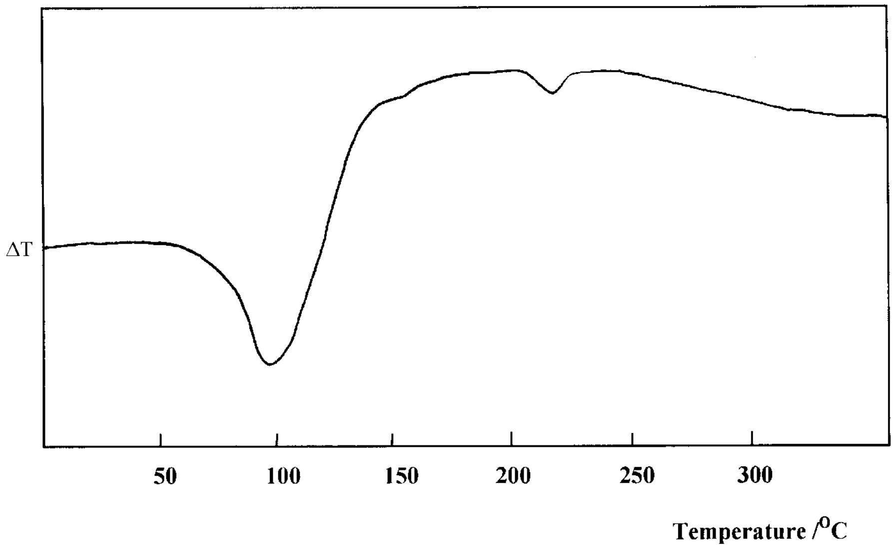

Fig. 3. DTA curve for Ca-montmorillonite.

that obtained by the Ca-M adsorption isotherms discussed earlier in this work. Also, it is interesting to note that the energy required for dehydration of the adsorbed water is determined from the area under the peak, which is observed between 50 and 200°C. In this region, heat is absorbed by the clay, required for the desorption (dehydration) of water adsorbed at the surface of the bentonite and coordinated with exchangeable Ca^{+2} cation. According to this phenomenon, the results show that, the energy storage of Ca-M systems increase as the pre-heating temperature increase. These values were obtained in the range between 435 and 487 cal/g as the pre-heating temperature increased from 125 to 250°C, respectively, as presented in Table 2.

Table 2
Summary of DTA data

Pre-heating temperature (°C)	Peak temperature (°C)	Peak area (cm^2)	Energy storage (cal/g)
125	100	14.1	435
160	100	14.5	447
200	100	14.5	447
250	100	15.8	487

The values of these energy storage densities for the used Ca-M system is high enough when compared to other systems applied for energy storage. For example, sodium salt hydrates which is considered as appropriate thermal energy storage materials, can store relatively about 43.0–65.0 cal/g. The stored value depends on the structure, which affects the water loss percent when the salt hydrates are subjected to the temperature swing above their melting points [28]. Also zeolites can exhibit a relatively high thermal energy storage density, from 40 to 70 cal/g depending on the pre-hydration temperature, when it was subjected to reversible direct hydration and dehydration [29]. Other new composite chemical heat storing materials were reported to have a capacity up to 478 cal/g [30].

The above mentioned data confirms that Ca-M clay can be considered as an efficient solar energy storage material and it fulfills the following criteria:

1. The material has heat-storing capacity up to 480 cal/g.
2. The handling of the materials is very easy and does not need sophisticated technology and/or equipment.
3. The material is commercially available at low cost.

Acknowledgements

The authors acknowledge the help of Prof. Dr. S.H. Kandil, Institute of Graduate Studies and Research, Alexandria University and Prof. Dr. F.F. Assaad, National Research Center, for their helpful suggestions and discussion during this study.

References

[1] J. Schröder, Thermal energy storage, in: Proceeding of the Third General Conference of the European Physical Society, Bucharest, Romania, 9–12 September 1975.

[2] R. Stockerl, H.H. Kohler, Dynamic investigations of the slow recrystallization of incongruently melting Glauber salt, Solar Energy 46 (1991) 167–173.

[3] T.L. Pryor, D.J. Close, Measurements of the behavior of adsorbed energy storage beds, Solar Energy 20 (1978) 151.

[4] A. Kanzawa, Y. Aria, Thermal energy storage by the chemical reaction augmentation of heat transfer and decomposition in CaO/CaOH powder, Solar Energy 27 (1981) 289.

[5] K. Kaygusuz, ö. Çomakli, T. Ayhan, Solar-assisted heat pump systems and energy storage, Solar Energy 47 (1991) 383–391.

[6] R.A. Shiggeishi, C.H. Langford, B.R. Hollebone, Solar energy storage using chemical potential changes associated with drying of zeolites, Solar Energy 23 (1979) 489–495.

[7] R. Gopal, B. Hollebone, C. Longford, R. Shigeishi, The rates of solar energy storage and retrieval in a zeolite water system, Solar Energy 27 (1981) 289.

[8] A.S.A. Ammar, M.A. El-osairy, A.A. Ghoneim, Comparison of measured and predicted performance of heat storage unit packed with spheres of a local material, Renewable Energy 2 (1992) 73–76.

[9] A.M. El-Shabiny, S.M. Hammad, I.A. Ibrahim, A.K. Ismail, Combined thermal and structural study of some Egyptian Bentonitic clays, J. Thermal Anal. 46 (1996) 1421–1435.

[10] C.T. Chiou, D.W. Rutherford, Effect of exchanged cation and layer charge on the sorption of water and EGME vapors on montmorillonite clays, Clays and Clay Minerals 45 (1997) 867–880.

[11] H. Van Olephan, Clay Colloid Chemistry, Interscience, New York, 1963.

[12] J.W. Kijne, On the interaction of water molecules and montmorillonite surfaces, Soil Sci. Soc. Am. Proc. 33 (1969) 539–543.

[13] J.M. Cases, I. Bèrend, M. François, J.P. Uriot, L.J. Michot, F. Thomas, Mechanism of adsorption and desorption of water vapor by homoionic montmorillonite. 3. The Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} exchanged forms, Clays and Clay Minerals 45 (1997) 8–22.

[14] W.K. Mekhamer, M.A. El-Gamal, M.A. Moussa, Effect of exchangeable cations on the properties of clay used in casting mold, in: Proceedings of the Second URE University Symposium on Materials Science, AL-AIN, 24–29 November 1998.

[15] R. Keren, I. Shainberg, Water vapor isotherms and heat of immersion of Na/Ca montmorillonite system. I. Homoionic clay, Clays and Clay Minerals 23 (1975) 193–200.

[16] R. Keren, I. Shainberg, Water vapor isotherms and heat of immersion of Na/Ca montmorillonite system. II. Mixed clay, Clays and Clay Minerals 27 (1979) 145–151.

[17] R.W. Moony, A.G. Keenan, L.A. Wood, Adsorption of water vapor by montmorillonite. I. Heat of adsorption and application of BET theory, J. Am. Chem. Soc. 74 (1952) 1367–1371.

[18] V.C. Farmer, Water on particle surface, in: D.J. Greenland, M.H. Hayes (Eds.), The Chemistry of Soil Constituents, Wiley, New York, 1978.

[19] P.L. Hall, D.M. Astill, Adsorption of water by homoionic exchange forms of Wyoming montmorillonite, Clays and Clay Minerals 37 (1989) 355–363.

[20] J.L. Bishop, C.M. Pieters, J.O. Edwards, Infrared spectroscopic analysis on the nature of water in montmorillonite, Clays and Clay Minerals 42 (1994) 702–716.

[21] V.C. Farmer, J.D. Russell, Interlayer complexes in layer silicates: the structure of water in lamellar ionic solution, Trans. Faraday Soc. 67 (1971) 2737–2749.

[22] L. Lerot, P.F. Low, Effect of swelling on the infrared absorption spectrum of montmorillonite, Clays and Clay Minerals 24 (1976) 191–199.

[23] C.T. Johnston, G. Sposito, C. Erickson, Vibrational probe studies of water interactions with montmorillonite, Clays and Clay Minerals 40 (1992) 722–730.

[24] A. Fudala, J. Halasz, I. Kiricsi, Thermogravimetric investigation, J. Thermal Anal. 47 (1996) 399–406.

[25] J. Bujdák, H. Slosiarikovà, Hydration and dehydroxylation of reduced charge montmorillonite, J. Thermal Anal. 41 (1994) 825–831.

[26] T. Daniels, Thermal Analysis, Kogan Page, UK, 1973.

[27] R. Keren, I. Shainberg, Water vapor isotherms and heat of immersion of Na/Ca montmorillonite system. III. Thermodynamics, Clays and Clay Minerals 28 (1980) 204–210.

[28] S.K. Sharma, C.K. Jotshi, S. Kumar, Thermal stability of sodium salt hydrates for solar energy storage applications, Solar Energy 45 (1990) 177–181.

[29] M. Selvidge, I.N. Miaoulis, Evaluation of reversible hydration reactions for use in thermal energy storage, Solar Energy 44 (1990) 173–178.

[30] E.A. Levitskij, Y.I. Aristov, M.M. Tokarev, V.N. Parmon, Chemical heat accumulators: a new approach to accumulating low potential heat, Solar Energy Mater. Solar Cells 44 (1996) 219–235.