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Thermal behavior and immersion heats of selected clays from Turkey

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Abstract Four clays (two bentonites and two kaolinites) from Turkey were investigated by X-ray diffraction (XRD), thermal analysis (DTA/TG-DSC) and surface area measurement techniques. Mineralogically bentonite samples were characterized low concentration of montmorillonite and high level of impurities. Both kaolinite samples mainly contained kaolinite and quartz as major mineral. TG-DTA curves of all clay samples were measured in the temperature range 30–1200 °C. The total % weight losses for the bentonite samples (B1 and B2) and the kaolinite samples (K1 and K2) were determined as 14.50, 13.42, 5.55 and 11.85%, respectively. Differential Scanning Calorimeter (DSC) analyses of samples were carried out by heating the samples from 30 to 550 °C. The immersion heats of clay samples were measured using with a Calvet-type C-80 calorimeter. The higher exothermic Q_{imm} values were determined for bentonite samples compared to kaolinite samples.

Keywords Bentonite · Kaolinite · Montmorillonite · Thermal analysis · XRD · Immersion heat

Introduction

Clay is usually defined as any very fine grained, naturally occurred material that becomes plastic when mixed with a small amount of water and hardens when dried or fired [1]. Bentonite and kaolinite are natural clay minerals-hydrated aluminium silicate. The most common dominant mineral in bentonite is montmorillonite which belongs to the group of silicate minerals known as dioctahedral smectites [2]. Montmorillonite is a group of smectite clay. Smectite group includes montmorillonite, beidelite, nontronite (dioctahedral smectites), and saponite, hectorite (trioctahedral smectites) [3]. Smectite is 2:1 layer clay mineral formed by one alumina octahedral sheet placed between two silica tetrahedral sheets. Feldspar, zeolites, carbonates and silica polymorphs (quartz and opals) may be found in bentonites in different extent as nonclay minerals. Minor clay minerals generally found in bentonites is illite (I) [4]. Bentonites and their major clay minerals smectites are among the most important industrial raw materials [5–7]. The application areas of bentonites depend on quality and quantity of their smectites and other clay and non-clay minerals [8, 9]. Some physico-chemical properties of bentonites as well as mineralogy are greatly affected by thermal treatment. Due to these effects, the investigation of thermal behavior of bentonite samples has a great importance.

Kaolinite has a 1:1 layer structure composed of a tetrahedral layer of SiO_4 and an octahedral layer with Al^{+3} as the octahedral cation [10]. The summits of the octahedra are exclusively hydroxyl units. The intermediate anion sites are occupied by both oxygens and hydroxyls [11]. Successive 1:1 layers are bound to each other by hydrogen bonding of adjacent silica and alumina layers [12].

Kaolinite clays are widely used in various industrial applications, such as production of ceramics, paper, pigments, cosmetics, etc. Knowledge of the structural and surface properties of kaolinite is essential in optimizing the above mentioned applications. The major property, which determines the utility of the clay for various applications, is its purity. Pure kaolinite ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$) is white in color and its theoretical composition expressed in terms of the oxides is 46.54% SiO_2, 39.50% Al_2O_3 and 13.96%

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H_2O. Presence of impurities, especially iron- and titanium-bearing materials, imparts color to kaolin. The mined kaolin is usually associated with various impurities like quartz, anatase, rutile, pyrite, siderite, feldspar, etc., depending on the origin and depositional environment [13]. These impurities damage the characteristics of the kaolin and affect its usefulness for various applications.

There are large bentonite and kaolinite reserves in different regions of Turkey. There are numerous studies regarding the thermal properties of clays [14–43]. However, there has not been enough study in literature about the thermal properties of Turkey clays. The main objective of this study is to investigate four clay samples from Turkey, in terms of their clay types, chemical compositions, immersion heats and thermal properties.

Experimental

Material

The bentonite samples named: B1 and B2. The B1 sample was obtained from Çankırı and the other bentonite sample (B2) was from Mihalıcık, Turkey. The kaolinite samples labeled as K1 and K2 obtained from Bilecik and Eskisehir regions, respectively. The samples were air dried at room temperature and ground to pass through a <100 μm sieve.

Instrumentation

The XRD diffractograms were obtained with a RINT-2200 instrument, using CuKα radiation ($\lambda = 1.54$ Å) at 40 kV and 20 mA, in the range 3–40° 2θ. The samples were scanned with a step of 0.02° 2θ.

Simultaneous TG-DTA experiments were carried out using a Setsys Evolution Setaram thermal analyzer. Approximately 40 mg of sample was used in each run. All experiments were performed at a linear heating rate of 10 °C min^{-1} over the temperature range of 30–1200 °C.

Differential Scanning Calorimetric (DSC) analyses of samples were carried out by heating the samples from 30 to 550 °C at 5 °C min^{-1} rate using a Setaram DSC 151 analyser.

BET surface areas were calculated from the first part of the N_2 adsorption isotherm ($P/P_o < 0.3$) obtained at liquid nitrogen temperature with N_2 in Autosorb-1C equipment previously degassed at 125 °C for 6 h prior to measurement. High-purity (99.99%) nitrogen was used in adsorption measurements.

The enthalpies of immersion (in water) of the clay samples were determined with a Setaram Calvet-type C 80 Immersion Calorimeter at 30 °C. In order to remove the adsorbed water, about 400 mg of material was heated for 24 h at 120 °C before each calorimetric experiment.

Results and discussion

Characterization of bentonite and kaolinite clays

Four local samples were investigated through chemical analysis. The chemical analysis of clay samples was carried out and the data were presented in Table 1. The chemical composition of bentonite samples indicates the presence of silica and alumina as major constituents, along with traces of sodium, potassium, iron, magnesium, calcium and titanium oxides in the form of impurities. As shown in this table, the weight percent of calcium contained in the bentonite samples is higher than that of sodium. The MgO content ranges between 2 and 4.5%. In both cases, the Fe_2O_3 content is high, about 4–8%.

The K1 clay is rich in SiO_2 (77.5%) and poor in Al_2O_3 (10%). Its loss on ignition (LOI) value is low (7.11%). The chemical composition indicates presence of considerable amounts of silica-bearing impurity in the clay. The SiO_2 (50.37%) content of the K2 sample are considerably less and Al_2O_3 (34.64%) content and LOI value (11.79%) are more than those of the K1 sample (Table 1). Some metals as Fe_2O_3, TiO_2, K_2O and MgO have higher content in the K1 sample than the K2 sample. As seen from Table 1, concentrations of SiO_2 greater than the theoretical value can be explained by the presence of various amounts of quartz in both of kaolinite samples as indicated by X-ray diffraction [13].

Table 1 Chemical analyses in oxides % for natural clay samples

Chemical analysis	B1	B2	K1	K2
SiO_2 (%)	50.32	42.46	77.57	50.37
Al_2O_3 (%)	13.86	10.82	10.05	34.64
Fe_2O_3 (%)	4.72	7.83	1.92	0.81
Na_2O (%)	2.72	2.23	–	0.16
K_2O (%)	0.90	2.29	0.57	1.31
CaO (%)	4.23	3.06	1.31	0.22
MgO (%)	2.46	4.59	0.78	0.31
TiO_2 (%)	0.61	0.83	0.40	0.19
SO_3 (%)	0.66	0.06	0.26	0.02
MnO (%)	0.03	0.12	–	–
P_2O_5 (%)	0.06	0.06	–	0.13
Others	0.25	0.30	0.03	0.05
LOI (%)	19.18	25.35	7.11	11.79

X-ray diffraction

The XRD patterns of the bentonite and kaolinite samples are illustrated in Figs. 1 and 2. The B1 sample (Fig. 1) mainly contained montmorillonite (14.96 and 4.45 Å). Some accessory minerals such as calcite (3.03 and 2.49 Å), albite as plagioclase (3.18 and 2.56 Å) and quartz (4.26, 3.34 and 2.28 Å) are observed. Besides containing clay minerals such as montmorillonite (13.50, 4.50 and 2.56 Å) and illite (2.95 Å), the B2 bentonite contained also quartz (4.26, 3.34 and 2.45 Å), albite (3.19 Å), cristobalite (4.03 Å) and dolomite (2.89 Å). These minerals were identified by their characteristic XRD peaks [13]. Mineralogically bentonite samples were characterized low concentration of montmorillonite and high level of impurities. The estimated montmorillonite contents are less than 50%.

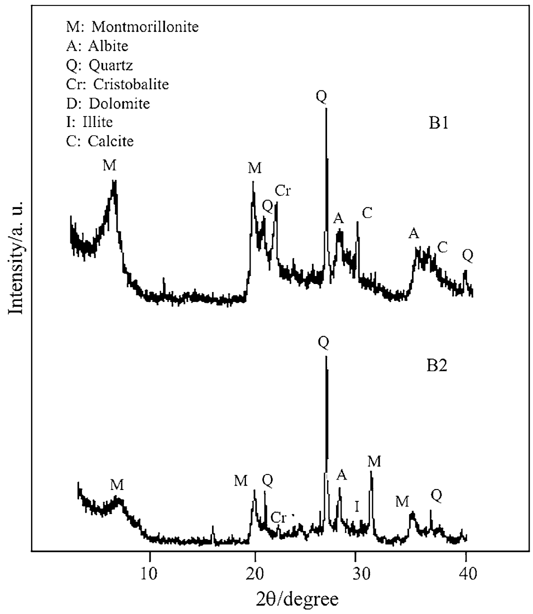

Fig. 1 XRD patterns of the natural B1 and B2 bentonite samples

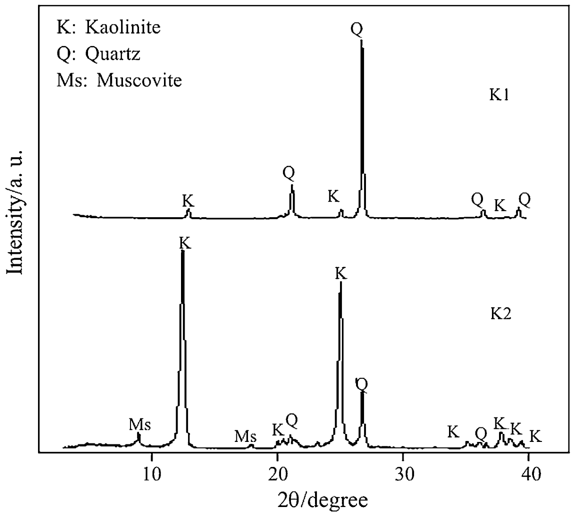

Fig. 2 XRD patterns of the natural K1 and K2 kaolinite samples

The XRD pattern of the K1 clay (Fig. 2) showed sharp peaks at $d = 7.15$, 4.45 and 3.57 Å due to kaolinite and $d = 4.25$, 3.34, 2.45 and 2.28 Å due to quartz, indicating that the later was the major contaminant of the clay. The XRD pattern of the K2 clay (Fig. 2) exhibited prominent peaks due to kaolinite ($d = 7.17$, 4.36, 3.85, 3.58 and 2.38 Å) and quartz ($d = 4.26$, 3.34 and 2.45 Å) and muscovite ($d = 10.03$ and 5 Å). The basal spacing of the K2 sample (7.17 Å) was slightly bigger than that of the K1 sample (7.15 Å).

Specific surface area

Applications of BET model give the specific surface areas of 94 m^2/g, 116 m^2/g, 9 m^2/g and 16 m^2/g for natural B1, B2, K1 and K2 samples, respectively. The nitrogen adsorption isotherms on all the samples at 77 K are given in Figs. 3 and 4. The shape of N_2 adsorption isotherms of the samples correspond to the type II [44] according Gregg and Sing [45]. It is found that BET surface area of the B1 bentonite was low compared to the B2 bentonite. The N_2-BET specific surface area for the K2 was nearly twice as large as obtained value for K1. The presence of considerable amount of quartz in the K1 sample may affect its surface area.

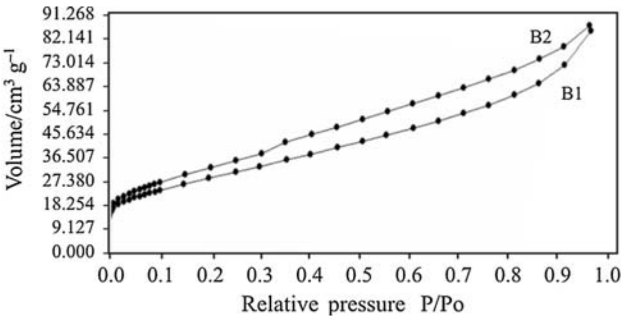

Fig. 3 The isotherms of the adsorption of nitrogen on the natural B1 and B2 bentonite samples

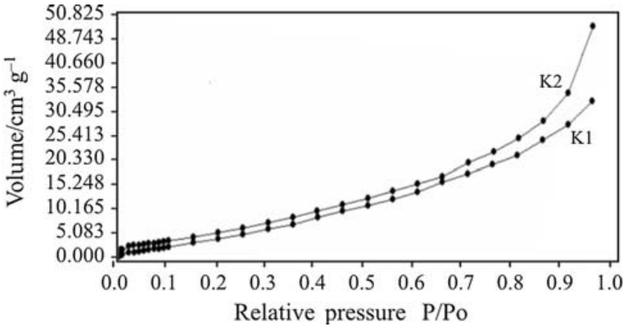

Fig. 4 The isotherms of the adsorption of nitrogen on the natural K1 and K2 kaolinite samples

Thermal properties

Any physical, physicochemical and/or chemical transformation takes place with a thermal effect, which leads to a difference between the sample and reference temperature. Thus, the respective endo- or exothermic peaks shown in DTA curves are very useful ways to establish transformations with or without mass loss and have been used as one of the major tools for qualitative clay characterization [46, 47].

Many studies have been devoted to the behavior of kaolinite on heating. Below 670 K, a reversible dehydroxylation event occurs. Above 670 K kaolinite undergoes an irreversible change containing the loss of structurally bonded water, indicated by an endothermic peak in a DTA curve [48].

The DTA curve of the K1 sample shows three endothermic peaks (Fig. 5a). The DTA curve of this sample shows two small endothermic peaks at 156 and 271 °C corresponding to the loss of adsorbed and interlayer water. The third peak at 577 °C corresponds to the loss of the structural OH of kaolinite. After the three endothermic events, only a less intense exothermic peak at ~1000 °C reflecting the crystallization of new phase is recorded.

DTA curve of K2 sample (Fig. 5b) shows a sharp endothermic kaolinite dehydroxylation peak at 539 °C and, as the mineral has a high purity degree, a sharp exothermic peak occurs at 994 °C. The K2 sample loses its constitutional-OH groups in the endothermic peak temperature range and forms metakaolinite. This endothermic peak (Fig. 5b) is in good agreement with the reported DTA curve shown by previous authors for well crystallized kaolinites [15]. The occurrence of exothermic peak was due to formation of spinal phase.

Mass changes of the samples studied plotted as a function of temperature are shown in Fig. 5a and b. The TGA curves for both samples exhibit a similar two-step weight loss. The first step (starting at 30 °C) corresponds to the thermodesorption of physically adsorbed water. The second one (starting at 400 °C) reflects the loss of structurally bonded water. The total loss of K1 and K2 were determined as 5.55 and 11.85%, respectively.

TG and DTA curves of the natural bentonite samples are given in the Fig. 6a and b for the temperature range of 30–1200 °C and the related mass losses are given in Table 2. Figure 6a and b shows the mass loss of bentonite samples with the increasing temperature.

The amount of water uptake of the bentonite samples depend on the relative humidity of the environment to which they are exposed [32]. The endothermic peaks of the B1 (Fig. 6a) are attributed to the evolution of moisture and interlayer water up to 200 °C. The structural OH groups are removed in the region 400–800 °C. The first endothermic mass loss 8.25% between 30 and 400 °C for the B1 sample is due to the dehydration of interparticle water, adsorbed water and interlayer water. The second endothermic mass loss 5.74% between 400 and 800 °C with the maximum rates at 492 and 703 °C are due to the formation of the dehydroxylation water.

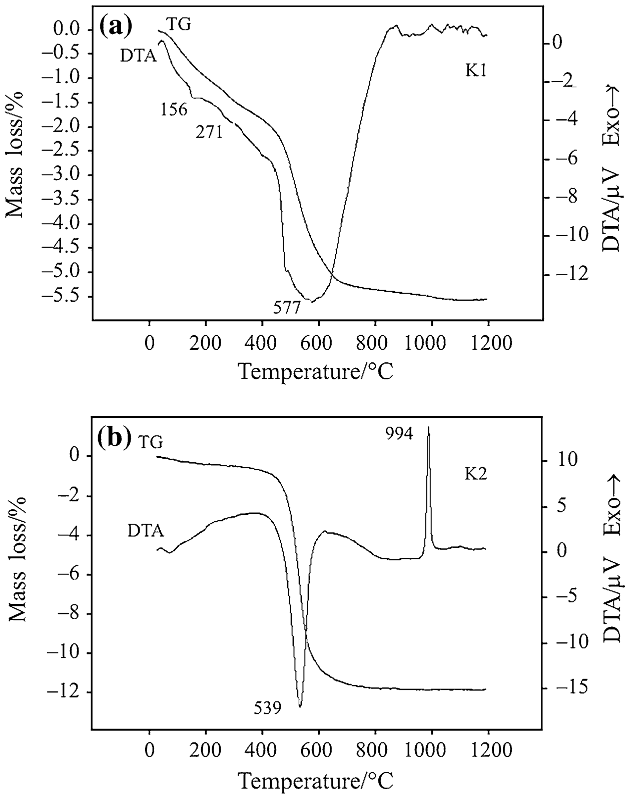

Fig. 5 Thermogravimetric analysis (TG) and differential thermal analysis (DTA) curves for the kaolinite samples

The thermal properties of the B2 are shown in Fig. 6b, where the DTA curve have the endothermic peaks at 107, 503 and 746 °C and exothermic peak at high temperature above 1000 °C. The DTA thermogram of the B2 sample exhibits low-temperature endothermic peak at about 107 °C within adsorbed and exchangeable cation coordinated water is released. Dual endothermic peaks at 503 and 746 °C represented dehydroxylation of sample. Exothermic peak at high temperature above 1000 °C corresponds mainly due to crystallization of new phases. The temperature interval and mass loss percentage by the dehydration, dehydroxylation, amorphization and recrystallization are observed from the DTA and TG curves as 30–400 °C and 5.51%, 400–800 °C and 7.58%, 800–1200 °C and 0.33%, respectively. The total water content of B1 and B2 were determined as 14.5 and 13.42%, respectively. The results are summarized in Tables 2 and 3.

The results of the DSC analysis for kaolinite and bentonite samples are presented in Figs. 7 and 8, respectively. The K1 sample (Fig. 7a) shows one endothermic peak at 179 °C, attributed to elimination of adsorbed (or absorbed)

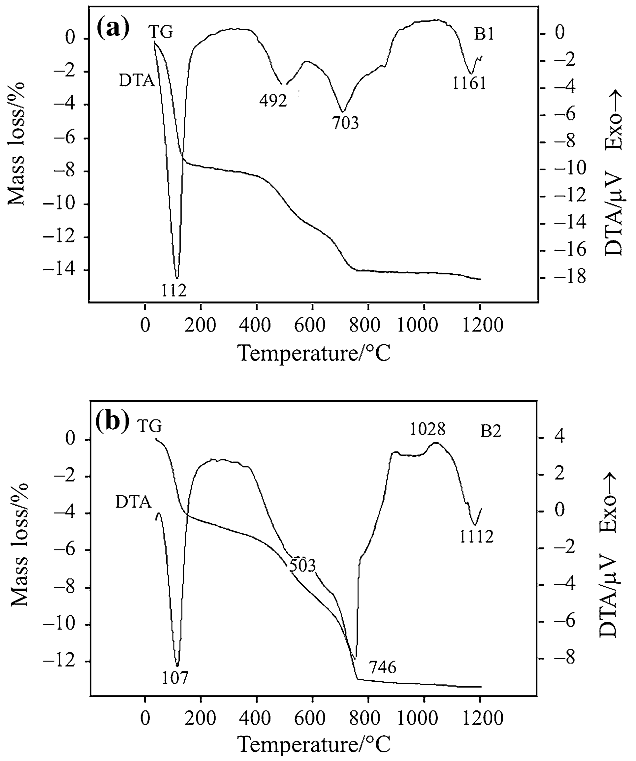

Fig. 6 Thermogravimetric analysis (TG) and differential thermal analysis (DTA) curves for the bentonite samples

Table 2 Water loss-TG of the kaolinite samples

Sample	30–400 °C	400–1200 °C	Total %
K1	1.84	3.71	5.55
K2	0.70	11.15	11.85

Table 3 Water loss-TG of the bentonite samples

Sample	30–400 °C	400–800 °C	800–1200 °C	Total %
B1	8.25	5.74	0.51	14.50
B2	5.51	7.58	0.33	13.42

water, and one peak centered at 508 °C, attributed to a dehydroxylation process to metakaolinite [49]. The K2 sample (Fig. 7b) shows one endothermic peak centered at 198 °C, corresponding to elimination of absorbed and adsorbed water. The other peak centered at 532 °C corresponds to elimination of crystallization water.

DSC curve for B1 sample (Fig. 8a) up to 450 °C showed an intense loss of water at 108 and 227 °C, which is attributed to the loss of interlayer water. The B2 sample (Fig. 8b) in the range of 50–270 °C exhibited two endothermic peaks at 125 and 217 °C. In this region, heat is absorbed for the dehydration of interlayer water contained in the bentonite samples. In addition, the B2 clay showed an endothermic peak at 486 °C, which was assigned to the dehydration and loss of crystal structure.

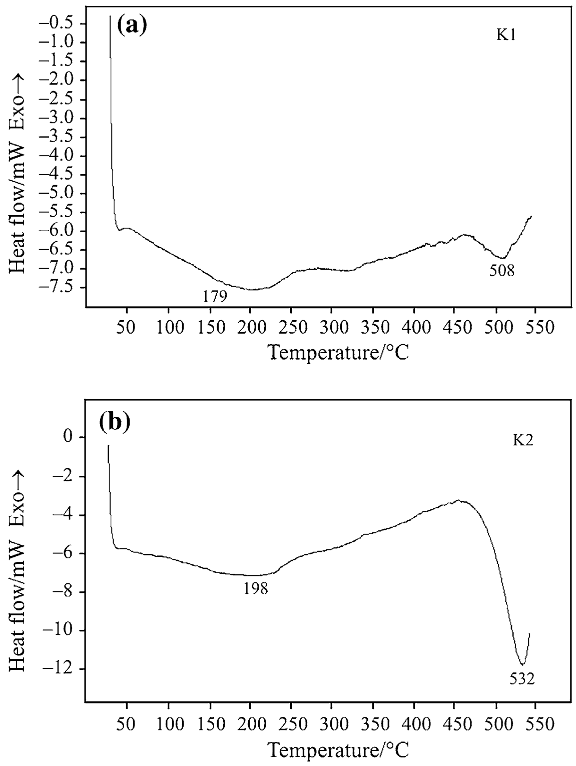

Fig. 7 Differential scanning calorimeter (DSC) curves for the kaolinite samples

Heats of immersion

The immersion is the process where a solid–liquid interface is created starting from a pure liquid surface and a pure solid phase [50]. When a solid is immersed into a non-reacting liquid a given amount of heat is evolved [51]. This measured heat is known as immersion heat, Q_{imm} (J/g). Many researchers have been investigated immersion heat values of clay minerals in liquid water [50, 52–58].

In these immersion experiments, water was used as immersion liquid for clay samples with hydrophilic surfaces. The whole system is located into the calorimeter and time is allowed for temperature equilibration between the sample set-up and the calorimeter. Once the thermal equilibrium was achieved in calorimeter, the ampoule of sample container was broken and the liquid water allowed to entering into the ampoule and wets the sample. The heat flow evolution was monitored as a function of time. Integration of this signal gives the total experimental heat of immersion.

The measurement of immersion heats with a Calvet calorimeter is a simple and convenient method. When montmorillonite clays are in contact with water or water vapor, the water molecules penetration between the unit layers through hydrogen bonds between water molecules and the hydroxyl group on clay structure cause an

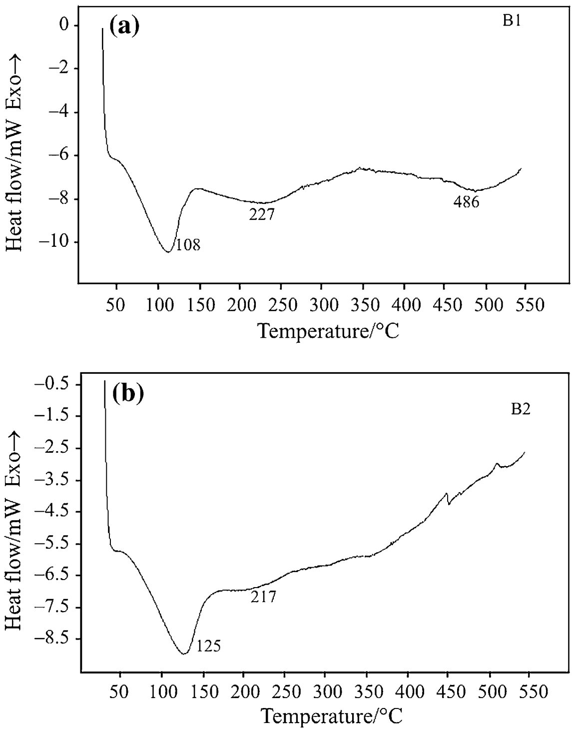

Fig. 8 Differential scanning calorimeter (DSC) curves for the bentonite samples

Table 4 BET surface areas and immersion heats of the natural clay samples

Sample	BET surface area/m^2/g	Immersion heat/J/g
B1	94	−39.19
B2	116	−30.45
K1	9	−3.18
K2	16	−5.13

exothermic reaction [59]. The heats of immersion of the bentonite samples (B1 and B2) and the kaolinite samples (K1 and K2) measured with a Calvet calorimeter at 30 °C were determined as −39.19 J/g, −30.45 J/g, −3.18 J/g and −5.13 J/g, respectively (Table 4). The presented values are generally the average values of three experiments.

Conclusions

In the present work, clay samples were characterized using X-ray diffraction (XRD), thermal analysis (DTA/TG-DSC) and surface area measurement methods. Both the mineral and chemical purities of the powder samples were established.

The results of this investigation show that the bentonite sample (B1) from Çankırı, Turkey, mainly consists of montmorillonite with varying amounts of quartz, albite, cristobalite and calcite. The other bentonite sample (from Mihalıcık, Turkey) contains montmorillonite as major clay mineral and less amount of illite as other clay mineral. The rest are albite as plagioclase, cristobalite, quartz and dolomite.

It was determined that the Bilecik kaolin (KI) mainly contained kaolinite and quartz as the major mineral. The K2 sample showed a predominant simple phase as kaolinite and also muscovite phases as clays, and quartz as impurity. Minor quartz was present in K2 sample compared to KI sample.

In the DTA/TG curves, both bentonite samples studied in this research exhibit three endothermic effects on heating. The first and dominant endothermic mass losses of 8.25 and 5.51% between 30 and 400 °C for the B1 and B2 bentonite samples, respectively are due to the dehydration of interparticle water, adsorbed water and interlayer water. The bentonite clay minerals showed two endotherms between 400 and 800 °C which evidences dehydroxylation of the silicate minerals. Above this temperature, the loss of water was accompanied by a slight change in the dimensions of the structure.

It was determined that the DTA curves of K1 and K2 clay samples showed two endothermic peaks between 100 and 300 °C corresponding to the loss of adsorbed and interlayer water. The peaks between 400 and 800 °C corresponded to the loss of the structural OH of kaolinite and associated with kaolinite–metakaolinite phase transition. The exothermic peak at 994 °C was related to the appearance of new crystallization.

It was observed that the DSC curve of the K1 and K2 samples showed one endothermic peak up to 200 °C, attributed to elimination of adsorbed water, and one peak in the range of 500–535 °C, ascribed to the dehydroxylation process to metakaolinite. DSC curves of bentonite samples exhibited that endothermic reaction took place between 100 and 250 °C corresponding to water loss from the clay surface and interlayered space. At about 500 °C, the second endotherm was concerning the beginning of the collapse of the interlayered structure.

The heats of immersion of the bentonite samples (B1 and B2) and the kaolinite samples (K1 and K2) were measured with a Calvet calorimeter at 30 °C. The higher exothermic Q_{imm} values were determined for bentonite samples compared to kaolinite samples.

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References

1. Guggenheim S, Martin RT. Definition of clay and clay mineral; joint report of the AIPEA nomenclature and CMS nomenclature committees. Clays Clay Miner. 1995;43:255–6.
2. Paluszkiewicz C, Holtzer M, Bobrowski A. FTIR analysis of bentonite in moulding sands. J Mol Struct. 2008;880:109–14.
3. Brown G. Crystal structure of clay minerals and related phyllosilicates. Phil Trans R Soc Lond A. 1984;311:221–40.
4. Moore DM, Reynolds RC. X-ray diffraction and the identification and analysis of clay minerals. 2nd ed. Oxford: Oxford University Press; 1997.
5. Murray HH. Applied clay mineralogy today and tomorrow. Clay Miner. 1999;34:39–49.
6. Murray HH. Overview: clay mineral application. Appl Clay Sci. 1991;5:379–95.
7. Grim RE. Applied clay mineralogy. New York: McGraw Hill; 1962.
8. Grim RE. Clay mineralogy. 2nd ed. New York: McGraw Hill; 1968.
9. Grim RE, Güven N. Bentonites-geology, mineralogy, properties and uses: developments in sedimentology, vol. 24. New York: Elsevier; 1978.
10. Pauling L. The structure of chlorites. Proc Natl Acad Sci USA. 1930;16:578–82.
11. Velde B. Introduction to clay minerals: chemistry, origins, uses and environmental significance. 1st ed. London: Chapman & Hall; 1992.
12. White GN, Dixon JB. Kaolin-serpentine minerals. In: Dixon JB, Schulze DG, editors. Soil mineralogy with environmental applications. Madison: Soil Science Society of America; 2000. p. 431–66.
13. Grimshaw RW. Physics and chemistry of clay. 4th ed. London: Ernest Benn; 1971.
14. Dweck J. Qualitative and quantitative characterization of Brazilian natural and organophilic clays by thermal analysis. J Therm Anal Calorim. 2008;92:129–35.
15. Chakraborty AK. New data on thermal effects of kaolinite in the high temperature region. J Therm Anal Calorim. 2003;71:799–808.
16. Kristóf J, Frost RL, Horváth E, Kocsis L, Inczédy J. Thermoanalytical investigations on intercalated kaolinites. J Therm Anal Calorim. 1998;53:467–75.
17. Castelein O, Soulestin B, Bonnet JP, Blanchart P. The influence of heating rate on the thermal behaviour and mullite formation from a kaolin raw material. Ceram Int. 2001;27:517–22.
18. Hart RD, Gilkes RJ, Siradz S, Singh B. The nature of soil kaolins from Indonesia and western Australia. Clays Clay Miner. 2002;50:198–207.
19. Sei J, Abba Touré A, Olivier-Fourcade J, Quiquampoix H, Staunton S, Jumas JC, et al. Characterization of kaolinitic clays from the Ivory Coast (West Africa). Appl Clay Sci. 2004;27:235–9.
20. Saikia NJ, Bharali DJ, Sengupta P, Bordoloi D, Goswamee RL, Saikia PC, et al. Characterization, beneficiation and utilization of a kaolinite clay from Assam, India. Appl Clay Sci. 2003;24:93–103.
21. Felhi M, Tlili A, Gaied ME, Montacer M. Minerological study of kaolinitic clays from Sidi El Bader in the far north of Tunisia. Appl Clay Sci. 2008;39:208–17.
22. Chakraborty AK. DTA study of preheated kaolinite in the mullite formation region. Thermochim Acta. 2003;398:203–9.
23. Souza GP, Sanchez R, de Holanda JNF. Characteristics and physical-mechanical properties of fired kaolinitic materials. Ceramica. 2002;48:102–7.
24. El-Shabiny M, Hammad SM, Ibrahim IA, Ismail AK. Combined thermal and structural study of some Egyptian bentonitic clays. J Therm Anal Calorim. 1996;46:1421–35.
25. Sinha MK, Gulha SK. Mineralogical studies on five plastic fire clays. J Therm Anal Calorim. 1992;38:1405–13.
26. Rue JW, Ott WR. Scanning electron microscopic interpretation of the thermal analysis of kaolinite. J Therm Anal Calorim. 1974;6:513–9.
27. Palomba M, Porcu R. Thermal behaviour of some minerals. J Therm Anal Calorim. 1988;34:711–22.
28. Lombardi B, Baschini M, Torres Sánchez RM. Bentonite deposits of Northern Patagonia. Appl Clay Sci. 2003;22:309–12.
29. Hassan MS, Abdel-Khalek NA. Beneficiation and applications of an Egyptian bentonite. Appl Clay Sci. 1998;13:99–105.
30. Tabak A, Afsin B, Caglar B, Koksal E. Characterization and pillaring of a Turkish bentonite (Resadiye). J Colloid Interface Sci. 2007;313:5–11.
31. Önal M, Sarikaya Y. Thermal behavior of a bentonite. J Therm Anal Calorim. 2007;90:167–72.
32. Kök MV. Thermogravimetry of selected bentonites. Energy Sources. 2002;24:899–907.
33. Noyan H, Önal M, Sarıkaya Y. Thermal deformation thermodynamics of a smectite mineral. J Therm Anal Calorim. 2008; 91:299–303.
34. Gates WP, Anderson JS, Raven MD, Churchman GJ. Mineralogy of a bentonite from Miles, Queensland, Australia and characterization of its acid activation products. Appl Clay Sci. 2002; 20:189–97.
35. Volzone C, Cesio AM. Structural modifications of OH-Cr smectites after thermal treatment up to 1000°C. Mater Chem Phys. 1997;48:216–9.
36. Volzone C, Torres Sanchez RM. Thermal and mechanical effects on natural and activated smectite structure. Colloids Surf A Physicochem Eng Asp. 1993;81:211–6.
37. Volzone C, Aglietti EF, Scian AN, Porto Lopez JM. Effect of induced structural modifications on the physicochemical behavior of bentonite. Appl Clay Sci. 1987;2:97–104.
38. Kloprogge JT, Evans R, Hickey L, Frost RL. Characterisation and Al-pillaring of smectites from Miles, Queensland (Australia). Appl Clay Sci. 2002;20:157–63.
39. Besq A, Malfoy C, Pantet A, Monnet P, Righi D. Physicochemical characterisation and flow properties of some bentonite muds. Appl Clay Sci. 2003;23:275–86.
40. Balek V, Malek Z, Yariv S, Matuschek G. Characterization of montmorillonite saturated with various cations. J Therm Anal Calorim. 1999;56:67–76.
41. Gal M. Quantitative estimation of kaolin in soil clays by differential thermal analysis. J Therm Anal Calorim. 1991;37: 1621–5.
42. Hlavaty V, Fajnor VS. Thermal stability of clay/organic intercalation complexes. J Therm Anal Calorim. 2002;67:113–8.
43. Malek Z, Balek V, Garfinkel-Shweky D, Yariv S. The study of the dehydration and dehydroxylation of smectites by emanation thermal analysis. J Thermal Anal Calorim. 1197;48:83–92.
44. Brunauer S, Deming LS, Deming DM, Teller E. On a theory of the van der Waals adsorption of gases. J Am Chem Soc. 1940; 62:1723–32.
45. Gregg SJ, Sing KSW. Adsorption, surface area and porosity. 2nd ed. London: Academic Press; 1982.
46. Harmelin M. La thermo-analyse. Paris: Presses Universitaires de France; 1968.
47. Santos PS. Science and technology of clays. 2nd ed. Sao Paulo: Edgard Blücher; 1989.
48. Fripiat JJ, Toussaint F. Prehydroxylation state of kaolinite. Nature. 1960;186:627–8.

49. Frost RL, Vassallo AM. The dehydroxylation of the kaolinite clay minerals using infrared emission spectroscopy. Clays Clay Miner. 1996;44:635–51.
50. Haouzi A, Salles F, Henry M, Douillard JM. Thermodynamic analysis of the immersion of a smectite substituted with Na or Ca: heat effect due to the cation. J Colloid Interface Sci. 2007; 307:531–42.
51. Silvestre-Albero J, Gomez de Salazar C, Sepulveda-Escribano A, Rodriguez-Reinoso F. Characterization of microporous solids by immersion calorimetry. Colloids Surf A Physicochem Eng Asp. 2001;187–188:151–65.
52. Salles F, Henry M, Douillard JM. Determination of the surface energy of kaolinite and serpentine using PACHA formalism—comparison with immersion experiments. J Colloid Interface Sci. 2006;303:617–26.
53. Kraehenbuehl F, Stoeckli HF, Brunner F, Kahr G, Mueller-Vonmoos M. Study of the water-bentonite system by vapour adsorption, immersion calorimetry and X-ray techniques; I, Micropore volumes and internal surface areas, following Dubinin's theory. Clay Miner. 1987;22:1–9.
54. Kahr G, Kraehenbuehl F, Stoeckli HF, Mueller-Vonmoos M. Study of the water-bentonite system by vapour adsorption, immersion calorimetry and X-ray techniques; II, Heats of immersion, swelling pressures and thermodynamic properties. Clay Miner. 1990;25:499–506.
55. Zoungrana T, Berrada A, Douillard JM, Partyka S. Competitive interactions between water and organic solvents onto mineral solid surfaces studied by calorimetry. Langmuir. 1995;11:1760–7.
56. Keren R, Shainberg I. Water vapor isotherms and heat of immersion of Na/Ca montmorillonite system. I. Homoionic clay. Clays Clay Miner. 1975;23:193–200.
57. Douillard JM, Salles F, Devautour-Vinot S, Manteghetti A, Henry M. Study of the surface energy of montmorillonite using PACHA formalism. J Colloid Interface Sci. 2007;306:175–82.
58. Medout-Marere V, Malandrini H, Zoungrana T, Douillard JM, Partyka S. Thermodynamic investigation of surface of minerals. J Pet Sci Eng. 1998;20:223–31.
59. Van Olephan H. Clay colloid chemistry. New York: Interscience; 1963.