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Spectroscopic and thermal studies of bentonites from Ünye, Turkey

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ABSTRACT

Three bentonites from Turkey were investigated by X-ray diffraction (XRD), X-ray fluorescence (XRF), differential thermal analysis (DTA), thermogravimetric analysis (TG), Fourier transform infrared (FT-IR), magic angle spinning nuclear magnetic resonance (MAS NMR) and surface area measurement techniques. The XRD patterns showed that all three bentonite samples (B1, B2 and B3) were mainly composed of montmorillonite accompanied by cristobalite. In addition, albite appears in B3 sample studied. The heats of immersion of the bentonite samples (B1, B2 and B3) measured with a Calvet calorimeter at 30 °C in water were determined as −75.70, −54.69 and −68.22 J/g, respectively.

1. Introduction

Bentonite contains mainly montmorillolinite which is the most common clay of the dioctahedral smectites group [1–3]. The smectite is the most important mineralogical component in bentonite and it is a 2:1 layer clay mineral formed by an octahedral (O) sheet containing Al^{+3} and Mg^{+2} ions placed between two Si tetrahedral (T) sheets [4,5]. The negative charge of the 2:1 (TOT) layers produced from the isomorphic substitution of Al^{+3} for Si^{+4} in the tetrahedral layer and Mg^{+2} for Al^{+3} in the octahedral layer is generally balanced by the exchangeable Na^{+} and Ca^{+2} cations between the TOT layers and around the edges [6–8]. The major smectite minerals are sodium montmorillonite, calcium montmorillolinite, saponite, nontronite, beidellite and hectorite [1,9].

Bentonites and their major clay mineral smectites have wide range of uses in many industrial applications in oil, petroleum, cosmetics, perfume, ceramics and paintings [2,6,7,10]. The applications areas of the bentonite vary depending on the kinds and amounts of its constituents such as smectites, other clay minerals and non-clay minerals such as quartz, calcite, dolomite and feldspar [2,11]. There are large bentonite reserves in different regions of Turkey. In order to use these bentonites more efficiently, their structural and thermal properties need to be investigated. The aim of this study is to present mineralogical, structural and thermal properties of clays from Ünye region of Turkey to evaluate their potential suitability as raw materials in various industrial applications.

2. Experimental

2.1. Material

Three bentonite samples from Kavaktepe, Tavkutlu and Yemişlitepe deposits of Ünye region of Turkey, coded as B1, B2 and B3, respectively, were used in this study. The samples were supplied from Ünye Mining Co., and crushed, ground and sieved to pass through a <45 μm sieve. The bentonite samples were washed with deionized water in order to remove the soluable impurities. Before the experimental procedure, the samples were dried in an oven at 110°C for 16 h and stored in a desiccator.

2.2. Instrumentation

The chemical analyses of bentonite samples were carried out using a Rigaku ZSX Primus model XRF instrument. The XRD diffractograms were obtained with a RINT-2200 instrument, using CuKα radiation (λ = 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).

The solid state spectra were obtained on a Bruker Avance 300 spectrometer operating at 78.17 MHz for ^{27}Al. All solids experiments were done at room temperature and were performed using hydrogen high power decoupling. Zirconium oxide rotor with a 4 mm diameter was used to acquire the NMR spectra of ^{27}Al. The

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spinning rate was kept at 6 kHz. The ^{27}Al spectra were carried out using the MAS technique with short delay between 90° pulses (2 s) and 2000 number of scans. Chemical shifts were quoted in ppm from external Al $(NO_3)_3{*}9H_2O$ (0 ppm). Infrared spectra of the bentonite samples were recorded (4000–400 cm^{-1}) with Perkin-Elmer FT-IR 2000 spectrometer at a resolution of 4 cm^{-1} using KBr pellet technique.

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 NOVA 2200 equipment previously degassed at 125 °C for 6 h prior to measurement. High-purity (99.99%) nitrogen was used in adsorption measurements.

Simultaneous TG–DTA experiments were carried out using a Setsys Evolution Setaram thermal analyzer. Approximately 30 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 30–1000 °C. The enthalpies of immersion (in 4 ml water) of the bentonite 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.

Table 1
Chemical analyses in oxides% for bentonite samples.

Chemical analysis (%)	B1	B2	B3
SiO_2	72.576	76.838	74.035
Al_2O_3	14.130	12.305	12.571
Fe_2O_3	1.262	1.115	1.181
MgO	1.858	1.529	2.036
CaO	2.379	1.403	1.973
Na_2O	–	0.347	–
K_2O	0.713	0.370	0.228
P_2O_5	–	–	0.018
TiO_2	0.161	0.110	0.137
MnO	0.069	–	0.036
SO_3	0.029	0.018	0.026
LOI	6.742	5.913	7.692

3. Results and discussion

3.1. Chemical analysis

Three local samples were investigated through chemical analysis. The chemical analysis of bentonite samples was carried out and the data were presented in Table 1. Loss ignition (LOI) was calculated by heating samples at 1000 °C for 2 h. The most abundant oxides are SiO_2 and Al_2O_3 whereas TiO_2, MgO, CaO, K_2O and Na_2O are present only in small quantities. The content of SiO_2/Al_2O_3 ratio is higher, may be due to the presence of cristobalite [12–15]. As shown in this table, the weight percent of calcium contained in the bentonite samples is higher than that of sodium.

3.2. X-ray diffraction

The X-ray diffraction patterns of the bentonite samples are illustrated in Fig. 1. The $d(0\,0\,1)$ values of B1, B2 and B3 samples were 15.00, 15.22 and 15.06 Å which corresponded to the main montmorillonite component (Fig. 1). The XRD patterns indicated that the B1 and B2 samples consisted of predominantly montmo-

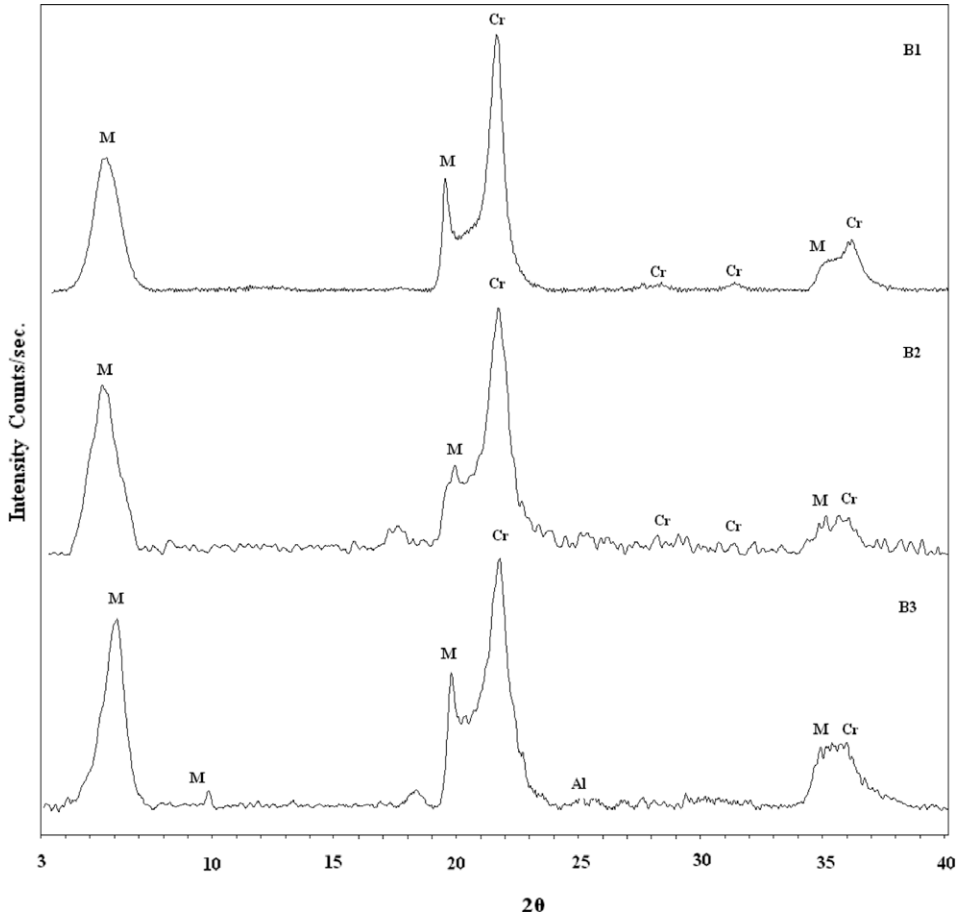

Fig. 1. X-ray diffraction patterns of the bentonite samples (M, montmorillolinite; Cr, cristobalite; Al, albite).