Characterization of bentonite clay from "Greda" deposit

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Abstract

Based on mineralogical and technological investigations of the deposit "Greda" important characteristics of bentonite clay were determined. Representative samples of the deposit were characterized with X-ray diffraction, low-temperature nitrogen adsorption, chemical analysis, differential thermal analysis and scanning electron microscopy. It was determined that the main mineral is montmorillonite and in subordinate quantities kaolinite, quartz and pyrite. The chemical composition generally shows high silica and alumina contents in all samples and small quantities of Fe^{3+}, Ca^{2+} and Mg^{2+} cations. Based on technological and mineralogical research, bentonite from this deposit is a high-quality raw material for use in the ceramic industry.

Keywords: bentonite, structural characterization

I. Introduction

Bentonite is a clay-based material derived from the alteration, over geological time periods, of glassy material emitted from volcanoes - tuff and ash. It can also be derived from alteration of silica bearing rocks such as granite and basalt. The environmental requirements for the formation of the clay, that is the main component found in bentonite, are only approximately known. Different climatic and hydrological environments together with the different ages and depths of occurrence produce subtle variations in this clay.

As it is well known, the clay minerals are hydrous aluminium silicate and are classified as phyllosilicates. They have a layered structure which can be described as constructed from two modular units: a sheet of corner-linked tetrahedra and a sheet of edge-linked octahedra. Each tetrahedron consists of M^{x+} cation, coordinated to four oxygen atoms, and linked to adjacent tetrahedra by sharing three corners [1]. The dominant M^{x+} cation in the tetrahedral sheet is Si^{4+}, but Al^{3+} substitutes it frequently and Fe^{3+} occasionally. The octahedral sheet can be thought of as two planes of closed-packed oxygen ions with cations occupying the resulting octahedral sites between two planes.

When we connect the centres of the six oxygen ions packed around an octahedral cation site, we have an octahedron. Sharing of neighbouring oxygen ions forms a sheet of edge-linked octahedra. The cations are usually Al^{3+}, Mg^{2+}, Fe^{2+} or Fe^{3+}, but all other transition elements and Li have been identified in cation sites of the octahedral sheet [2]. Smectites are a group of clay minerals able to expand and contract their structure while maintaining the two-dimensional crystallographic integrity. Montmorillonite is a mineral from this group, which has an ideal chemical formula:

$$R_{0.33}(Al_{1.67}Mg_{0.33}) Si_4O_{10}(OH)_2$$

Bentonites are clays rich in smectite regardless of their origin [3], which are valued for their properties such as crystal shape and size, cation exchange capacity (CEC), hydration and swelling, thixotropy, bonding capacity, impermeability, plasticity and tendency to react with organic compounds [4,5]. As a result, they have many industrial applications in oil drilling, iron ore and animal and poultry feed pelletization, civil engineering, paints, cosmetics and pharmaceuticals, as foundry sand bonding material and many others [6]. Their applica-

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tions are heavily dependent on their structure, composition, and physical properties [7]. Therefore, it is very important to examine the qualitative properties of bentonite (indication of the expected performance in various applications), and to determine the mineral composition and physicochemical parameters which control their behaviour.

In this study the main goal is to characterize bentonite clay from the deposit "Greda" and to estimate its quality and potential use.

II. Experimental

The bentonite raw material was collected from a quaternary sedimentary basin situated in "Greda", which is located between Donji and Gornji Čuklići, 4 km northeast Šipovo, Bosnia and Herzegovina. Chemical composition was determined with classical silicate (AAS) and energy dispersive X-ray analysis (EDAX). The cation exchange capacity (CEC) of the bentonite sample was determined by the method of Ming and Dixon [8]. In order to better define the present clay minerals, clay fraction < 2 μm was separated from the raw clay sample by sedimentation and centrifugation [9]. This fraction was used for X-ray powder diffraction measurement (XRPD), thermal analysis (DTA) and low-temperature nitrogen adsorption measurement.

X-ray powder diffraction measurement (XRPD) of samples was carried out by a Siemens D-500 diffractometer. Cu K_α radiation was used in conjunction with a Cu K_β nickel filter. Two sets of 2θ angle ranges were used. The range of 4–65° 2θ was used for the raw sample to determine mineral composition. For more precise determination of present clay mineral, oriented samples of fraction < 2 μm were used and X-ray data was collected in the range of and 2–40° 2θ. Three oriented solid particles of fraction (untreated, glycolated and heated to 450°C) were used to identify clay mineral associations [10].

The thermal behaviour (DTA) of the bentonite clay from "Greda" deposit was investigated using a Netzsch simultaneous analyzer; model STA-409 EP and DTA cells at a heating rate of 10 °/min. Sample was heated from room temperature to 1100°C.

Adsorption and desorption isotherms of N_2 were measured on the obtained powder at −196°C using the gravimetric McBain method. An adsorption isotherm consists of a series of measurements of the adsorbed amount as a function of the equilibrium gas pressure at a constant temperature. The amount of adsorbate can be determined gravimetrically after degassing of the sample solids above 373 K [11]. From the isotherms different powder characteristics were determined, such as: the specific surface area, S_{BET}, pore size distribution, mesopore including external surface area, S_{meso} and micropore volume, V_{mic}. Pore size distribution was estimated by applying BJH method [12] to the desorption branch of isotherms. Mesopore surface area and micropore volume were estimated using the high resolution α_s plot method [13–15]. Micropore surface area, S_{mic}, was calculated by subtracting S_{meso} from S_{BET}.

Investigations of crystal morphology and chemical composition of the bentonite sample (SEM/EDAX analyses) were carried out using a JEOL JSM-6610-LV scanning electron microscope. The accelerating potential was 15 kV, the beam current 20 mA. Quantitative analyses were done by an INCA Energy 350 EDS Microanalysis System. Sample was prepared by dispersing dry powder on double-sided conductive adhesive tape. Samples were coated with gold by arc-discharged method for SEM/EDAX.

III. Results and discussion

The bentonite "Greda" is a sedimentary deposit, formed during devitrification of the volcanic tuffs in Miocene. Layers within these Miocene deposits are vertical and lateral. One sediment unit is composed of layers of higlhy porous limestone and marly limestone with minor amouts of bentonites and clayiey-marly coal. Another sediment unit is composed of bentonite clay with minor amouts of gravel, tuffs, sandstones and clayey marl [16]. Economically, the most important Miocene lithological unit in this deposit is the bentonite clay.

Table 1. Chemical composition of initial raw bentonite from deposite "Greda"

Classical silicate analysis (AAS)										
Oxide	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	SO_3	I.L
[%]	58.6	24.8	0.25	2.89	2.60	2.13	0.27	0.2	0.05	0.1	8.20

EDAX analysis							
Element	Si	Al	Ti	Fe	Ca	Mg	K	Na
[%]	27.89	13.39	0.26	2.5	1.86	1.33	0.25	0.0

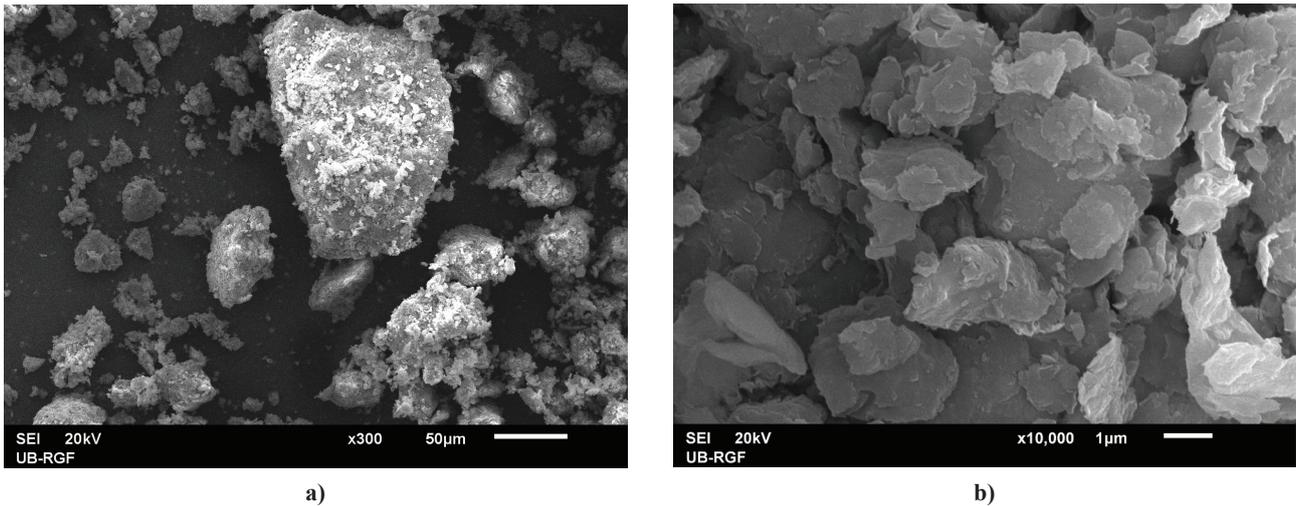| Cation exchange capacity (CEC)			
Cation	Ca^{2+}	Mg^{2+}	Na^+	K^+
[meq/100g]	90.1	9.4	0.15	0.5

a)   b)

Figure 1. SEM micrographs of raw bentonite at different magnifications: a) 300× and b) 10000×
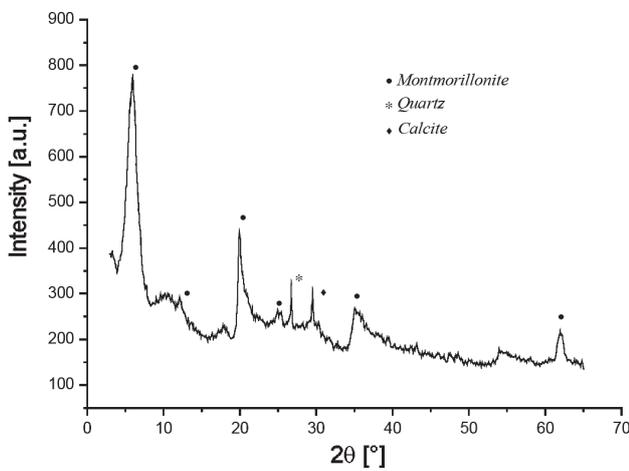

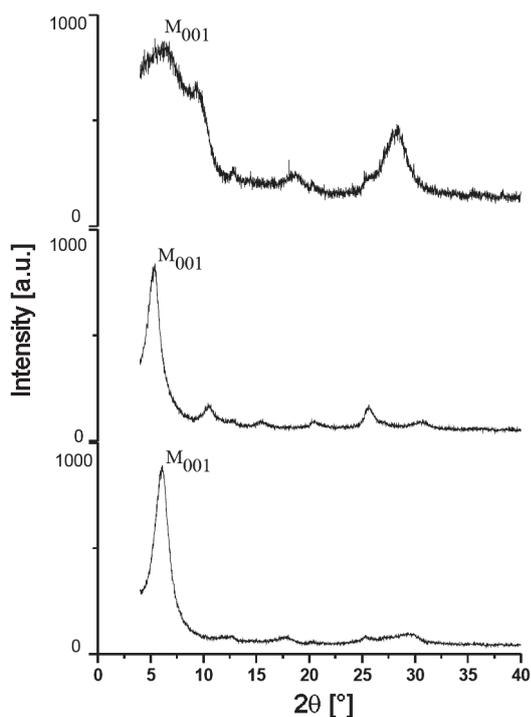**Figure 2. XRPD diagram of initial raw bentonite from deposit "Greda"**

Figure 3. Comparative diagram of oriented samples

Mineralogical analysis of the bentonite showed that the deposit "Greda" contains dioctahedral smectite (montmorillonite) as the main phase, associated with kaolinite, quartz, calcite and pyrite. The results of EDAX, AAS chemical analysis and cation exchange capacity of initial raw bentonite sample are presented in Table 1. The results of EDAX analysis are in agreement with chemical analysis (see Table 1). The analysis shows high silica content and the presence of oxides of alkali and alkaline earth metal. It was found that the sample has a small amount of P_2O_5 and SO_3 which can be attributed to impurities. Based on the results of the analysis of cation exchange capacity (Table 1), the major cations in the bentonite sample are Ca^{2+} and Mg^{2+}.

The sample of initial raw bentonite was examined by SEM and XRPD analysis and results are presented in Figs. 1 and 2. Clay platelets of varying size are clearly visible (Fig. 1). They are arranged in face-to-face patterns. Some well crystalline pseudohexagonal edges are also observed. XRPD pattern of raw sample shows presence of minerals montmorillonite, quartz and calcite (JCPDS cards for observed phase are: montmorillonite 13-0135, quartz 89-8936, calcite 83-0578). The comparative X-ray powder diffraction diagram (untreated, glycoleted and heated to 450°C) of clay fraction is presented in Fig. 3. The XRPD pattern of untreated oriented sample (Fig. 3a) clearly shows (001) peak on $d = 14.5$ Å which is characteristic for montmorillonite. After glycol addition (Fig. 3b), the basal spacing of montmorillonite expanded from 14.5 Å to 16.4 Å. The basal reflection of montmorillonite collapsed to 9.4 Å after heating for 1 h at 450°C (Fig. 3c). Peaks corresponding to other minerals present in the raw bentonite sample are not observed on this diagram. However, other bentonite deposits like the ones in Turkey and Serbia [17−19], still have minerals which are present in this fraction of the raw sample.

The results of thermal stability of the bentonite, obtained in the range from ambient temperature to 1100°C,
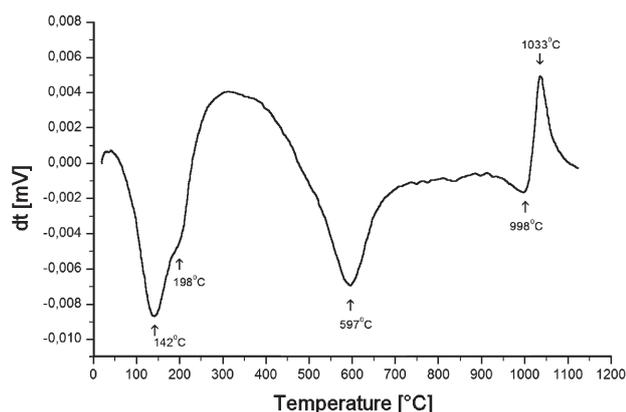
Figure 4. DTA curve of bentonite clay from "Greda"
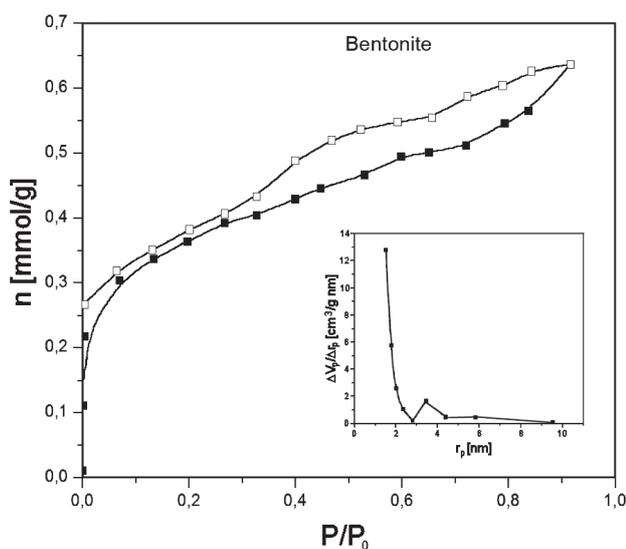

Figure 5. Nitrogen adsorption isotherm and pore size distribution (solid symbols – adsorption isotherm; open symbols - desorption isotherm; insert - pore size distribution)
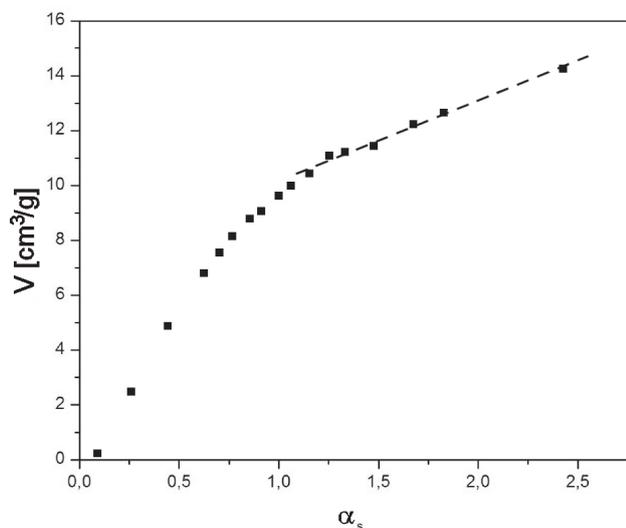

Figure 6. α_s-plots for nitrogen adsorption isotherm

are shown in Fig. 4. A significant endothermic peak at 142°C can be attributed to the removal of adsorbed and interlayer water of the clay. Also, on 198°C the small peak-limb can be observed, which represents simultaneous reaction, such as boiling reaction of water [20]. In addition, a large exothermic reaction between 250 and 450°C is related to the decomposition of organic matter. A broad endothermic band centred at 597°C was due to the dehydroxylation. An exothermic peak was obtained at 1033°C due to recrystallization of montmorillonite. The DTA curve shows a slight endothermic peak around 998°C, immediately before the exothermic peak, due to the breakdown of the montmorillonite structure [20].

Nitrogen adsorption isotherm as a function of relative pressure at −196°C is shown in Fig. 5. According to IUPAC classification which recommends the six types of the adsorption isotherms [11] the observed isotherm is of type-IV with hysteresis loop which is associated with mesoporous materials. Specific surface areas calculated by BET equation are: $S_{BET} = 28$ m²g⁻¹, $S_{meso} = 8$ m²g⁻¹ and $S_{mic} = 20$ m²g⁻¹, whereas $V_{mic} = 0.011$ cm³g⁻¹. Pore size distribution is shown in the insert of Fig. 5. The distribution for these sample shows that the bentonite clay is microporous with a certain amount of mesoporosity. Based on the standard nitrogen adsorption isotherms, which is shown in Fig. 5, α_s-plots are obtained (Fig. 6). The slope of straight line in the medium α_s region gives a mesoporous surface area (S_{meso}) including the contribution of external surface, while micropore volume (V_{mic}) is determined by its intercept. Subtraction S_{meso} from S_{BET} gave micropore surface (S_{mic}).

IV. Conclusions

The clay from "Greda", was characterized by chemical, mineralogical and thermal analysis. All used methods are in agreement. This bentonite possesses high adsorption characteristics and thermal stability, which makes it a promising material for application such as adsorbent and catalyst. It also shows monomineral composition in fraction < 2 μm which makes it a good starting material for further modification and application. The additional work is presently being performed in the laboratory on further characterization of material and its modification for catalyst and adsorption.

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