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## EFFECT OF THERMAL TREATMENT ON THE BENTONITE PROPERTIES

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### ABSTRACT

The main objective of this study is to investigate the changes in structure, surface area and porosity of monomineral fraction of the local bentonite upon heating at 300, 500 and 650 °C. IR spectroscopy, DTA, XRD and N<sub>2</sub> adsorption method were employed for the analyses. The non-heated montmorillonite was characterized by a basal spacing of 1.50 nm, after thermal treatment of 0.98 nm. This decrease was attributed to the loss of interlamellar water, finally a phase transformation occurred. Changes of the crystal structure related with the decrease of the value of specific surface area and total pore volume.

Keywords: *bentonite, thermal treatment, surface properties.*

## UTICAJ TERMIČKE OBRADÉ NA BENTONITSKA SVOJSTVA

### REZIME

Glavni cilj ovog istraživanja je ispitati promjene u strukturi, površine i poroznosti monomineralnih djeliću lokalnih bentonita nakon zagrijavanja na 300, 500 i 650 ° C. IR spektroskopija, DTA, XRD i N<sub>2</sub> adsorpcione metode su uključene za analize. Nezagrijani montmorilonit karakteriše bazalni razmak od 1,50 nm, a nakon termičke obrade 0,98 nm. To smanjenje pripisuje se gubitku interlamelarne vode, koji nastaje nakon faze transformacije. Promjene kristalne strukture vezane se za smanjenje vrijednosti specifične površine i ukupne zapremine pora.

Ključne riječi: *bentonit, termička obrada, površinska svojstva*

### INTRODUCTION

Bentonite is one of the clay minerals, hydrated aluminium silicate. Its major component is montmorillonite, which belongs to the group of silicate minerals known as dioctahedral smectites. Structure of this material is formed from two tetrahedral sheets with Si(IV) as a central atom and one octahedral sheet containing Al(III), which can be substituted by Fe(III) or/and Mg(II). This kind of structure exhibits cation exchange properties, swelling ability, plasticity, cohesion, compressibility, adsorptive properties and catalytic activity.

The application areas of bentonites vary depending on the amount of their constituents. Bentonites are used as selective adsorbents [1], ion exchangers, catalysts [2], catalysts support, for production of pillared clays [3] and organoclays [4].

Bentonites may be subjected to high temperatures when are used in ceramic [5-6] or foundry industry [7]. In these processes, the structure as well as the physicochemical properties could be affected by thermal treatment [8-12]. Therefore, the aim of this study is to investigate the effect of the heating on the structural, surface and porous properties of the local natural bentonite.

## EXPERIMENTAL

The natural bentonite originated from the deposit of locality Jelšový potok (Slovakia). For the investigation < 20  $\mu\text{m}$  fraction was used. Montmorillonite was the only mineral detected in this fraction. Its structural formula as calculated from chemical analysis is:  $[\text{Si}_{7.95} \text{Al}_{0.05}] [\text{Al}_{3.03} \text{Fe}_{0.22} \text{Mg}_{0.75}] \text{O}_{20} (\text{OH})_4 (\text{Ca}_{0.42} \text{Mg}_{0.04} \text{Na}_{0.01} \text{K}_{0.01})$  [13].

The sample was heated for 2 hours at three selected temperatures 300, 500 and 650  $^{\circ}\text{C}$  in inert atmosphere.

Room temperature Mössbauer measurement was made in transmission geometry. A  $^{57}\text{Co}/\text{Rh}$ -ray source was used. The velocity scale was calibrated relative to  $^{57}\text{Fe}$  in Rh. Mössbauer spectral analysis software "Recoil" [14] was used for the quantitative evaluation of the spectra. The Voigt-based fitting method was applied.

Morphology of the natural sample was observed by the scanning electron microscope (SEM) of the type JSM-6400 (JEOL Ltd., Japan).

Infrared (IR) spectra of the bentonite samples were taken on a spectrometer AVATAR 330 (Thermo Nicolet Corp., USA) equipped with DGTS/KBr detector at a resolution 4  $\text{cm}^{-1}$ . The spectra were collected with spectral resolution in the region from 4000 to 400  $\text{cm}^{-1}$  on potassium bromide (KBr) pellets.

Powder X-ray diffraction (XRD) patterns were recorded with a Philips PW1820 diffractometer (The Netherlands) equipped with a  $\text{CuK}\alpha$  radiation (40 kV, 40 mA). The JCPDS PDF database was used for the phase identification.

Differential thermal analysis (DTA) was carried out using the Derivatograph-C (MOM, Hungary). Measurement was done in real atmosphere up to the temperature 800  $^{\circ}\text{C}$  with heating gradient 10  $^{\circ}\text{C}/\text{min}$ . Obtained data were processed by the WINDER software.

Adsorption and desorption isotherms were measured with the Micrometrics ASAP 2400 apparatus (USA) by the method of physical adsorption of nitrogen at 77 K. Experimental data were processed by the BET (Brunauer, Emmett, Teller) isotherm [15] in the range of relative pressure 0.05–0.2  $p/p_0$ . The micropore volume  $V_{\text{micro}}$  and the external surface area  $S_t$  were calculated from the t-plot method using Harkins-Jura standard isotherm [16]. The value of total pore volume  $V_a$  was estimated from the maximum adsorption at relative pressure close to the saturation pressure. The pore size distribution was obtained from the BJH (Barret–Joyner–Halenda) method [17].

## RESULTS AND DISCUSSIONS

The sample of the natural bentonite was first investigated by the Mössbauer spectroscopy. Clay minerals can contain structural iron in concentrations from less than 1 to over 10 % which is usually octahedrally and less frequently tetrahedrally coordinated. Most clay minerals (except for extremely

iron-rich species, which may be magnetically ordered below about 20 K) are paramagnetic down to 4.2 K. Depending on the valence of iron and the number of sites in the structure, Mössbauer spectra of clay minerals therefore consist of one or several Fe(II) and/or Fe(III) doublets [18]. This technique can provide the information on  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratios and in favourable cases the Fe coordination [19].

The room temperature Mössbauer spectrum of the natural bentonite, Figure 1, was asymmetric, consisting of two doublets suggesting two different iron cations positions in montmorillonite structure. Therefore, it was fitted by two spectral components. On the basis of the obtained hyperfine parameters: isomer shifts  $\text{IS}_1 = 0.28 \text{ mm/s}$ ,  $\text{IS}_2 = 0.23 \text{ mm/s}$ ; quadrupole splittings  $\text{QS}_1 = 1.39 \text{ mm/s}$ ,  $\text{QS}_2 = 0.52 \text{ mm/s}$ ; relative intensities  $I_1 = 33.7 \%$ ,  $I_2 = 66.3 \%$ , it can be stated that present iron cations are trivalent.

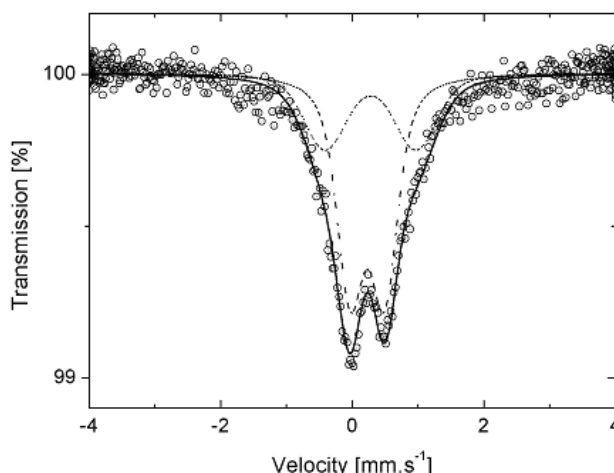


Figure 1 Mössbauer spectrum of the natural bentonite

Slika 1. Mössbauerov spektar prirodnih bentonita

The scanning electron microscopic data for most samples of the bentonite can be summarized as follows: montmorillonite occurred either as ultrafine, thin, leaf-like crystals forming a dense aggregate or in a more open honeycomb texture [20]. The SEM micrograph of the sample used for the investigation showed its sheet structure, Figure 2, corresponding with the first mentioned type.

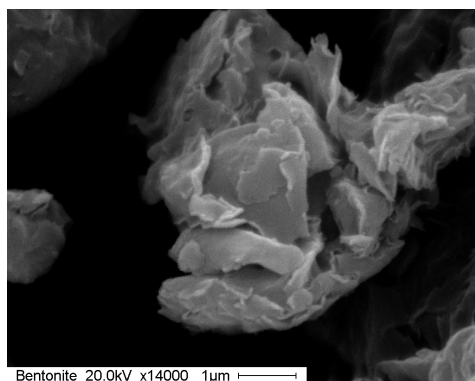


Figure 2 SEM micrograph of the natural bentonite

Slika 2. SEM mikrograf prirodnog bentonita

IR spectroscopy has significantly contributed to the understanding of the structure, bonding, and reactivity of clay minerals. The examination for the IR spectra in the range  $4000 - 400 \text{ cm}^{-1}$  provides information on fundamental vibrational modes of the constituent units of these materials. OH stretching and bending vibrations occur in the spectral region of  $3750 - 3500$ , resp.  $950 - 600 \text{ cm}^{-1}$ . Si-O and Al-O stretching modes are found in the  $1200 - 700 \text{ cm}^{-1}$  range, while Si-O and Al-O bending modes dominate in the  $600-400 \text{ cm}^{-1}$  region [21]. Figure 3 shows the infrared spectrum of the

bentonite samples. The IR spectrum of the natural bentonite did not show significant difference in comparison with the samples heated at 300 and 500 °C. The absorption band at the position about  $3626\text{ cm}^{-1}$  is due to the stretching vibrations of structural OH groups of montmorillonite. The intensity of this peak for the sample heated up to 650 °C is negligible. The bands corresponding with the AlAlOH and AlMgOH bending vibrations were observed at  $916$  and  $840\text{ cm}^{-1}$ , respectively. A complex band at  $1040\text{ cm}^{-1}$  is related with the stretching vibrations of Si-O groups, while the bands at  $523$  and  $470\text{ cm}^{-1}$  are due to the Al-O-Si and Si-O-Si bending vibrations, respectively. The band at the position  $625\text{ cm}^{-1}$  was assigned to the couple Al-O and Si-O out-of-plane vibrations. The shift of these peaks was observed for sample heated at 650 °C (vibration at  $916\text{ cm}^{-1}$  for AlAlOH was not present). Water in montmorillonite gave a broad band at about  $3420 - 3450\text{ cm}^{-1}$  corresponding with the H<sub>2</sub>O-stretching vibrations. The shoulder close  $3330\text{ cm}^{-1}$  is due to an overtone of the bending vibration of water observed at  $1635\text{ cm}^{-1}$ .

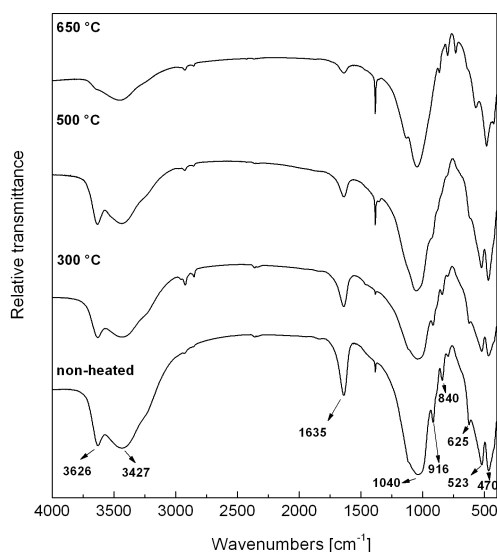


Figure 3 Infrared spectra of the natural bentonite and bentonite heated at selected temperatures  
Slika 3. Infracrveni spektri prirodnog bentonita i bentonita zagrijanog na odabranim temperaturama

TG and DTA curves of the bentonite are given in Figure 4. The first dominant mass loss is due to the dehydration of interparticle water, adsorbed water and interlayer water [22].

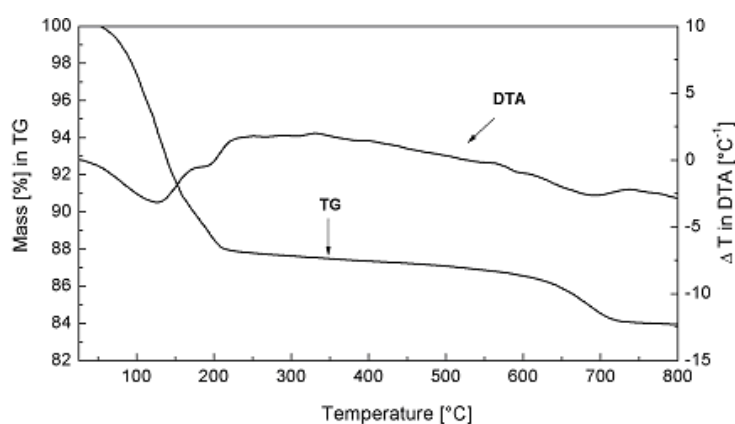


Figure 4 TG and DTA curves for the natural bentonite  
Slika 4. TG i DTA krivulje za prirodne bentonite

The DTA doubled endothermic peak corresponded to this change was observed at 130 and 190 °C. The next, smaller mass loss due to dehydroxylation is evident in the temperature range 640 – 730 °C, and the corresponding endothermic peak with its maximum at about 690 °C is related to the release of OH groups of the octahedral layer. The exothermic peak resulting from the started recrystallization was detected at 740 °C.

The XRD patterns of the bentonite samples showed the presence of montmorillonite phase with differences in the crystallographic parameters in dependence on the heating temperature caused by the dehydration of the bentonite, Figure 5, observed by DTA method. It is well shown by the decrease in intensity of the 001 basal reflection, Figure 6. The basal spacing changed from  $d(001) = 1.5$  nm for non-heated montmorillonite to  $d(001) = 0.98$  nm for sample heated at 650 °C. It means that the heating caused the phase transformation and obtained XRD reflections correspond to reference pattern of the heated bentonite.

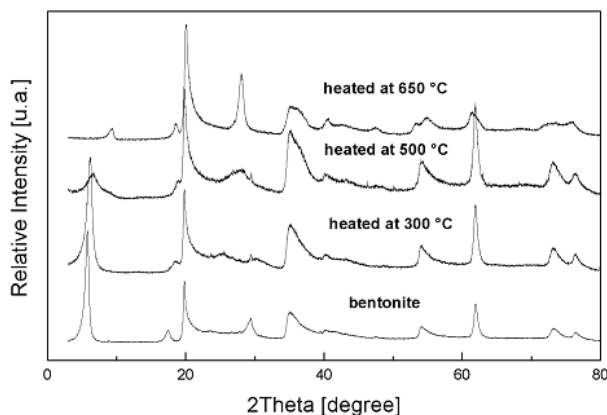


Figure 5 XRD Patterns of the natural bentonite and bentonite heated at selected temperatures  
Slika 5. XRD Obrasci prirodnog bentonita i bentonita zagrijanog na odabranim temperaturama

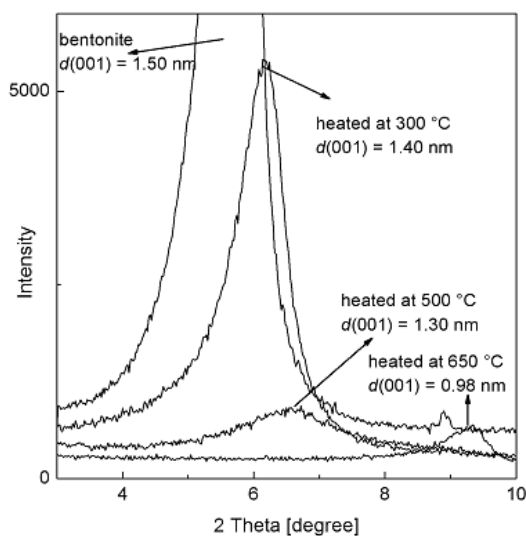


Figure 6 Comparison of the positions of (001) reflection peaks of the non heated and heated bentonite samples  
Slika 6. Poređenje pozicija (001) refleksije vrhova nezagrijanih i zagrijanih uzoraka bentonita

The mesoporous character of the bentonite is preserved after the heating, what is observable from the hysteresis loop between the adsorption and desorption isotherms. The volume of adsorbed gas in relation with the relative pressure decreased, Figure 7. This corresponds with the changes in values of total pore volume after the thermal treatment, as well as with the pore size distribution analysis.

The variation of the values of specific surface area, total pore volume and micropore volume with heating temperature is given in Figure 8. The values of specific surface area calculated from the adsorption data show a "zig-zag" variation with increasing temperature up to 500 °C and a rapid decrease above this temperature. The value of total pore volume is not influenced rapidly by the temperature of heating. The same was observed for the micropore volume. The curves of pore size distributions of the natural bentonite and sample heated at 650 °C are shown in Figure 9. The bentonite

preserves its mesoporous character during the thermal treatment, but volume of mesopores decreased after the heating and new macropores occurred in comparison to the non-heated sample.

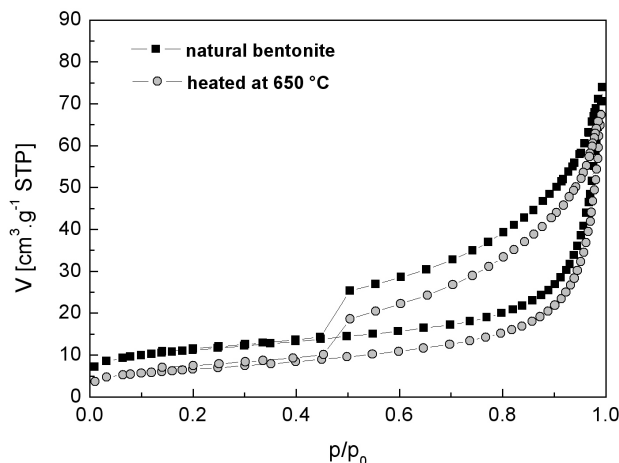


Figure 7 Adsorption and desorption isotherms of the non-heated and heated bentonite up to 650 °C  
Slika 7. Adsorpcije i desorpcije izoterme za nezagrijane i grijane bentonite na 650 °C

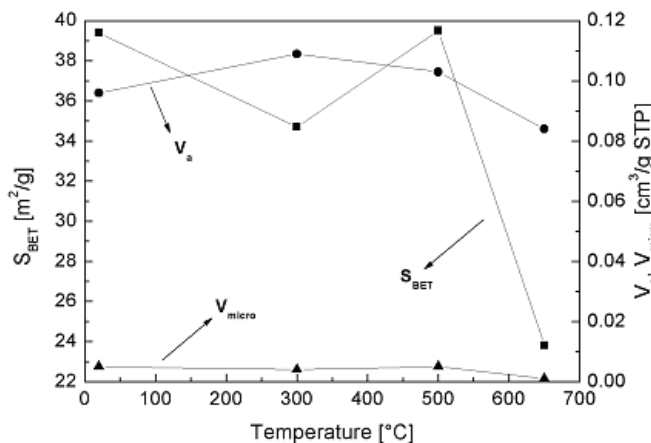


Figure 8 Comparison of the surface parameters of the natural bentonite and bentonite heated at selected temperatures  
Slika 8. Poređenje površinskih parametara prirodnih bentonita i bentonita zagrijanih na odabranim temperaturama

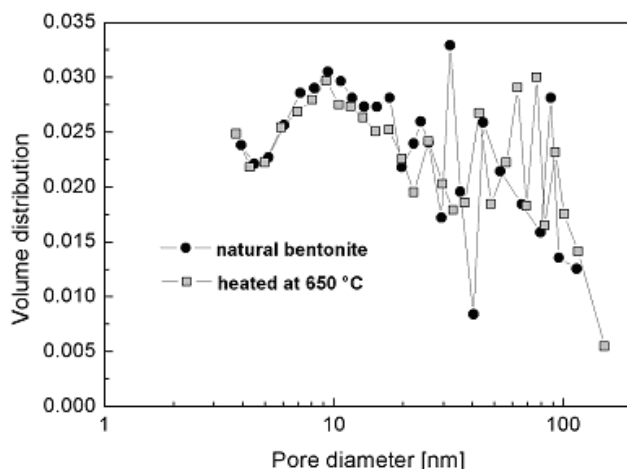


Figure 9 Pore size distribution curves for the natural bentonite and bentonite heated at 650 °C  
Slika 9. Raspodjela veličine pora krivulje za prirodne bentonite i bentonita grijane na 650 °C

## CONCLUSION

Heating of the natural bentonite up to 500 °C caused its dehydration, which was completed at the temperature 650 °C. It was evident from the shift of the reflection peaks indicating the changes in the basal spacing  $d(001)$  from the value 1.5 nm for non-heated bentonite to 0.98 nm for sample heated at 650 °C. The DTA results showed that the further thermal treatment could lead to the dehydroxylation of OH groups.

Thermal treatment up to 500 °C did not influence so much the surface and porous properties of the bentonite. The noticeable changes were observed after the heating up to 650 °C when the values of the specific surface area decreased rapidly. Because of the possible applicability of the heated bentonite, it will be very interesting to study the mechanical properties of bentonite heated up to the temperature 650 °C.

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