

The effects of the fine grinding on the physicochemical properties and thermal behavior of bentonite clay

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Abstract: In this study, the results obtained by the mechanical treatment of bentonite clay Zavidinci, Serbia in a laboratory vibration mill with rings for different periods of time are presented. The successive structural changes of the minerals were studied by X-ray diffraction analysis, DTA analysis, IR spectroscopy and particle size distribution. The reactivity changes were controlled by CEC. The starting material and the material mechanically treated for 30 min were sintered at several temperature and for different time periods examined by X-ray diffraction. Mechanical treatment by fine grinding of bentonite clay produces structural changes of the powdered material and influences its behavior in further processing steps in particular after thermal treatment.

Keywords: bentonite clay, grinding, properties.

INTRODUCTION

Mechanical treatment by grinding of clay minerals produces important changes of powdered materials and influences their behavior in further processing steps.

The processes involved have been widely studied, especially for kaolinite.^{1–4} Dry grinding causes a decrease in the degree of crystallinity of kaolinite crystals, leading to the formation of reactive surfaces or changes in the physicochemical behavior.

With respect to bentonite, Köller *et al.*⁵ studied grinding in a ball mill, under dry and wet conditions. Novak *et al.*⁶ observed parallel texture in smectite crystals after short time of vibration grinding. Čičel and Kranz⁷ described the process of mechanical treatments of montmorillonite. The destruction can be described as a series of parallel changes occurring at various rates.

Volzone *et al.*⁸ studied the effect of milling on the structure and texture of a natural bentonite and in several monoionic forms. When pyrophyllite is submitted to mechanical and thermal treatments,⁹ significant changes take place, according to X-ray diffraction and DTA results.

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The objective of the present work was the characterization of the physicochemical changes produced during mechanical treatment of a natural bentonite clay in a vibro mill and the influence of the grinding on the behavior this raw material during thermal treatment.

EXPERIMENTAL

Material and methods of analysis

The starting material used for the experimental work was a natural raw material of bentonite clay from Zavidinci-Pirot, Serbia, which contains predominantly montmorillonite mineral (> 60 %) with accompanying minerals (feldspar, quartz, cristobalite and illite).

The chemical composition of the starting material is given in Table I.

TABLE I. The chemical composition of the starting material

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	L.o.I
mass-%	56.56	17.06	1.86	0.18	6.17	0.92	1.30	0.97	14.96

The bentonite clay was mechanically treated in a laboratory vibration CAP mill, Type Mn 953/3-KHD Humbolt Wedag, for 10, 30, 60 and 120 min. During the grinding, the mill and the sample formed a closed system preventing the evaporation of water.

The structural properties of the starting and mechanically treated bentonite clay were determined by X-ray diffraction analysis. The X-ray diffractograms (XRD) were obtained on a Philips PW-1710 with a copper tube operating at 40 kV and 35 mA. The instrument was equipped with a diffracted beam curved graphite monochromator and a Xe-filled proportional counter. Diffraction data were collected in the range of 2θ from 4° to 15°.

Thermal analysis was performed in an air atmosphere with a Netzsch STA-409 EP instrument at heating rate of 10 °C/min.

Infrared absorption spectra were recorded on a Perkin-Elmer model 377 spectrophotometer using the KBr pellets technique.

Changes in particle size distribution were determined on a Coulter Multisizer.

The cation exchange capacity was determined by the standard ammonium acetate method.

The starting material and mechanically treated samples were shaped into laboratory testing bodies in the shape of pallets using a hydraulic press under a pressure of 20 MPa. The dried samples were then sintered at temperatures of 1050, 1100 and 1150 °C. Retention time at determined temperatures was 15, 30, 60 and 120 min. Characterization of both non treated and treated sintered materials were performed by X-ray diffraction analysis.

RESULTS AND DISCUSSION

Thermal analysis

The DTA curves of the starting bentonite clay Zavidinci and samples mechanically treated for different treatment times (10, 30, 60 and 120 min) are presented in Fig. 1. The first endothermic effect results from a dehydration reaction. The second effect is associated with dehydroxylation, third endo effect simultaneously included decarbonisation and dehydroxylation which are overlapping. The fourth endo-reaction is connected to the disappearance of the layered structure of the montmorillonite mineral. After 120 min grinding exothermic effect at 970 °C occurs, it is characteristic of development of high temperature phases with a spinel-type structure.

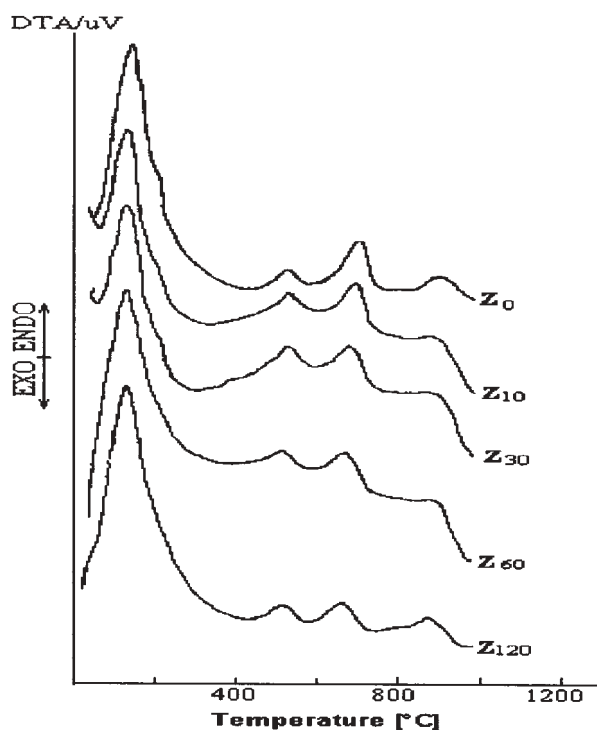


Fig. 1. Changes in the DTA curves as a function of treatment time.

The DTA analysis showed that with increasing mechanical treatment time, dehydroxylation reaction and the disappearance of the layered structure occur at lower temperatures. This is probably caused by a decrease of the energy of the OH-group bond in the structure of the bentonite clay resulting from mechanical treatment.

X-Ray diffraction

The X-ray diffractograms of the starting natural material and the product of 120 min grinding are given in Fig. 2. The changes of the intensity and width of diffraction reflection maximum (001) in montmorillonite mineral was monitored. The intensity of the diffraction line of the sample ground for 120 min decreased relative to the untreated sample and the peak width increased becoming more diffusive. This indicates a gradual disturbance of the crystal structure.

IR-Spectroscopy

Infrared absorption spectra of starting and mechanically treated samples are given in Fig. 3. It can be seen that with increasing mechanical treatment time, changes in the shape and width of the absorption bands are observed, indicating a progressive structural degradation.

The IR spectrum of the natural sample showed, ranges besides bands characteristic for montmorillonite, also bands within the wave numbers from 950 to 1200 cm^{-1} and from

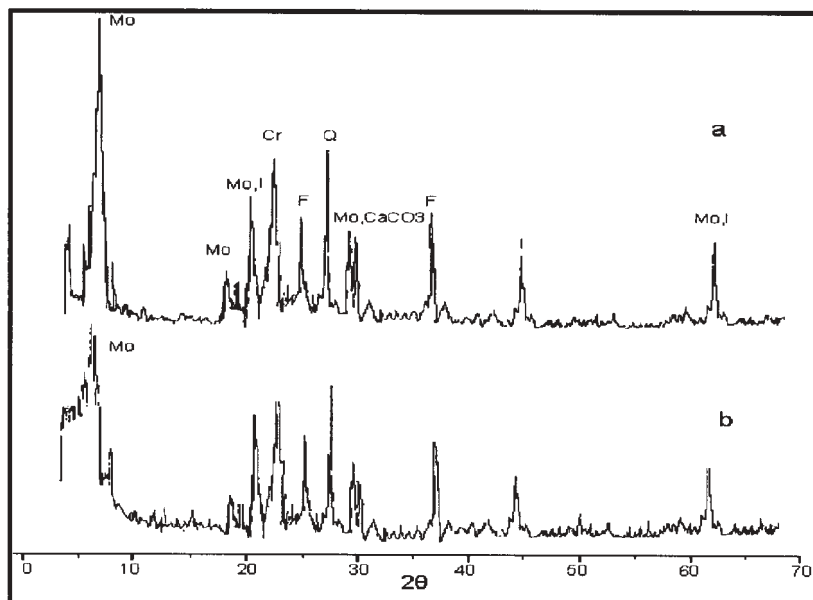


Fig. 2. XRD Patterns of, a) starting material and b) material ground for 120 minutes (Mo–montmorillonite, Cr–crystalobalite, I–illite, F–feldspar, Q–quartz, CaCO_3 –calcite).

800 to 808 cm^{-1} , which were overlapped and modified, but belong to $\alpha\text{-SiO}_2$. With prolonged mechanical treatment, the intensity of the 855 cm^{-1} band, which belongs to Al–O–H vibrations decreases and disappears entirely after 120 min grinding. The bands, which belong to $\alpha\text{-SiO}_2$ are changed giving one band of 800 cm^{-1} and the band at 629 cm^{-1} caused by Si–O vibrations in the tetrahedral layer decreases in intensity. Similar ef-

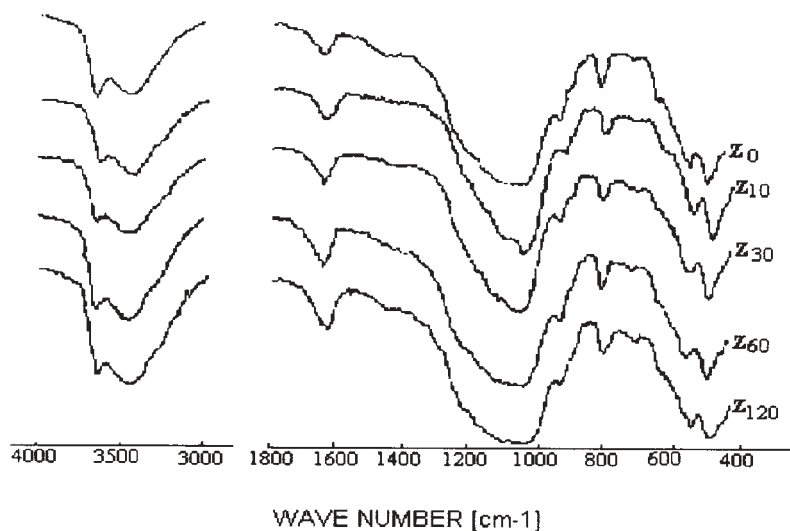


Fig. 3. Changes in the IR spectra as a function of treatment time.

fects are observed with the bands at 530 cm^{-1} and 478 cm^{-1} which are for montmorillonites of high intensity (they result from Si–O–Al, Si–O–Si and Si–O vibrations).¹⁰ This was not the case in this work due to the presence of accompanying minerals and overlapping of bands. During mechanical treatment of the samples, they lose in intensity and sharpness and, after 60 min fragmentation, a shoulder appears at 490 cm^{-1} .

Particle size distribution

As shown in Fig. 4, extending the grinding time led to an increasing content of finer particles for samples mechanically treated for 10 and 30 min. With prolonged grinding time, 60 and 120 min, an anomaly occurs which is the consequence of agglomeration. In other words, the curves of these blips shifted to the right when going from the sample treated for 30 min to the samples subjected to prolonged grinding.

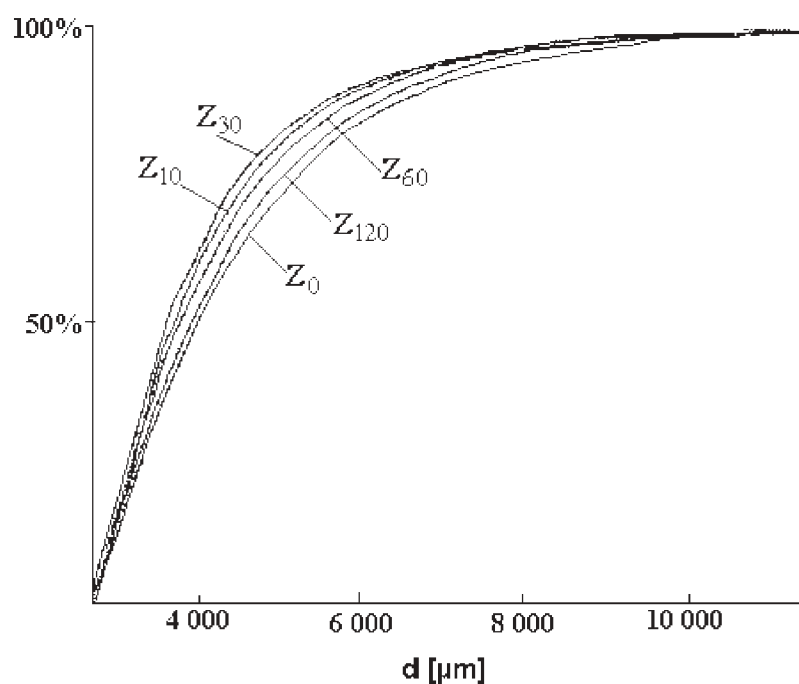


Fig. 4. Cumulative curves of the particle size distribution after different treatment times.

Cation exchange capacity

The reactivity changes were controlled by CEC. The cation exchange capacity (CEC) for all the samples is given in Table II.

The data given in Table II show that mechanical treatment of the sample causes an increase of the CEC from 65.28 meq/100 g for the starting sample to 85.29 meq/100 g for the treated sample for 120 min. This increase in the CEC is explained by the production of extensive crystal defects in the Al^{3+} octahedral position.

TABLE II. Cation exchange capacity

Treatment time/min	CEC/(meq/100 g)
0	65.28
10	66.06
30	69.47
60	72.86
120	85.29

Thermal treatment

In the paper shown a comparative X-ray diffractograms of the starting sample and a sample mechanically treated for 30 min, both thermally treated at 1150 °C for 60 min, are given in Fig. 5. Another results were not described and no comment on, because there were abundant of dates.

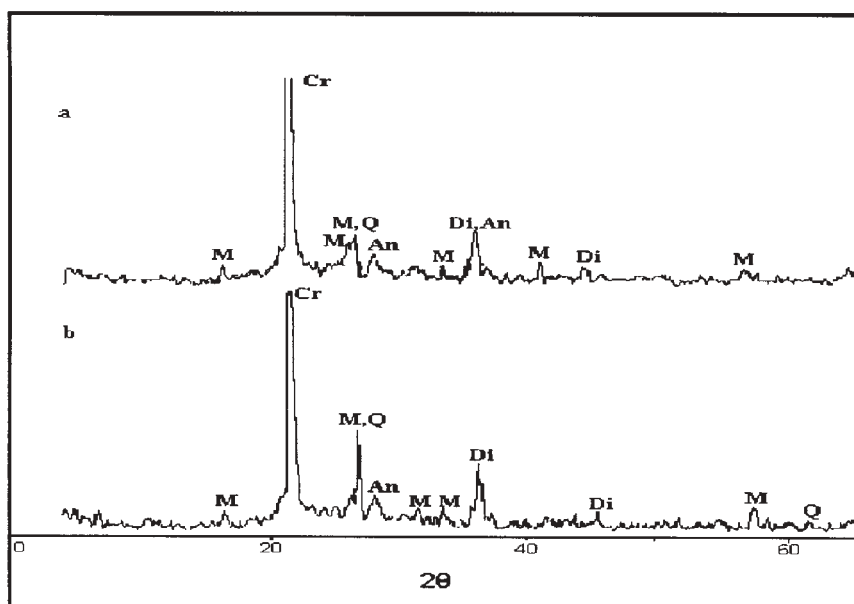


Fig. 5. X-Ray diffractogram of samples treated thermally at 1150 °C for 60 min a) starting material, b) material ground for 30 min. (M–mullite, Cr–cristobalite, Q–quartz, An–anortite Di–diopside).

X-Ray diffraction analysis of the starting material sintered at 1150 °C showed that cristobalite, mullite, quartz and diopside were the predominant high temperature phases. The mineralogical composition of the material ground for 30 min and sintered at 1150 °C was same, but the intensity of the diopside and mullite reflections increased. It is known that the intensity of the mullite reflections is never very great and that this phase is not abundant and very well crystallized in pure montmorillonite.

CONCLUSION

Fine grinding of bentonite clay in vibration mill produces changes in its physical and chemical characteristics:

– With prolongation of the grinding time, the crystallinity of the monitored mineral decreases.

– Thermal analysis shows that some OH groups become unstable during grinding, which results in a decrease of the temperature of dehydroxylation of bentonite clay. The appearance of an exothermic effect which is not present in unground samples can be seen.

– The intensity of the vibration bands in the range 400–1200 cm⁻¹ in the IR spectrum show gradual structural changes.

– The reactivity of bentonite clay, monitored by CEC, increase during the grinding.

By grinding of bentonite clay, the course of happenings in solid-state reactions which occur during further heating can be influenced. The intensity of mullite formation, which represents the high temperature phase desirable in ceramic systems, was much higher in the ground samples than in natural bentonite clay.

ИЗВОД

ЕФЕКАТ ФИНОГ СИТЊЕЊА НА ФИЗИЧКОХЕМИЈСКЕ ОСОБИНЕ И ТЕРМИЧКО ПОНАШАЊЕ БЕНТОНИТСКЕ ГЛИНЕ

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У овом раду су представљени резултати који су добијени механичким третманом бентонитске глине Завидинци, Србија, у вибро млину са прстеновима и различитим временским периодима млевења. Промене у структури испитиване сировине су праћене рендгенском дифракцијом, ДТА анализом, ИР спектроскопијом, расподелом величине честица, а промене реактивности су праћене контролом капацитета катјонске размене. Полазни испитивани материјал и материјал механички обрађен 30 минута су топлотно третиран на неколико температура и различитих времена. Након тога су проучени рендгенском дифракцијом. Механичка обрада бентонитске глине, финим млевењем, доводи до структурних промена у прашкастом материјалу и утиче на следеће процесе прераде као што је термички третман.

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