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Study of montmorillonite and cationic activators sistem rheological characteristic change mechanism

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Abstract

The aim of this work is to examine changes of the montmorillonite mineral rheological characteristics during its activation with sodium carbonate and magnesium hydroxy carbonate. In order to foresee the mechanism of these processes, it was necessary to study the following:

- The change of the rheological characteristics of the investigated system, i.e. viscosity and thixotropy, with respect to the initial montmorillonite and water system,
- structural changes caused by migration of Al^{3+} ions from the octaedric positions into the interlamellar region, by using the structural analysis methods and by monitoring the cation exchange capacity increase during the activation of this mineral,
- formation of the new anionic clay types, as well as their synthesis and structure in an independent system and
- formation and emergence of new structures during particle interaction, during which various products are created, in the form of "card house", "band type", "networked band type" or connected by a "latching" mechanism.

The changes in rheological characteristics has been studied for the montmorillonite obtained from "Jelenkovac" bentonite by separating fractions smaller than 2 μm, with Ca^{2+} and Mg^{2+} mostly being the exchangeable cations.

Keywords: Spectroscopy; X-ray methods; Silicate; Traditional ceramics; Bentonite

1. Introduction

Significant changes in the rheological characteristics of bentonite are influenced by various admixtures used in the industrial processes of bentonite activation, thus determining the practical characteristics of commercial bentonites. The most important properties of the montmorillonite-water system are: viscosity, thixotropy, swelling potential and flow behavior. The basis of the alkaline activation process of bentonite is the reaction of exchange of Ca-ions from montmorillonite with Na-ions from the salt solution. During process a metastable balance is established. The montmorillonite mineral particle size is decreased, which enhances the ion exchange reaction.[1]

For different pH values the suspensions of thin hexagonal laminar particles develop a certain type of structures which results in significant changes of rheological properties. In the acidic medium a "card house" structure is formed, while "band type" structure is formed in the alkaline medium.[2] The electroviscous effect, created by the double diffusion layer, is important for the clay particle migration.

By introduction of alkaly magnesium carbonate into the Na activated montmorillonite and water system an additional effect on the change of rheological properties is obtained. The presence of alkaline-magnesium salts in the alkaline medium leads to a certain structural changes of the montmorillonite and to emergences of new phases, which act as additional activators and influence the system's rheological properties. Drzaj et al.[3] relate activating mechanism to the presence of zeolites in bentonites, with the possibility of tobermorite synthesis. French authors [4] suggest that, within the alkaline medium containing hardly soluble magnesium salts, montmorillonite is transformed into pseudochlorite over a longer time period. Further investigations proved that the migration of Al-ions from the octaedric layer of montmorillonite into the exchangeable position [5] releases a small quantity of Al^{3+} ions into the system, thus enabling the appearance of hydrotalcite.

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A multidisciplinary approach was assumed in investigating the alkaline-magnesium activation mechanisms. The phenomena related to the changes in rheological properties of the montmorillonite-water-electrolyte system were explained using several approaches: ion exchange, structural changes of the montmorillonite mineral, appearance of the anionic clay phase and the anionic and cationic clay particle interaction, which is a new concept in this field. Since the Na-montmorillonite develops the “band type” structure in the alkaline medium containing Ca^{2+} ions, anionic clay serves as cationic activator.[6] Small anionic clay particles, catalitically very active, serve as “latches” between the chains of the created “band structure”.

2. Materials and methods

As starting materials, montmorillonite obtained from bentonite “Jelenkovac” (Serbia) with fractions below 2 μm and natural montmorillonite “Jelenkovac”, which is mainly in biionic form (Ca, Mg), were used.

The capacity of cation exchange, determined by ammonium acetate method is 98.0 mmol M+/100 g, and the exchangeable cations of montmorillonite are presented in Table 1.

The results of the montmorillonite chemical analysis are shown in Table 2.

The structural formula of montmorillonite was obtained on the basis of the data from Tables 1 and 2.[7]

The structural formula of montmorillonite is:

$$[Ca_{0.25}Mg_{0.06}Na_{0.07}K_{0.03}][Al_3Fe_{0.26}Mg_{0.61}Ca_{0.07}][Si_8O_{20}(OH)_4]\cdot 2.28SiO_2$$

Natural montmorillonite was treated with different quantities of Na_2CO_3 (2–4%) and $Mg_2(OH)_2CO_3$ (1–3%) in the pulp. The mass is then conditioned and dried for about 20 h in the drying oven heated to 40° and turned off. The changes of viscosity, as main rheological property, were followed by a multifactor experiment of second order. Viscosity of the 6% montmorillonite and water suspension was determined using a rotational viscosimeter.

Table 1
Exchangeable cations of montmorillonite

	mmol M^+/100 g
Ca	68.7
Mg	17.6
Na	9.2
K	3.4
Σ	98.9

Table 2
Chemical composition of the montmorillonite

	L.O.I.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
Percentage	6.6	68.5	17.0	2.33	2.0	3.0	0.65	0.15
Mol/elem.cell	–	10.78	3.01	0.26	0.32	0.67	0.19	0.33

The structural changes of the investigated system were determined using methods:

- X-ray diffraction analysis,
- IR-spectroscopy, and
- TGA analysis.

3. Results

3.1. Rheological properties – viscosity

Raw bentonite (6% suspension) has low viscosity of 4 mPa, while montmorillonite (<2 μm) has a slightly higher value of 5 mPa. Sodium activation of bentonite (4% of Na_2CO_3) increases viscosity to 9.6 mPa.

Samples of bentonite were activated using Na_2CO_3 in the concentrations of 2–4%, and then in the second stage using $Mg_2(OH)_2CO_3$ in the concentrations of 1–3%.

A maximum viscosity of 26 mPa was obtained for the bentonite activated with 3% Na_2CO_3 and 2% $Mg_2(OH)_2CO_3$. Montmorillonite activated with 3% Na_2CO_3 and 2% $Mg_2(OH)_2CO_3$ has viscosity of 116 mPa. In further text this sample will be referred to as activated montmorillonite.

3.2. Suspension pH values

Suspension pH values were also measured. Montmorillonite has a pH value of 8.1, while activated montmorillonite has a much higher value of 10.5.

3.3. CEC and exchangeable cations

Cationic exchange capacity (CEC) and exchangeable cations for montmorillonite are given under MATERIALS AND METHODS. Activated montmorillonite has a CEC coefficient of 110 mmol M^+/100 g.

The quantities of Ca^{2+} and Mg^{2+} in exchangeable positions were determined for the activated montmorillonite and they are 18 mmol M^+/100 g for Ca^{2+} and 27 mmol M^+/100 g for Mg^{2+}.

3.4. X-ray diffraction analysis

Characteristic values for d of the natural montmorillonite and for the heated sample are 1.520 nm and 0.966 nm, respectively. The characteristic d for the activated natural montmorillonite has a smaller value of 1.267 nm, while for the heated activated sample it is somewhat bigger than for the nonactivated sample and has a value of 0.976 nm.

Characteristic peaks for the montmorillonite indicates the Ca-montmorillonite. The activated montmorillonite pattern shows the spreading of the basic peak to 1.267 nm, with teeth at 1.32 and 1.45 nm (Fig. 1). This indicates the superposition of several diffraction peaks and the presence of Mg- and Ca-montmorillonite, besides Na-montmorillonite. X-ray diffractogram of the activated montmorillonite indicates, besides the dominant presence of montmorillonite, the appearance of new phases, which are weakly crystallized. Low peaks at 4.80 and

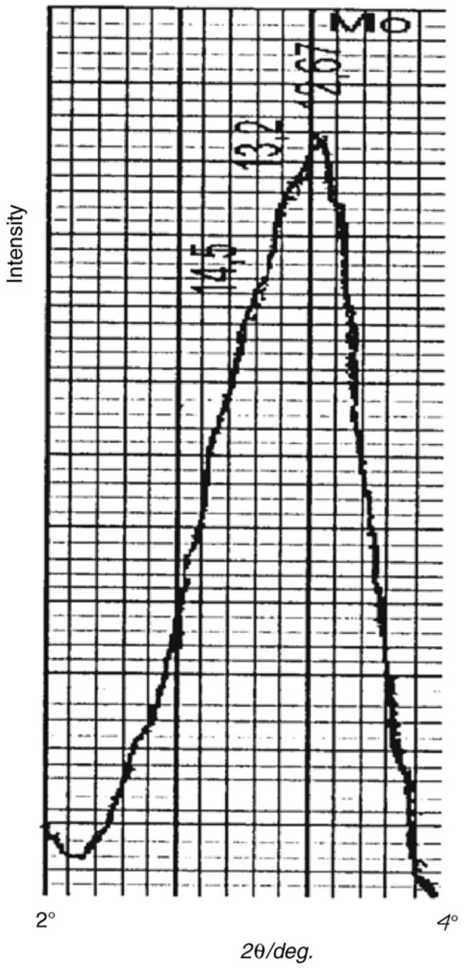

Fig. 1. d_{001}-Peak of the activated montmorillonite "Jelenkovac".

7.81 nm suggest the formation of weakly crystallized hydrotalcite.

3.5. IR analysis

Characteristic absorption bands indicate the dominant presence of the montmorillonite in both cases. Figs. 2–4 show parts of the spectrum shows differences and indicates certain structural changes and possible new phases. The intensity drop of the absorption band at 520 cm^{-1} for the activated montmorillonite indicates the possibility of migration of a small quantity of Al^{3+} from the montmorillonite octaedric layer (decreased Si–O–Al bond intensity) (Fig. 2.). Significant difference between the IR-spectrums of montmorillonite and activated montmorillonite occurs in the range of 1350–1700 cm^{-1} (Fig. 3). That region is characteristic for carbonate ions.[8] Besides the band at 1635 cm^{-1}, activated montmorillonite has two additional bands, with peaks at 1420 and 1480 cm^{-1}. These peaks correspond to the carbonate ions, but having different coordinations and levels of orderliness. The small degree of splitting of the bands (60 cm^{-1}) indicates that the remaining carbonates coordinate weakly with cations. The carbonate anion symme-

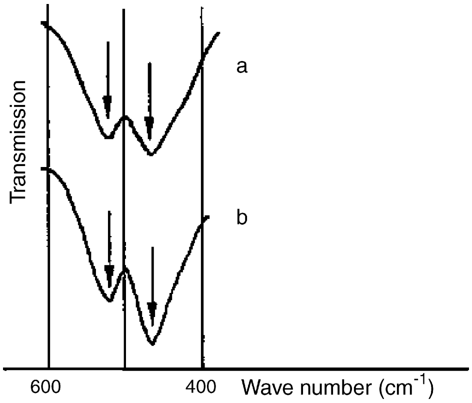

Fig. 2. IR spectrum of the region 400–600 cm^{-1} montmorillonite "Jelenkovac" activated montmorillonite "Jelenkovac".

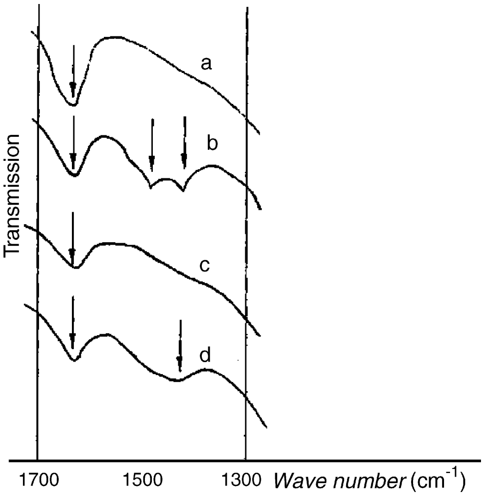

Fig. 3. IR spectrum of the region 1300–1700 cm^{-1}.

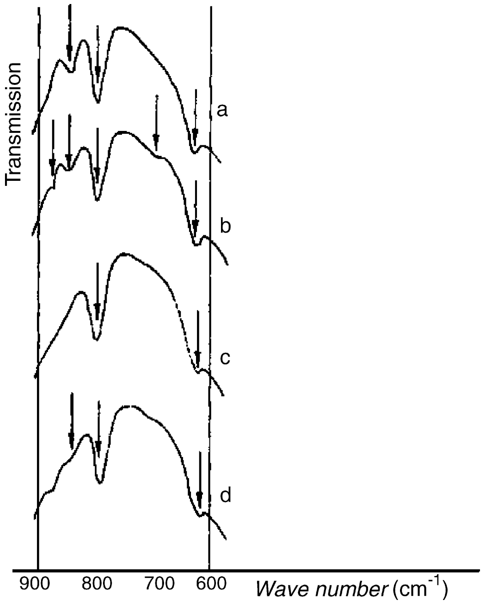

Fig. 4. IR spectrum of the region 600–900 cm^{-1}: (a) montmorillonite "Jelenkovac" (dried at 80 °C), (b) activated montmorillonite "Jelenkovac"(dried at 80 °C), (c) montmorillonite "Jelenkovac" (heating at 450 °C), and (d) activated montmorillonite "Jelenkovac" (heating at 450 °C).

try resembles to the sodium carbonate symmetry (1480 cm^{-1}). This indicates the presence of carbonate anions having the same orientation as hydrotalcite. When samples are heated to 450 °C the peak sharpness is lost and the remaining rounded absorption band indicates the weak bonds between residual carbonate anions (like hydrotalcite). Activated montmorillonite displays absorption bands in concave form at 870 and 690 cm^{-1}, which correspond to the free carbonate anion absorption (Fig. 4).

3.6. Thermogravimetric analysis (TGA)

Montmorillonite and activated montmorillonite were also subject to the thermogravimetric analysis. TG curves show a significantly smaller mass loss up to 200 °C for the activated sample, thus indicating higher interlayer water content in the nonactivated sample. However, if the 300–450 °C region is observed, the activated sample mass loss becomes evident. It corresponds to the H_2O and CO_2 loss from hydrotalcite.[9] Constitution water loss regions are practically identical.

3.7. Hydrotalcite synthesis

Characterization of activated montmorillonite showed the appearance of a new phase in the system, of the anionic clay type.[10,11] An attempt of synthesizing hydrotalcite in an independent system was made. Starting raw materials were admixtures for activating montmorillonite with the addition of aluminum salts. Conditions for hydrotalcite synthesis were equivalent to those of the montmorillonite activation process. Synthesis was completed under room conditions, with medium pH of 10.5 and drying and crystallization temperature of 60 °C.

3.8. Characterization of synthesized hydrotalcite

Characterization of hydrotalcite included: chemical analysis, X-ray diffraction and IR spectroscopy. The chemical analysis results: Al_2O_3: 16.27%, MgO: 35.23%, CO_2: 16.94%, H_2O (110 °C): 8.80%, H_2O (1000 °C): 22.79%.

X-ray diffractograms of the synthesized sample are given in Fig. 5. Hydrotalcite (H) was identified along with nonreacted alkaly magnesium carbonate (C). Quantitative yield of hydrotalcite was approximately 70%. Dimensions of the synthesized hydrotalcite crystal lattice are: $a = 0.302$ (0.3) nm; $c = 2.331$ (4.2) nm; $V = 0.190$ nm^3.

Hydrotalcite IR spectrum is given in Fig. 6. There is a pronounced wide absorption band in the 3000–3700 cm^{-1} region, characteristic for OH vibrations of the basic hydrotalcite layer. Absorption at 1630 cm^{-1} is the consequence of interlayer water existence in hydrotalcite. Peaks at 1365, 1420 and 1485 cm^{-1} are characteristic for carbonate anions that are differently bonded in hydrotalcite and basic magnesium carbonate.

Absorptions at 890, 850 and 680 cm^{-1} are due to the carbonate anion. Absorption band at 400 cm^{-1} is characteristic for hydrotalcite.

Assuming that the synthesis process yielded 70% of hydrotalcite and 30% of basic magnesium carbonate, the following structural formula was derived from the results of chemical analysis: $[Mg_{0.64}Al_{0.31}(OH)_2][(CO_3)_{0.16}0.62H_2O]$.

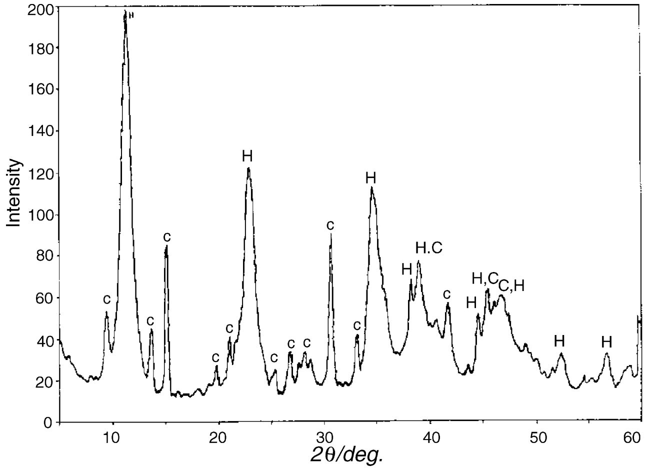

Fig. 5. X-ray diffractograms of the synthesized hydrotalcite.

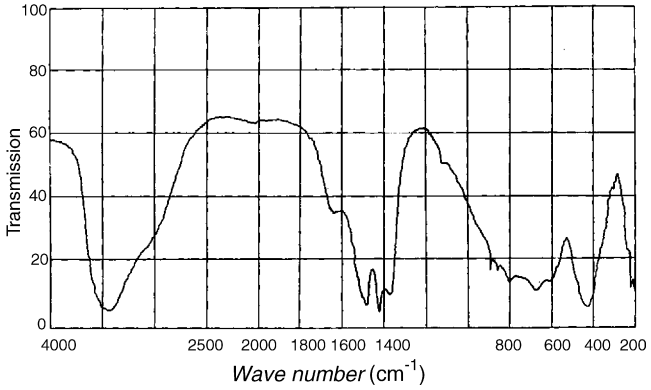

Fig. 6. IR spectrum of the synthesized hydrotalcite.

4. Discussion of results

Natural bentonite has low viscosity and no thixotropic properties. Sodium activation enhances rheological properties, but not significantly. Sodium magnesium activation (with Na_2CO_3 and $Mg_2(OH)_2CO_3$) enables a significant change of rheological properties (viscosity). Activation of montmorillonite with 3% of Na_2CO_3 and 2% of $Mg_2(OH)_2CO_3$) increased the water suspension viscosity up to the 116 mPa.

The basis of the chemical process of alkaline activation of bentonite is the ion exchange reaction between the montmorillonite and the soluble salts in water. Sodium activation of montmorillonite causes particle deagregation and increase of number of thin particles in hexagonal laminar form. Introduction of $Mg_2(OH)_2CO_3$ into the system causes a significant change of the system pH value, from 8.5 to 10.5 and increase in CEC value from 98 to 110 mmol M^+/100 g. The exchangeable cations ratio is Na:Ca:Mg = 55:18:27. A detailed structural analysis of the activated montmorillonite proves the appearance of certain structural changes due to the Al^{3+} ion migration from the montmorillonite octaedric position into the interlayer region.

A new phase of the anionic clay appears in the investigated system. Anionic clay particles are positively charged and positive charge is compensated by exchangeable anions. The investigation results proved the possibility of hydrotalcite synthesis $[Mg_{0.64}Al_{0.31}(OH)_2][(CO_3)_{0.16}0.62H_2O]$ from hardly soluble magnesium salt $Mg_2(OH)_2CO_3$, with pH 10.5.

The anionic clay obtained during the activitation of montmorillonite serves as an additional cation activator. In alkaline medium (pH 10.5), activated montmorillonite develops a "band structure" under the dominant influence of Ca^{2+} ions and a somewhat "networked structure" under the influence of Mg^{2+} ions. Anionic clay particles serving as cation activators secure the formed networked "band structure" according to the "latch" model. The explained model leads to a significant change in rheological properties of the activated montmorillonite.

5. Conclusion

The research of the behavior of dispersive systems such as the montmorillonite, $Mg_2(OH)_2CO_3$, Na_2CO_3 and water system requires a multidisciplinary approach. There is a trend in modern literature called "clay particle engineering" which covers a whole range of scientific fields, such as: colloid chemistry, physical chemistry of solid state surfaces, rheology and others. Chemical processes that take place during bentonite activation or clay pillared provoke certain structural changes in clay minerals thus enabling the obtaining of modern materials based on clay particles but having much better properties than classical materials of this type. Anionic clay structures have an extremely important place in modern research.

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