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Columnar Clays Intercalated With Iron Compounds

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ABSTRACT.The structural characteristics of montmorillonite clay of the Krantau deposit, intercalated with iron hydroxocations in various ways, which were conventionally called dry and ash, were studied. The dependence of the thermal behavior and adsorption characteristics of pillar montmorillonites on the structure, in particular on the size of the interplanar space and the nature of the introduced oligomeric oxides, has been established. The XRD results showed that the d_{001} value, which determines the size of the slit micropores, depends on the method of clay intercalation. The interplanar distance d_{001} for the samples synthesized by the first method is 14,7-15,1 Å, while for the samples based on the second method it is 13,7-14,3 Å. Various changes in the interplanar spacing show the possibility of synthesizing an intercalating cation of various nature and size. Heat treatment of the samples according to the first method does not lead to a noticeable change in the interplanar space of intercalated montmorillonites, due to the formation of a more complex structure than the classical periodically columnar structure.

KEYWORDS.Intercalation, Fe-clay, benzene, adsorption, X-ray phase analysis, interplanar spacing, montmorillonite, textural characteristics.

I. INTRODUCTION

A wide range of researchers in the field of clay materials are aware of the ability of smectite group minerals to be filled with oligomeric cations of polyvalent metals and ammonium organic compounds [1, 2]. Due to the process of introduction - intercalation of foreign ions, the properties of clay minerals change: thermal stability, adsorption and catalytic capabilities, etc. To date, depending on the needs of clay materials, methods have been developed for the purposeful implementation of some intercalation processes [3-5]. The cavities or pores formed during the intercalation of columnar clays of a zeolite-like structure mainly depend on the nature, size and shape of the intercalated particles and, as a rule, are much larger than typical pores of zeolites [6-9]. Columnar clays have a relatively large specific surface area compared to the starting materials [10]. The high specific surface area and surface acidity of columnar clays make them attractive as adsorbents, catalysts, and their carriers. In this respect, Fe-intercalated montmorillonites (MM) are of potential interest. Such systems were presented as catalysts for the reductive and oxidative removal of nitrophenol [11, 12], thiocyanates [13], organic dyes [14], and adsorbents [15, 16]. The aim of the research was to study the synthesis processes of intercalated montmorillonites and their surface properties..

II. SIGNIFICANCE OF THE SYSTEM

The article presents the kinetics of sorption of lead ions in a solution of lead nitrate with composite polymer sorbents. The study of literature survey is presented in section III, methodology is explained in section IV, section V covers the experimental results of the study, and section VI discusses the future study and conclusion.

III. METHODOLOGY

Natural clays of the Krantau deposit (KR2) [17, 18] were subjected to enrichment by elutriation until the complete removal of non-clay impurities. The enriched forms of clays were dried at a temperature of 104 ± 1 °C and crushed. The intercalation of Fe^{3+} cations into the interlayer space of montmorillonite was carried out under different conditions: 1) Dry method: calculated amounts of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ salt (from 1 to 10 mmol Fe^{3+} per 1 g of clay) were added to a suspension of bentonite, where the mass content of the solid and liquid phases was 1:15, with constant stirring on a magnetic stirrer at room temperature. A 1 M NaOH solution was added dropwise to the resulting suspension at the ratio $\text{OH} / \text{Fe}^{3+} = 2$ and left alone at room temperature for 24 hours. Before the separation of the solid phase, the suspension was sonicated with a wave frequency of 50 kHz for 5 min. Then the resulting mass was washed until negative reaction from Cl^- ions and dried; 2) Ash method: solutions containing an intercalating agent were prepared by dissolving 67,625 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ salt in distilled water and bringing the solution volume to 500 ml. A 1 M NaOH solution was added dropwise to the resulting solution with constant stirring and at a temperature of 50 °C until the molar ratios $\text{OH}/\text{Fe}^{3+} = 2$ were reached, then it was kept at rest at room temperature for 24 hours. A suspension of bentonite was prepared by dispersion using ultrasound with a wave frequency of 50 kHz for 5 min and at a mass ratio of solid and liquid phases of 1:10. Certain amounts of the intercalating solution (from 1 to 10 mmol Fe^{3+} per 1 g of clay) were added dropwise to this suspension with constant stirring on a magnetic stirrer. The resulting suspension was left at rest for 24 hours. Then the solid phase of the suspension was separated from the liquid by centrifugation, washed until the Cl^- ions were completely removed, and dried at a temperature of 100 ± 1 °C. The resulting samples were milled and then sieved through a 170 mesh screen. The sieved intercalated clays were calcined at temperatures from 200 to 500 °C for 2 hours at a heating rate of 2 °C / minute. To determine structural changes in the intercalation process in order to purposefully change stability and porosity, complex analytical methods were used, including X-ray phase (XRD), spectrophotometric and electron microscopic (scanning electron microscope EVO MA10 SEM) analysis methods. X-ray diffraction patterns were obtained on an XRD Empyrean PANanalytical X-ray diffractometer. At the same time, an Al 1200 atomic adsorption spectrophotometer was used for the chemical analysis of the sample. The IR spectra of the synthesized materials were recorded on an Avatar 360 FT-IR Nicolet iS50 Thermo Fisher Scientific spectrometer with Fourier transform in the frequency range 400-4000 cm^{-1} . The textural characteristics are determined by the amount of adsorption of water and benzene vapors on the McBen vacuum adsorption unit

IV. EXPERIMENTAL RESULTS

The XRD results showed that the d001 value, which determines the size of the slit micropores, depends on the method of clay intercalation. The interplanar distance d001 for the samples synthesized by the first method is 14,7-15,1 Å, while for the samples based on the second method it is 13,7-14,3 Å. Various changes in the interplanar spacing show the possibility of synthesizing an intercalating cation of various nature and size. The study of the effect of heat treatment on the thermal stability of the samples showed that the thermal behavior of materials is also determined by the nature of the intercalating cation. For a sample of 10 mmol Fe/g clay (10-Fe-KP2-1), the d001 value decreases only to 13,4 Å, and the intensity of the first basal reflection falls from 100 to 83% upon heating to 500 °C (Fig. 1), which indicates the preservation of the microporous structure. The thermal stability of these intercalated systems is due to the fixation of nanosized particles of Fe (III) oxides formed during the dehydration of iron polycations in the interlayer space of montmorillonite. On the X-ray diffraction patterns of dried (unheated) samples 10-Fe-KR2-1; 5-Fe-KP2-1 and 2-Fe-KP2-1 there are lines characteristic of oligomeric acaganeite (7,4; 331 Å). XRD results have shown the retention of the structure of the oligomer to a large extent during heat treatment up to 300 °C [19, 20]. With a further increase in heat treatment (more than 300 °C), the intensity of the lines characteristic of iron hydroxides (goethite-4,14; 2,7 Å and acaganeite-3,31; 2,54 Å) decreases and additional lines characteristic of iron oxides (hematite 2,696; 2,518 Å). In the case of the second method, with such ratios of complex cations and clay, the samples (10-Fe-KR2-2) are less stable even when heated at temperatures of 200; 300; 400 and 500 °C d001 drops to 13,8; 12,1; 11,7 and 10,9 Å, respectively, and the intensity of the first basal reflection decreases to 23-40%. Only in the case of intercalation of iron ions at ratios of less than 5 mmol/g of clay does the d001 value fall to 9,6, the intensity 4-11%, which indicates the destruction of the initial structure during heat treatment of clays (Table 1; Fig. 1). The intensity of the lines characteristic of compounds of iron oxide and hydroxide groups is very insignificant, which indicates a low content of these nanoparticles in the interlayer space of heat-treated clays. Changes in structure depending on the amount of intercalating solution and the temperature of heat treatment are given in table.1.

Table 1
Change in the interplanar spacing of intercalated clays, depending on the iron content and processing temperature

Sample	Heating temperature, °C	d_{001} , Å	I/I_0 , %	ContentFe, %
KP2	500	9,9	6	5,8
2-Fe-KP2-1	100	13,1	88	7,1
	200	12,1	76	7,1
	300	11,6	71	7,1
	500	10,6	65	7,0
5-Fe-KP2-1	100	14,7	90	8,4
	200	12,9	82	8,6
	300	12,5	80	8,6
	500	12,1	78	8,6
10-Fe-KP2-1	100	15,1	94	12,6
	200	15,0	90	12,6
	300	14,6	88	12,6
	500	13,4	83	12,7
2-Fe-KP2-2	100	12,7	72	6,8
	200	11,8	36	6,7
	300	11,4	25	6,7
	500	10,0	13	6,7
5-Fe-KP2-2	100	12,8	81	7,6
	200	12,4	46	7,6
	300	11,2	34	7,6
	500	10,1	18	7,6
10-Fe-KP2-2	100	13,8	78	10,8
	200	12,1	40	10,9
	300	11,7	29	11,0
	500	10,9	23	11,1

Heat treatment of the samples probably causes the transformation of the columns of iron oxyhydrates into larger and more ordered clusters by dehydroxylation. In [21], data are given on the successful intercalation of Fe^{3+} ions between layers of montmorillonite crystals and the formation of a more complex structure than the classical periodically located structure. The authors concluded that they are responsible for the high basal distances of Fe^{3+} aggregates with a globular structure. Probably, in our case, the intercalation of the initial montmorillonite according to the first method promotes the formation of oligomeric polyoxocations of the metal, which under certain temperature conditions form clusters not of the usual columnar structure, but of more complex ones. The formation of a more complex structure is responsible for maintaining the interplanar spacing between the layers of intercalated montmorillonites.

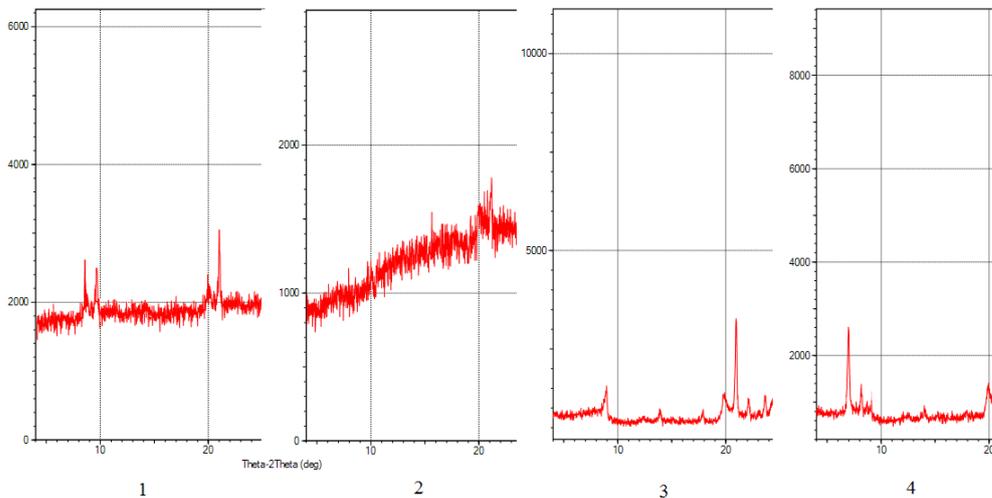


Fig. 1. Diffraction patterns of samples: 1) natural KP2; 2) calcined at 500 ° C KP2; 3) 5-Fe-KP; 4) 10-Fe-KP.

Spectrophotometric studies were carried out to reveal the structural features of Fe³⁺ nanoparticles in the montmorillonite matrix, which cannot be refined by XRD. Nevertheless, the existing difficulty of studying these nanoparticles by IR spectroscopy is associated with insignificant differences in the vibration frequencies of Si-O and Fe-O. At the same time, the frequencies can change depending on the amount of water and hydroxyl groups, which depends on the conditions of the intercalation process.

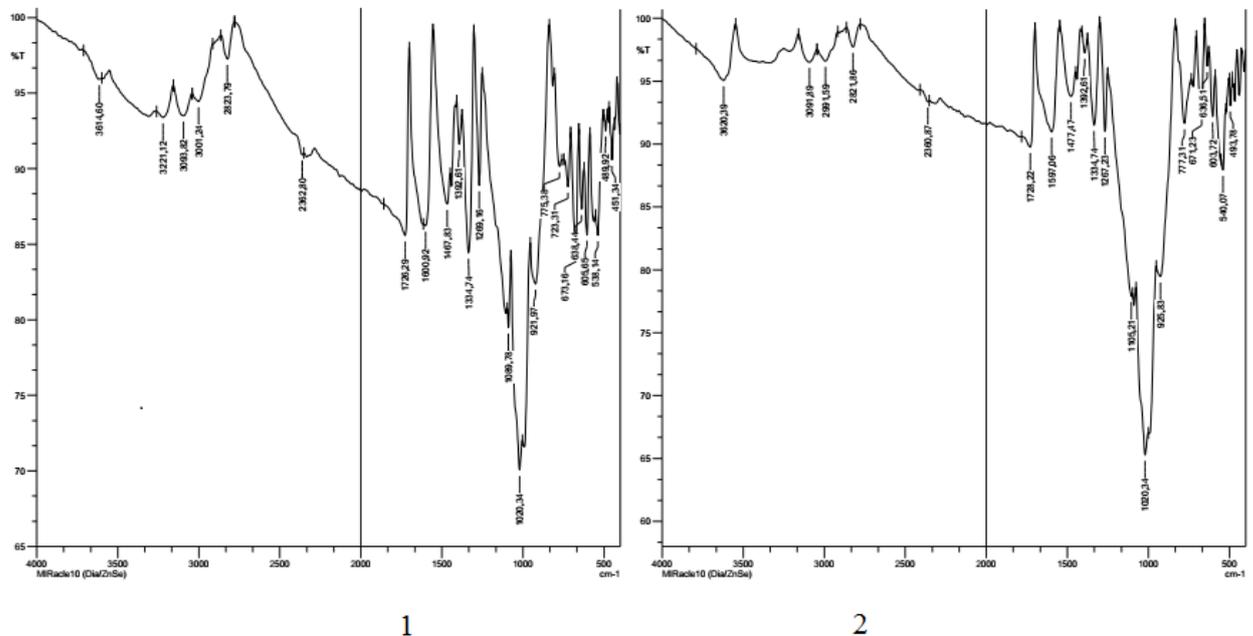


Fig. 2. IR spectra of 5-Fe-KR-1 samples heat treated at temperatures, °C: 1) 100; 2) 300.

Deciphering the above spectrum of the enriched Raman sample shows that the main bands displayed on them belong to the valence bonds of silicon and hydrogen with oxygen atoms. A well-pronounced broad band at 1040 cm⁻¹ corresponds to stretching vibrations of Si-O-Si tetrahedra of the silicon-oxygen framework, and the bands at 467 and 524 cm⁻¹ to bending vibrations of Me-O bonds. The band at 797 cm⁻¹ corresponds to Si – O – Si vibrations of rings of SiO₄ tetrahedra. High-intensity bands in the range of 3100-3500 and 1638 cm⁻¹ are related to OH-stretching and bending vibrations of free and bound water. In the range 860–798 cm⁻¹, stretching Al – O vibrations of condensed AlO₄ tetrahedra are manifested [22, 23]. The IR spectroscopic data showed a significant difference in the intensity of



the absorption bands depending on the conditions of intercalation. The appearance of new chemical bonds is observed in the spectra of intercalated clays. Thus, after intercalation of iron polycations, the absorption bands at 2823, 3001, and 3093 cm^{-1} are explained by the stretching of hydroxyl groups, and the band at 1467 cm^{-1} is associated with bending vibrations of Al-O- or Si-O- groups and their hydrogen bonds with hydroxyl groups. The detection of the peak at 3322 cm^{-1} allows one to associate it with the presence in the structure of Fe^{3+} cations bound to OH groups. In all samples dried only at 100 °C in the wavenumber range of 1610-1600 cm^{-1} , a polymeric form of water was found, which mixes in the 1590 region when heated to 200 °C, and in the samples heated at higher temperatures (>400 °C), this peak is not observed, which indicates the disappearance of the elements contributing to the manifestation in the composition of the samples. At the same time, in the region of 1060–920 cm^{-1} (a peak at 1020 cm^{-1}), there is a peak corresponding to the bending vibration of hydroxyl groups bound to the aluminum atom (Al – OH). The peak at 3620 cm^{-1} corresponds to in-phase stretching vibrations of internal OH-groups or 2Al-OH-bonds of montmorillonite. The presence of an interaction between the intercalated component and montmorillonite is reflected in a change in the characteristics of the vibration frequencies of silicon-oxygen bonds. In samples with higher Fe^{3+} contents (10-Fe-KP2-1 and 10-Fe-KP2-2), an absorption band is observed at 605 cm^{-1} , which is not observed in the spectra of other samples of intercalated clays. Calcination leads to an increase and shift of this band to the region of 612 cm^{-1} . Probably, this absorption band is caused by the vibration of the Fe-O bond in the composition of the formed crystal structure of Fe_2O_3 . Apparently, in other samples with lower Fe^{3+} contents in the interplanar space, the bands of stretching Fe-O vibrations are not detected against the background of intense absorption bands characteristic of Si-O. The study of the adsorption of water and benzene vapors on intercalated clays showed the distinctive nature of the adsorption isotherm (Figs. 3 and 4). The isotherms of water vapor adsorption on the initial and initial calcined samples (500 °C) belong to type II according to the IUPAC systematics. Intercalation of clays promotes an increase in the sorption of water vapor at low values of relative pressure, which indicates the formation of new micropores. The isotherm of water vapor adsorption on sample 10-Fe-KR2-1 (100 °C) has the form of hysteresis, which indicates the occurrence of irreversible capillary condensation. The maximum amount of adsorbed water is 8.36 mol/kg. The adsorption and desorption isotherms of 5-Fe-KR2-1 and 2-Fe-KR2-1 are characteristic of slit pores and also show the occurrence of irreversible polymolecular adsorption on an inhomogeneous surface. The hysteresis loop on the desorption isotherm for the 10-Fe-KR2-2 sample closes at a relative pressure of 0.19, which indicates the presence of micropores. The maximum amount of adsorbate on the surface of adsorbents 10-Fe-KR2-2; 5-Fe-KP2-2 and 2-Fe-KP2-2 is: 7.23; 4.218 and 3.42, which is lower than the values of those characteristics of the samples synthesized by the first method. High values of the amount of water adsorption in intercalated systems are associated with the presence of a strong intermolecular effect between the molecules of the adsorbate and adsorbent. Calcination led to a decrease in active sites with respect to water molecules due to dehydroxylation of the formed interlobular columns. As it turned out, the final dehydroxylation at temperatures above 500 °C, in addition to a decrease in active hydrophilic centers, leads to a noticeable decrease in the size of accessible pores.

Undoubtedly, according to the amount of adsorption of hydrophobic benzene, all studied objects have relatively low values. However, it can be seen that the adsorption isotherm of benzene vapors on intercalated samples in the region of lower values of relative pressure has a relatively convex structure and is higher than the adsorption isotherm of the initial sample KP2, which indicates an increase in micropores as a result of the incorporation of Fe^{3+} cations. The amount of benzene adsorption of the initial clay KP2 and its calcined form (500 °C) is 0,638 and 0,448 mol/kg, respectively. As it turned out, calcination of intercalated samples, on the contrary, promotes an increase in adsorption activity with respect to the hydrophobic agent. So, for samples 10-Fe-KR2-1 and 10-Fe-KR2-2, these indicators have the highest values and are 1,205 and 1,123, and for their forms calcined at 200 °C, the amount of adsorption increased by 16,8 and 12,1%, respectively. A further increase in processing temperature contributes to an increase of another 2-3%. With an increase in the relative pressure p/p_s from 0 to 0,2, a phenomenon was observed when adsorption in adsorbents approaches the state of micropore saturation. It was determined that these adsorption isotherms belong to type I classification proposed by BDDT. Probably, the improvement in the adsorption characteristics of calcined intercalated clays is associated with a decrease in hydroxyl groups, which prevent the physical adsorption of benzene molecules in accessible pores, as well as the formation of complexes with iron atoms in the composition of pillars from oxides. At the same time, for samples 5-Fe-KR2-1 and 2-Fe-KR2-1 calcined at 500 °C, an increase in the amount of adsorption by 13,1 and 4,5%, respectively, is characteristic. However, the calcined adsorbents obtained by the second method with similar ratios of the starting materials do not show noticeable improvements in adsorption performance. On the contrary, for sample 2-Fe-KR2-2, a decrease in benzene adsorption is observed with an increase in the calcination temperature above 300 °C, which indicates the absence of pores with the

corresponding characteristics and the necessary iron atom in the composition of pillar clays. Table 2 shows the results of determining the texture characteristics of some of the samples studied.

Table 2.
Changes in the texture properties of clay depending on the method of intercalation and calcination temperature

Sample	Calcination temperature, °C	Texture characteristics					
		A _∞ , mol/kg	S, m ² /g	V _a , sm ³ /g	V _b , sm ³ /g	ΣV, sm ³ /g	ΔR, nm
By adsorption of water vapor							
KP2	100	0,518	74,20	0,045	0,016	0,061	2,11
	500	0,511	70,50	0,021	0,022	0,045	2,18
5-Fe-KP2-1	100	2,436	158,36	0,100	0,030	0,131	1,66
	500	1,597	103,80	0,080	0,030	0,114	2,20
5-Fe-KP2-2	100	1,534	101,10	0,081	0,030	0,111	1,88
	500	1,443	93,20	0,075	0,020	0,095	2,34
By adsorption of benzene vapor							
KP2	100	0,213	51,33	0,022	0,027	0,050	2,36
	500	0,188	41,32	0,011	0,030	0,041	3,01
5-Fe-KP2-1	100	0,465	108,80	0,080	0,018	0,098	2,11
	500	0,452	111,97	0,091	0,020	0,111	1,75
5-Fe-KP2-2	100	0,402	99,50	0,074	0,011	0,085	2,01
	500	0,416	102,40	0,080	0,012	0,092	1,98

It should be noted, as the water vapor adsorption data shows, the intercalation method has little effect on the mean mesopore volume (V_b) of the obtained samples 5-Fe-KP2-1 and 5-Fe-KP2-2 and is 0,03. However, calcination of the 5-Fe-KR2-2 sample leads to a decrease in the values of this indicator to 0,0197 or less, while for the first sample, calcination does not lead to noticeable changes. All of these values are higher than the corresponding values of the original sample. The results of the experiments showed that intercalation of Fe³⁺ ions into the interlayer space of montmorillothy clay KP2 can be used to obtain samples with the largest volume of micropores. As a result, the development of sorption characteristics with respect to hydrophilic and hydrophobic adsorbates is due to the formation of both micropores and mesopores between disordered fragments of clay layers. As the authors note, new layers can be formed due to the destruction of lamellar particles during ion exchange and heat treatment [24]. Micrographs of intercalated clay samples show agglomerate particles with a size of no more than 30-40 microns, while for the original sample, the sizes of these particles exceed 50 microns.

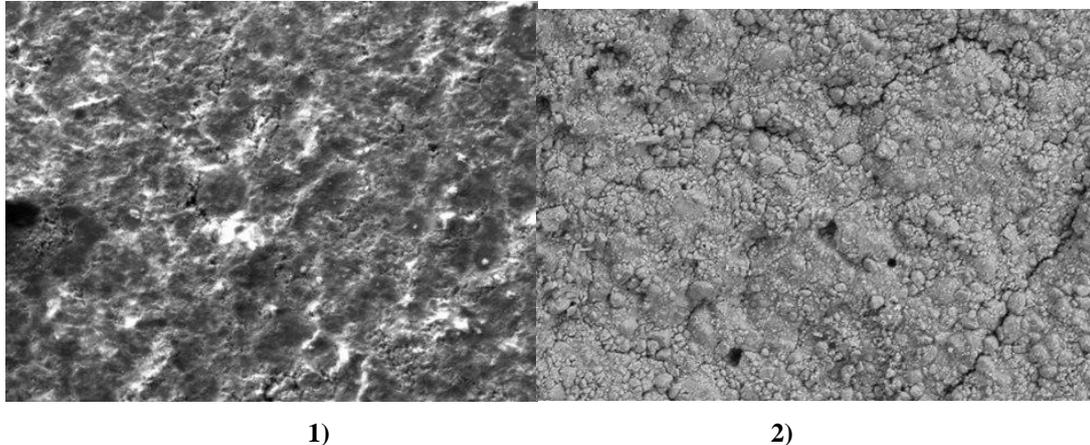


Fig. 3. Electron microscopic images of the 5-Fe-KR2-1 sample: 1) without calcination; 2) after calcining at 500 ° C.

V. CONCLUSION AND FUTURE WORK

Thus, an experimental study of the structural characteristics of Fe-pillar montmorillonites showed that by regulating the intercalation process, it is possible to purposefully change these characteristics. Obtaining pillar clays by the first method contributes to the formation of more stable pillars with large values of the volume of micro and mesopores. Heat treatment of these samples does not lead to a noticeable change in the interplanar space of intercalated montmorillonites, due to the formation of a more complex structure than the classical periodically columnar structure.

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