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Formation of the Kaolin Structure Treated by Pressure

Valerii V. Seredin[1], **Andrey V. Andrianov**[1], **Sharibzan Kh. Gaynanov**[1], **Vladislav I. Galkin**[2], **Sergey S. Andreyko**[2]

[1]Perm State National Research University (15 Bukireva st., Perm, 614068, Russian Federation)
[2]Perm National Research Polytechnic University (29 Komsomolskiy av., Perm, 614990, Russian Federation)

Формирование структуры каолина, обработанного давлением

В.В. Середин[1], **А.В. Андрианов**[1], **Ш.Х. Гайнанов**[1], **В.И. Галкин**[2], **С.С. Андрейко**[2]

[1]Пермский государственный национальный исследовательский университет (Россия, 614068, г. Пермь, ул. Букирева, 15)
[2]Пермский национальный исследовательский политехнический университет (Россия, 614990, г. Пермь, Комсомольский пр., 29)

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To form the technological properties of clays, various methods of their activation have been developed, the essence of which is that when processing clays, their structure (defectiveness) changes, which forms the energy potential of clay particles, and the latter is realized in the form of "specified" physicochemical properties of clays. In this regard, the effect of stress pressure on the change in the defectiveness of structural elements of kaolin was studied.

Experimental studies showed that the pressure value $P = 150$ MPa was the boundary value at which different conditions for the formation of defectiveness of structural elements of kaolin were observed. High pressure has a multidirectional effect on the defectiveness formation of the kaolin structural elements: a package, a mineral, a colloid and an aggregate.

In a package of kaolinite mineral, the defectiveness increases with increasing pressure. Defects are formed due to the removal of Al, Fe, Mg, Si ions from the octahedral and tetrahedral sheets. Al ions are the most sensitive to pressure. The removal of ions entails deformation of the packet and the formation of "hole" energy centers. Pressure up to 0–150 MPa has a greater effect on the formation of defectiveness (calculated correlation coefficient $r_c = 0.86$) than in the range 150–800 MPa ($r_c = 0.82$).

In the kaolinite mineral at pressures up to 150 MPa, a decrease in defectiveness is observed due to the ordering of the structure under pressure ($r_c = 0.67$). At pressures above 150 MPa, an increase in the defectiveness of the kaolinite mineral ($r_c = –0.72$) is observed due to the destruction of hydrogen bonds between the packets, which entails the sliding and rotation of the structural packets among themselves.

In a colloid (particle), with an increase in pressure to 150 MPa, the structural defect decreases due to an increase in the colloid density ($r_c = 0.67$). In the pressure range of 150–800 MPa, it is rather difficult to reveal the effect of pressure on the formation of defectiveness ($r_c = 0.37$).

In the aggregate, with an increase in pressure to 150 MPa, the defectiveness of the structure increases due to crushing of particles, sliding and displacement of particles among themselves ($r_c = 0.95$). In the pressure range of 150–800 MPa, it is rather difficult to reveal the influence of pressure on the formation of defectiveness ($r_c = 0.58$), although the tendency increases with increasing pressure, the defectiveness of the aggregate remains.

Ключевые слова:
глина, каолин, давление, структура, дефектность, химический состав, ионные связи, дефекты структурного пакета, минерал, коллоид, агрегат, техногенная обработка, активация глин.

Для формирования технологических свойств глин разработаны различные способы их активации, суть которых заключается в том, что при обработке глин изменяется их структура (дефектность), которая формирует энергетический потенциал глинистых частиц, а последний реализуется в виде «заданных» физико-химических свойств глин. В связи с этим изучено влияние стрессового давления на изменение дефектности структурных элементов каолина.

Экспериментальные исследования показали, что значение давления $P = 150$ МПа является граничным, при котором наблюдаются различные условия формирования дефектности структурных элементов каолина. Высокое давление оказывает разнонаправленное воздействие на формирование дефектности структурных элементов каолина: пакета, минерала, коллоида и агрегата.

В пакете минерала каолинита с увеличением давления дефектность возрастает. Дефекты формируются за счет выноса из октаэдрического и тетраэдрического листов ионов Al, Fe, Mg, Si. Наиболее чувствительными к давлению являются ионы Al. Вынос ионов влечет за собой деформации пакета и формирование «дырочных» энергетических центров. Давление до 0–150 МПа оказывает большее влияние на формирование дефектности ($r_p = 0,86$), чем в интервале 150–800 МПа ($r_p = 0,82$).

В минерале каолините при давлениях до 150 МПа наблюдается уменьшение дефектности за счет упорядочивания структуры под давлением ($r_p = 0,67$). При давлениях больше 150 МПа наблюдается увеличение дефектности минерала каолинита ($r_p = –0,72$) за счет разрушения водородных связей между пакетами, что влечет за собой скольжение и вращение структурных пакетов между собой.

В коллоиде (частице) при увеличении давления до 150 МПа дефектность структуры уменьшается за счет увеличения плотности коллоида ($r_p = 0,67$). В диапазоне давления 150–800 МПа выявить влияние давления на формирование дефектности достаточно сложно ($r_p = 0,37$).

В агрегате при увеличении давления до 150 МПа дефектность структуры возрастает за счет дробления частиц, скольжения и смещения частиц между собой ($r_p = 0,95$). В диапазоне давления 150–800 МПа выявить влияние давления на формирование дефектности достаточно сложно ($r_p = 0,58$), хотя тенденция с ростом давления возрастает, дефектность агрегата сохраняется.

Valerii V. Seredin (Author ID in Scopus: 56974744000) – Professor, Doctor in Geology and Mineralogy, Head of the Department of Engineering Geology and Subsoil Protection (tel.: +007 912 988 83 09, e-mail: seredin@nedra.perm.ru). The contact person for correspondence.
Andrey V. Andrianov (Author ID in Scopus: 57143872200) – PhD Student at the Department of Engineering Geology and Subsoil Protection (tel.: +007 342 211 51 55, e-mail: Andrianov@nedra.perm.ru).
Sharibzan Kh. Gaynanov – PhD in Geology and Mineralogy, Associate Professor at the Department of Engineering Geology and Subsoil Protection (e-mail: seredin@nedra.perm.ru).
Vladislav I. Galkin (Author ID in Scopus: 55418067700) – Doctor in Geology and Mineralogy, Professor, Head of the Department of Oil and Gas Geology (tel.: +007 902 472 95 81, e-mail: vgalkin@pstu.ru).
Sergey S. Andreyko (Author ID in Scopus: 55922205900 (Andreyko), 6506180352 (Andreiko)) – Doctor of Engineering, Professor, Head of the Department of Development of Mineral Recourses Fields (tel.: +007 912 882 43 93, e-mail: rmpi@pstu.ru).

Середин Валерий Викторович – профессор, заведующий кафедрой инженерной геологии и охраны недр, доктор геолого-минералогических наук (тел.: +007 912 988 83 09, e-mail: seredin@nedra.perm.ru). Контактное лицо для переписки.
Андрианов Андрей Владимирович – аспирант кафедры инженерной геологии и охраны недр (тел.: +007 342 211 51 55, e-mail: Andrianov@nedra.perm.ru).
Гайнанов Шарибзан Хатинович – доцент, кафедры инженерной геологии и охраны недр, кандидат геолого-минералогических наук (тел.: +007 342 211 51 55, e-mail: seredin@nedra.perm.ru).
Галкин Владислав Игнатьевич – профессор, заведующий кафедрой геологии нефти и газа, доктор геолого-минералогических наук (тел.: +007 902 472 95 81, e-mail: vgalkin@pstu.ru).
Андрейко Сергей Семенович – профессор, заведующий кафедрой разработки месторождений полезных ископаемых, доктор технических наук (тел.: +007 912 882 43 93, e-mail: rmpi@pstu.ru).

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Introduction

Properties of clays are largely defined by their composition and structure [1, 2]. There are various methods devised to activate clays that enhance their technological properties. In a nutshell, when clays are processed, it changes their structure (defectiveness) that shapes up the energy potential of clay particles, and this potential manifests itself as preset physicochemical properties of clays.

Namely, the studies found [3–5] that when clays are heated to 400–600 °C it unlocks high-energy centers on the surface of the mineral, which increases their adsorption activity. During UV-activation of clays [6] metal ions leave the octahedral positions due to the weakened bonds in the crystal lattice of minerals. This helps to increase the adsorption activity of clays by a factor of 1.3. Ultrasound treatment of clays destroys the aggregates and extends the crystal structure, which leads to higher absorption activity of clays [7, 8].

There are only a few studies that concern changes in defectiveness of pressurized kaolinite. The most detailed research of the matter was accomplished by A.G. Kossovskaya et al. back in 1963 [9], E.A. Goylo et al. in 1966 [10], K.J. Range et al. in 1969 [5], V.A. Frank-Kamenetsky et al. in 1970 and 1983 [11, 12], A. La Iglesia in 1993 [13], E. Galan et al. in 2006 [14]. Specifically, A. La Iglesia in 1993 [13] found that kaolin under pressures below 2000 MPa fails to show any noticeable structure defectiveness changes, whereas at pressures over 4000 MPa such changes do occur. Electron microscopy revealed that kaoline pressurized at 100-2000 MPa is characterized by a large number of defects (cracks, bends, deformations, compacted layers, sheet slips and rotations, etc.). Fang et al. in 2017 [15] stated that pressures up to 0.600 GPa break the structure of kaolin that gets restored at 66.2 GPa. When under pressure, the Al–O bond is weaker than Si–O, and the bond strength of the hydroxyl groups in kaolinite decreases as the pressure rises. The study of Welch et al. [16] in 2012 showed that kaolinite under pressure up to 9.5 GPa undergoes polymorphic changes that are registered by IR spectroscopy (v = 3.595 cm^{-1}).

Works by E. Galan et al. in 2006 [14] proved that kaolin treated at pressures up to 1320 MPa manifests structural changes and defects. At 400 MPa, the average number of layers (crystallites) grew from 25 to 36. While researching kaolin at 1500–2300 MPa, E.A. Goylo [10] concluded that stress pressure is the main cause of its defectiveness. Similar conclusions were drawn by V.A. Frank-Kamenetsky et al. in 1970 and 1983 [11, 12], V.V. Boldyrev in 2006 [17], and others. When pressurized, kaolinite transforms, for instance, into dickite, potassium feldspar, etc. [18, 19]. The mentioned findings indicate that the nature of how pressure affects the defectiveness of kaolinite's structural package remains understudied. Therefore the purpose of this study is to investigate the influence of stress pressure on the changes in the defectiveness of kaolin structural elements.

Methodology

In terms of methodology, the research was conducted in the following order: at first, samples of kaolin clay rich in clay particles were subject to compression and displacement within the range of pressures from 0 to 800 MPa following the procedure described by V.V. Seredin et al. in 2017 [20]. Then one group of samples was screened for their chemical composition using X-ray analysis [21], while the other group was studied for deformation and valency bonds between ions using IR-spectroscopy [22–24].

IR spectra were registered using the FT-IR spectrometer FSM 1201 made by Infraspec LLC in the range of 400–4000 cm^{-1} with resolution of 2 cm^{-1} (FT-IR) and Fspec software [22, 25].

The X-ray diffraction analysis was carried out according to V.A. Frank-Kamenetsky's technique [12].

Study subjects

The subject of the study is the kaolin clay rich in clay particles from the Chelyabinsk field. The grain size and mineral compositions of the natural and enriched clays are presented in Table 1.

Effect of Pressure on Changes in the Structural Package of Kaolinite

Changes in the structure at the level of the pressurized kaolinite package can be caused by the removal and displacement of Al, Fe, Mg, Si atoms that make up the octa- and tetrahedral sheets of kaolinite. To estimate the defectiveness in the structural package, pressurized kaolin was studied in terms of its chemical composition. The defectiveness caused by the displacement of atoms that make up the octa- and tetrahedral sheets of kaolinite was researched by means of IR spectroscopy.

Effect of Pressure on Changes in the Chemical Composition of Kaolin. The results of the bulk chemical composition of enriched kaolin clay are given in Table 2.

As the data presented in Table 1 suggest, kaolin is mainly made up of SiO_2 (59.48 %), Al_2O_3 (25.45 %) and Fe_2O_3 (2.42 %). The rest of the components are of minor importance.

Figure 1 demonstrates the results of experimental studies into the enriched kaolin clay exposed to stress pressure.

The retrieved data show that, as the pressure rises to 800 MPa, the oxide content of Al_2O_3 decreases correspondingly from 25.47 to 23.49 %, and MgO, from 0.31 to 0.24 %. The content of SiO_2 increases from 58.95 to 59.89 %, while the remaining oxides (Fe_2O_3 and others) change diversely.

Table 1

Grain size and mineral compositions of kaolin

	Fraction content, %							
Clay	$F_{<0.1}$*	$F_{0.1–0.2}$	$F_{0.2–0.5}$	$F_{0.5–1}$	$F_{1–2}$	$F_{2–5}$	$F_{5–50}$	$F_{50–100}$	$F_{>100}$
Natural	44.50						45.70	9.55	0.25
Enriched	0.70	1.22	5.54	14.8	30.10	41.22	6.42	0	0

	Mineral content, %				
Clay	Quartz	Montmorillonite	Kaolinite	Potassium feldspar	Illite
Natural	19.0	1.0	73.9	0	6.1
Enriched	7.6	15.6	76.7	0.1	0

Note: Fraction size is given in micrometers.

Table 2

Chemical composition of enriched kaolin clay

Clay	Oxide, mass fraction, %										
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	Na_2O	K_2O	P_2O_5	Other impurities
Enriched kaolin	59.48	1.73	25.45	2.42	0.01	0.31	0.31	0.29	0.49	0.02	9.49

Table 3

Correlation coefficients

Parameter	Class 1						Class 2					
	Al_2O_3	SiO_2	MgO	$Fe_2O_{3\ total}$	$Al_2O_3/\ SiO_2$	Wc	Al_2O_3	SiO_2	MgO	$Fe_2O_{3\ total}$	$Al_2O_3/\ SiO_2$	Wc
P, MPa	–0.86	0.64	–0.50	–0.53	–0.83	0.67	–0.82	0.20	–0.80	0.52	–0.80	–0.75

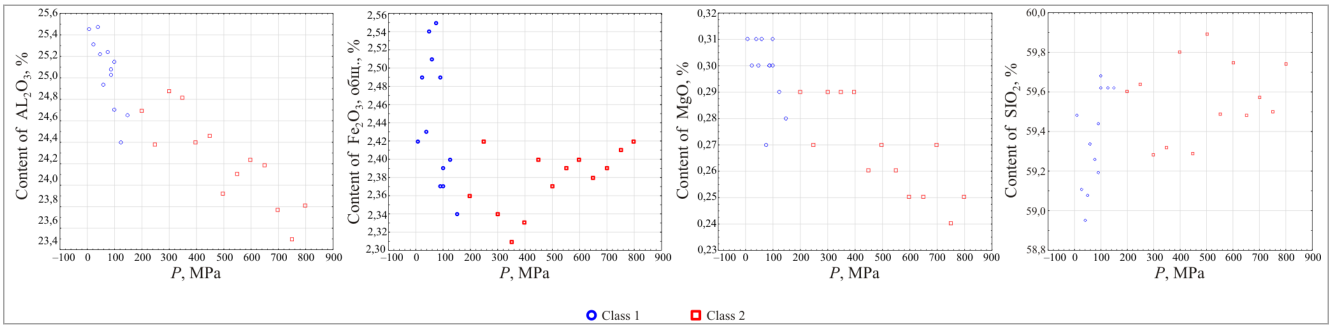

Fig. 1. Changes in the chemical composition of enriched kaolin clay exposed to stress pressure

The decrease of oxides Al_2O_3 is probably due to the removal of Al atoms from the octahedral lattice of kaolinite across the entire range of imposed pressures. The change in the content of Fe_2O_3 follows the same pattern: as pressure goes up to 150 MPa, ferric oxides drop. It can be interpreted as a removal of Fe atoms from the crystal lattice of kaolinite. The further increase in pressure from 150 to 800 MPa brings up the content of Fe, which apparently has to do with the Fe atoms entering the crystal lattice of the mineral.

The increase in silicon oxides is probably triggered by the higher content of quartz [26] resulting from Si atoms in the tetrahedral lattice of kaolinite. Quartz may be generated when the clay is put under pressure up to 150 MPa, so that the octahedral sheet loses its Al atoms and the tetrahedral sheet loses Si atoms, which is in line with the findings of previous studies [27]. Since shell vacancies left by Si atoms have high energy, Al atoms fill them up while the free Si atoms enter into a reaction with oxygen atoms and make new tetrahedrons (quartz). At the same time the quartz content increases by 1 %.

Therefore, when stress pressure is exerted on kaolin clay, the structural package of kaolinite develops defects caused by the removal of Al, Fe, Mg, ans Si atoms from the octahedral and tetrahedral sheets. The defects go by as "shell vacancies" formed by the removal of atoms from the crystal lattice and manifest themselves as "hole"-like energy centers that to a great extent define the physicochemical properties of kaolin [28, 29]. The atom removal triggers deformations in the crystal lattice of kaolinite.

To determine the influence of pressure on changes in the chemical composition of kaolinite, we used the correlation analysis that is based on the following principle: if stress pressure has a significant influence on the chemical composition, the estimated value of correlation coefficient r_p will be higher than critical $r_т$ obtained at $k = n^{-2}$ (degree of freedom) and $\alpha = 0.05$ (degree of significance). The resulting matching correlation coefficients are presented in Table 3.

The data given in Table 3 show that in Class 1 ($P = 0$–150 MPa) pressure significantly affects the changes in Al_2O_3 ($r_p = –0.86 > r_т = 0.34$), MgO ($r_p = –0.50 > r_т = 0.34$), Fe_2O_3 ($r_p = –0.53 > r_т = 0.34$) and SiO_2 ($r_p = 0.64 > r_т = 0.34$), i.e. the formation of defects in the octahedral and tetrahedral lattices of kaolinite. Class 2 ($P = 150$–800 MPa) demonstrates another pattern: stress pressure mainly triggers defects in the octahedral lattice, which proves the statistical correlation between pressure and the content of aluminum oxide ($r_p = –0.82 > r_т = 0.34$) and MgO ($r_p = –0.80 > r_т = 0.34$). The tetrahedral lattice did not reveal defectiveness, which is confirmed by the insignificant statistical correlations between P and SiO_2 ($r_p = 0.20 < r_т = 0.34$).

So, when stress pressure is exerted on kaolin, the structural package of kaolinite develops defects caused by the displacement of Al, Fe, Mg, Si. That said, the most significant influence of pressure is seen on the removal of Al atoms from kaolinite.

From the physical point of view, the atoms are supposed to be removed from the octa- and tetrahedral sheets simultaneously with the weakening of bond "strength" up to its disruption between atoms (ions) in the structural package. For this reason let us consider changes in this "strength" of bonds between atoms using infrared spectroscopy (IR).

Effect of Pressure on Changes in Defectiveness in the Kaolinite Package based on IR Spectroscopy. The defectiveness in the structural package of kaolinite was estimated using the method of infrared spectroscopy. The IR-spectrogram shows the bond between atoms in the structural package as peaks (spikes) that can be characterized through the following indicators: wave number (ν) and peak area (S).

From the physical point of view, the peak area S (integral absorption rate) is seen as the oscillation range of each atom in the studied group, for instance, Al–OH. With S tending to zero, the oscillation range of atoms in the studied group reaches such an extent that the bond between them breaks completely. Therefore, the S indicator can be used as a parameter to estimate the "strength" of bonds in atom (ion) groups that make up the kaolinite package, which is in line with previous studies [30, 31].

The wave number characterizes the resonance frequency between atoms in the studied group; in other words, it indicates the intensity of valency or deformation oscillations in the atom groups. The change in the resonance frequency suggests that the valency or deformation oscillations in atom groups change, which implies that the structure of the

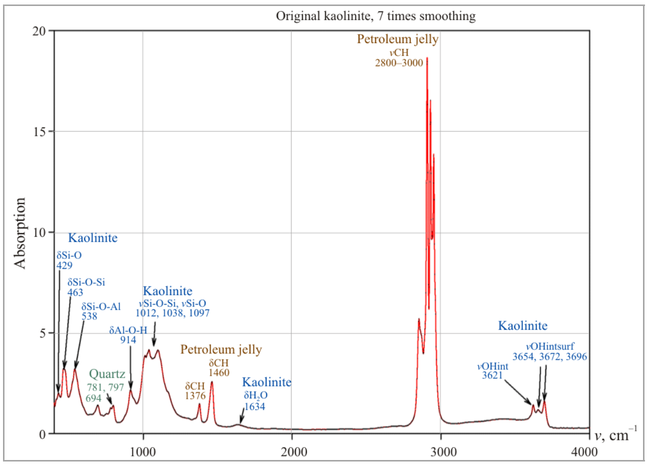

Fig. 2. Infrared spectrum of original kaolinite: $\nu = 400–1200$ cm^{-1} and $\nu = 3600–3720$ cm^{-1}

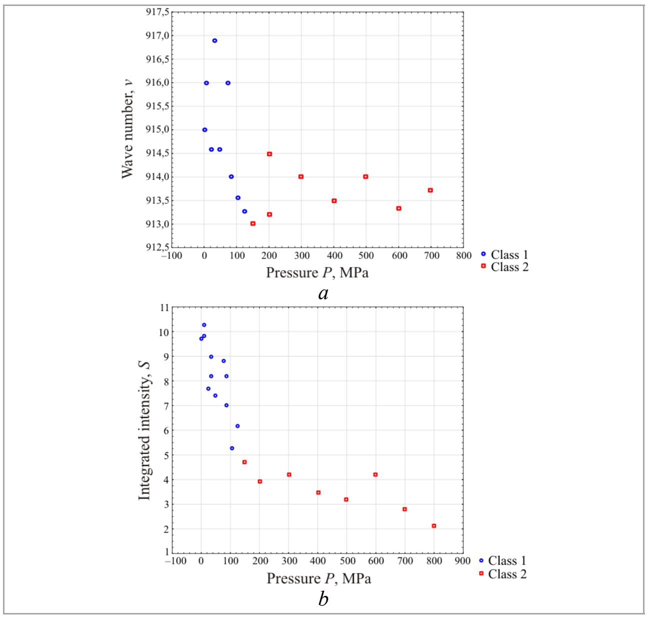

Fig. 3. Change in the bond "strength" between δAl–OH–Al under pressure (P) as per parameters: a – wave number (ν); b – integral absorption rate (S)

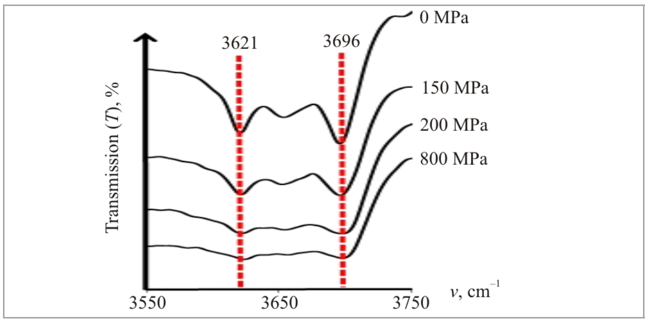

Fig. 4. Infrared spectrum of kaolinite samples under pressure in the range of wave numbers of 3550–3750 cm^{-1}

kaolinite package alters as well. At the same time, the decrease in the wave number is supposed to imply the loss of bond between atoms. Therefore, the ν indicator can be used as a parameter that shows changes in the structure of the kaolinite package.

The other parameter that indicates the change in the package structure can be the bands of valency oscillations of hydroxyl groups (OH) in the octahedral sheet. Defect-free (ordered) kaolinite has four well-defined bands of OH absorption at wave numbers of 3695; 3670; 3650 and 3620 cm^{-1}. Increasing defectiveness of kaolinite causes the bands 3670 and 3650 cm^{-1} to merge into one inexplicit peak [22, 32].

Parameter $K_3 = I_{3695}/I_{3620}$, i.e. relation of absorption band intensities in the intrasurface hydroxyl groups νOH$_{\text{i.s.}}$ (I_{3695}) to the inner hydroxyl groups νOH$_{\text{in.}}$ (I_{3620}), also, $K_4 = I_{3695}/I_{915}$ stands for the relation of the intrasurface hydroxyl groups νOH$_{\text{i.s.}}$ (I_{3695}) to δAl-OH-Al (I_{915}) that can be used to estimate defectiveness in the kaolinite structure [33]. These parameters are interpreted in the following manner: the lower their values are, the more defective the structural package of kaolinite is.

Estimation of Structure Defectiveness in the Octahedral Sheet based on δAl–OH–Al. The structure of the octahedral sheet involves Al ions that are located in the center of the octahedron, and ions of hydroxyl groups. The results of the experimental study into the "strength" of δAl–OH–Al bonds at the wave number of 914 cm^{-1} in kaolinite affected by stress pressure in the transmission mode are presented in Fig. 3.

Fig. 3 shows that when pressure is increased to 150 MPa, the peak area (S) and wave number (ν) decrease significantly, whereas at pressures 150–800 MPa the effect of P on the change in S and ν is hard to detect. It points to the fact that the decrease in the bond "strength" between δAl–OH–Al ions is affected by pressures below 150 MPa to a greater extent than those exceeding 150 MPa (Table 4).

As we see, at pressures < 150 MPa the indicators S and ν show reduced strength of bonds between Al and OH to the extent of their disruption, which explains the mechanism of how the Al ions are removed from the octahedral sheet of kaolinite and goes in line with the study findings [34].

Estimation of Defectiveness of the Kaolinite Package Structure based on the Valency Oscillations in Hydroxyl Groups. The results of the experimental study showed that the original sample of kaolinite has three distinct peaks of oscillations in OH-groups: 3696; 3654; 3620 cm^{-1} and one less defined peak – 3672 cm^{-1} (Fig. 4).

Kaolinite exposed to stress pressure of 10 to 400 MPa shows a poorly defined peak of 3672 cm^{-1} that extends to the arm. At pressures from 450 to 700 MPa, the arm of 3672 cm^{-1} merges with the peak of 3654 cm^{-1}, which is typical of the defective structure of kaolinite. At higher pressures (up to 800 MPa) there are only two peaks – about 3696 and 3621 cm^{-1}. It suggests the influence of pressure on the increase in defectiveness of the kaolinite structure package. The obtained results do not contradict the findings [31, 35].

Estimation of Kaolinite Defectiveness based on the Intensity of Absorption Bands of Hydroxyl Groups. Figure 5 shows the results of research into changes in intensities of absorption bands of hydroxyl groups K_3 = I3695/3620 and K_4 = I3695/915 under pressure. It can be observed that increased pressures tend to lower K_3 = I3695/3620 from 1.3 to 0.88, and K_4 = I3695/915 from 0.8 to 0.6. The most significant changes take place in the range of pressures from 0 to 150 MPa (Class 1), as opposed to 150 to 800 MPa (Class 2), which is in accordance with the study carried out by V.V Seredin et al. [36].

The identified downward pattern of $I_{3695}/_{3620}$ and $I_{3695}/_{915}$ at increased pressures suggests that when kaolinite is under pressure the bonds between Al and OH ions are disrupted: the ions are removed from the octahedral sheet, which leads to higher defectiveness of the kaolinite package. This finding is fully in line with the results obtained by Fang et al. [15].

The qualitative estimation of the effect of pressure on $K_{3\,(3695/3620)}$ and $K_{4\,(3695/915)}$ was carried out by means of a correlation analysis (Table 5).

Table 4

Effect of pressure on the development of defectiveness of kaoline structural elements

Structural element	Defectiveness indicator	Structural element defectiveness	
		$P =$ 0–150 MPa	$P =$ 150–800 MPa
Package	Content of Al ions, %	Increases	Increases
Mineral	Area of coherent scattering, Wc, Å	Decreases	Increases
Colloid	Zeta-potential, mV	Decreases	Not defined
Aggregate	Adhesive power, $F_{п}$	Increases	Increases

Table 5

Correlation matrix

Parameter	Class 1		Class 2	
	$K_{3\,(3695/3620)}$	$K_{4\,(3695/915)}$	$K_{3\,(3695/3620)}$	$K_{4\,(3695/915)}$
P, MPa	–0.84	–0.87	0.27	–0.56

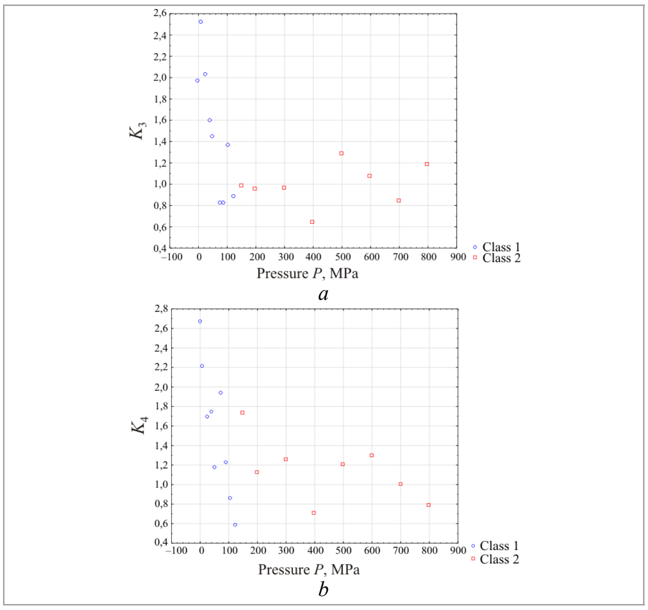

Fig. 5. Change in the intensity of absorption bands: a – $K_{3\,(3695/3620)}$; b – $K_{4\,(3695/914)}$ under pressure (P)

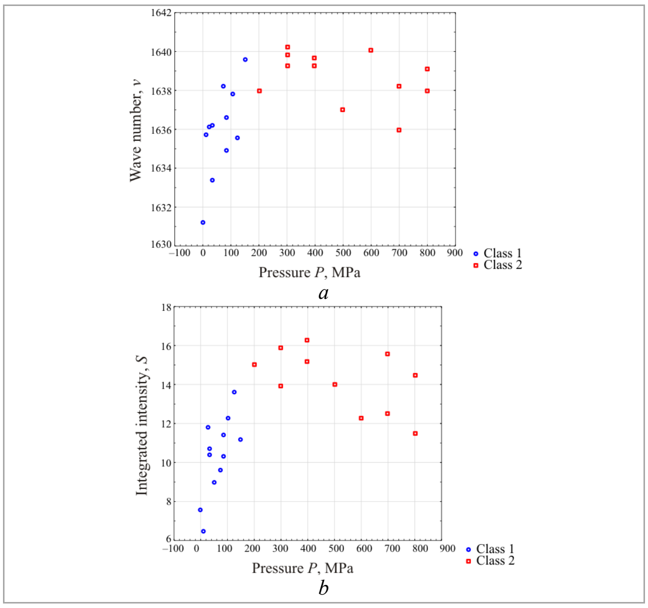

Fig. 6. Changes in the "strength" of bonds between δH–O–H ions under pressure (P) as per parameters: a – wave number (v); b – integral absorption rate (S)

It can be seen that based on the obtained data pressure and $K_{3\,(3695/3620)}$, $K_{4\,(3695/915)}$ are statistically related. It indicates that pressure has a significant effect on the formation of defects at the level of structural packages of kaolinite.

Therefore, when kaolin clay is pressurized at 800 MPa the package suffers the removal of Al and Si ions from the octahedral and tetrahedral sheets to form local "hole"-like defects accounting for 2–3 % in volume. The detected displacement (deformation) of ions in the kaolinite package is suggested by the decrease in integral transmission intensity S at increased pressures. Effect of Pressure on Structural Changes in Kaolinite Mineral.

The influence of pressure on changes in the structure of kaolinite was studied using IR spectroscopy and diffraction analysis. The change in the structure of crystallite (mineral) implies compaction, slips, and rotation of kaolinite packages in relation to one another. These changes can be interpreted as defectiveness of kaolinite mineral.

Estimation of mineral defectiveness using δH–O–H. It is well known that kaolinite packages are bound to one another though a hydrogen bond, so that ions of the OH surface hydroxyl groups in the octahedral sheet of one package are bound to atoms of oxygen O in the tetrahedral sheet of another package. Therefore, when the bond between O–H–O ions is disrupted, it quite likely indicates that we face an event of kaolinite packages rolling, sliding, and rotating in relation to one another.

The results of the experimental study are given in Fig. 6.

As is seen from Fig. 6, the pressure of up to 150 MPa increases the integral absorption rate S, whereas when the pressure goes up to 800 MPa S, on the contrary, drops. This kind of pattern points towards the fact that when kaolinite is affected by pressures up to 150 MPa its structure is aligned so its defectiveness goes down. It can be explained the following way: at pressures up to 150 MPa the kaolinite package loses about 2 % of Al ions as a result of the disruption in the bond between Al and OH. The hydroxyl groups, while dissociating, deliver hydrogen ions to the inter-package space, which strengthens the bond between the kaolinite packages.

As the pressure grows from 150 to 800 MPa the bonds between H–O–H ions are disrupted, which leads to higher defectiveness of the kaolinite mineral as a result of the packages being displaced in relation to one another. The resulting data go in line with the studies [37].

Estimation of Mineral Defectiveness based on the Data Drawn from Diffraction Analysis. The X-diffraction patterns (Fig. 7) show that the most sensitive indicators that characterize changes in the mineral structure under pressure are: peak half-width (h_1), integral intensity – peak area (s_1), interplane spacing (d_1) and the angle 2θ (a_1) of maximum diffraction incidence [38].

To enhance the reliability and accuracy of estimation of the kaolinite mineral structure defectiveness we used the complex indicator of the area of coherent scattering (ACS).

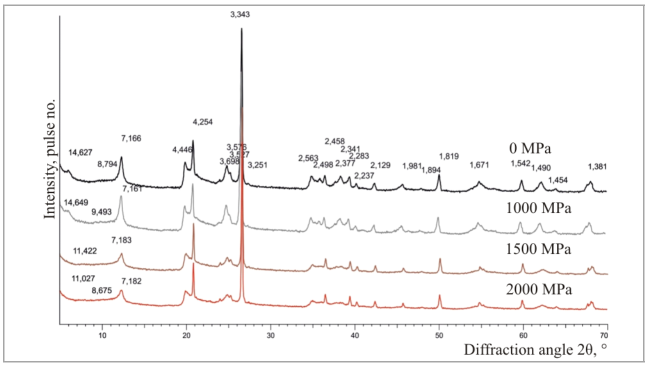

Fig. 7. X-ray diffraction patterns in kaolin clay samples: original and pressurized

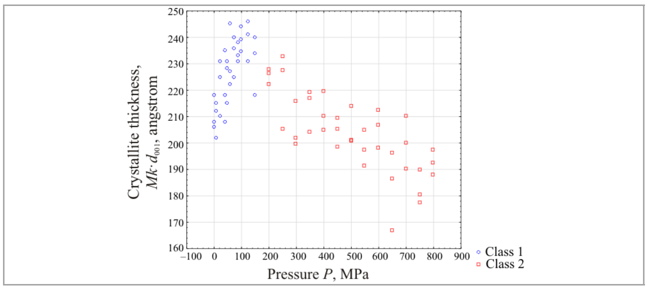

Fig. 8. Influence of pressure on changes in the width (*Wc*) of crystallite

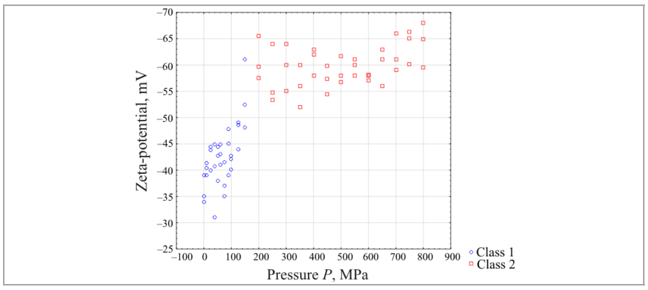

Fig. 9. Influence of pressure on changes in zeta-potential (ζ) of the colloid

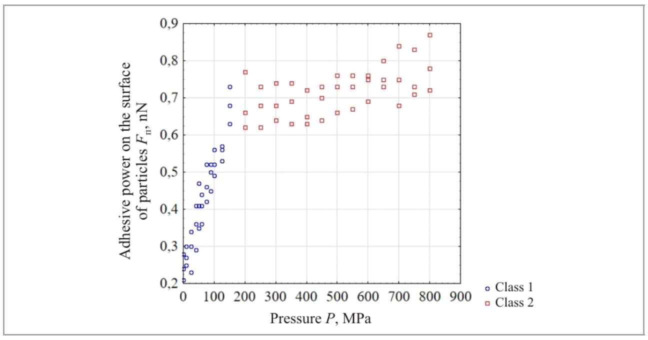

Fig. 10. Changes in adhesion strength (F_s) on the surface of kaolin aggregates under pressure (P)

The area of coherent scattering implies crystal with the defect-free structure. This indicator correlates with the energy activity of particles. Small values of ACS indicate that the microblocks are small in size and have high capacity for cation exchange [38], which points to a high energy potential of the particle. Besides, the study conducted by V.G. Shlykov [39] notes that small values of ACS generally suggest that there are water molecules between the microblocks that facilitate random displacement of packages in relation to one another, which leads to higher energy activity on the surface of particles. Namely, with ACS expressed by means of the indicator $Wc > 40$ (number of packages in defect-free crystallites), the cation exchange capacity (CEC) is 2–5 mg-eqv/100 g, at $Wc = 40–25$ the capacity grows to CEC = 6–12 mg-eqv/100 g, and at $Wc < 25$ the capacity has low values – CEC > 12 mg-eqv/100 g [38].

Therefore, the parameter *Wc* (area of coherent scattering) can be used as a complex indicator as it combines the peak half-width, angle of maximum diffraction incidence and X-ray radiation wavelength. *Wc* is calculated using the Scherrer equation based on the width of the first basal peak [12]:

$$Wc = \lambda/\cos\Theta \cdot h_1,$$

where λ = 1,54060 Å – the length of the X-ray radiation wave; Θ – the angle of diffraction; h_1 – basal peak half-width.

Fig. 8 shows the correlation field between the parameters *Wc* and *P* in kaolin clay: as pressure rises to 125–150 MPa, it thickens the crystallite (*Wc*); further increase of pressure to 800 MPa lowers the value of *Wc*.

In other words, whenever pressure rises to 150 MPa, it aligns the kaolinite structure, which brings the structure defectiveness down by 20 %, whereas at pressures climbing up to 800 MPa the crystallite defectiveness increases by 15–20 % compared with the original level.

Therefore, when kaolin clay is pressurized at up to 150 MPa, the mineral (crystallite) made up of 20–40 packages shows a better aligned structure, which suggests lower defectiveness. At pressures > 150 MPa, there is higher crystallite defectiveness due to the displacement of packages in relation to one another (see Table 4).

Influence of Pressure on Changes in Kaolin Structure at the Colloid (Particle) Level

Clay particles (colloids) are known to form a double electric layer on their surface that is largely defined by the energy potential of the particle surface. One of the indicators of the energy potential is zeta-potential [40] that is formed on the slip boundary between the absorption and diffusion layers. Zeta-potential is characterized by the charge (defectiveness) of the particle and thus can be used as an indicator of the particle defectiveness.

Fig. 9 presents the results of the experimental studies on the influence of pressure on the zeta-potential of kaolin particles: with the pressure increase to 150 MPa, the structure defectiveness goes down due to the increase in the colloid density ($r_p = 0.67$). In the range of 150–800 MPa, it is quite hard to identify the effect pressure has ($r_p = 0.37$) on the defectiveness formation (see Table 4).

Influence of Pressure on Changes in Kaolin Structure at the Aggregate Level

The change in the aggregate structure takes place due to the fragmentation of large structural elements and processes of compression and compaction of kaolin particles under externally exerted pressure. Such changes manifest as morphological alterations on the aggregate surface that can be expressed using the indicator of aggregate surface roughness. The aggregate surface roughness is manifested through the surface energy, therefore the aggregate structure defectiveness can be estimated using the energy indicator: adhesive strength of the aggregate surface (F_s). Adhesive strengths were measured using the atomic-force microscope (AFM) NT-MDT NTEGRA Prima (Russia). The resulting AFM-images were processed and quantitatively analyzed on Nova 1.1.1 Revision 14785 NT-MDT Tech.

The results of the experimental research into forces of adhesive interaction (F_s) between the cantilever and the aggregate surface under pressure are presented in Fig. 10.

As the data in Fig. 10 suggest, there is a rise in adhesion strength across the entire range of pressures. At the same time, in the range of 0–150 MPa, the influence of pressure on adhesive strength is higher that in the pressure range of 150–800 MPa.

The results of the correlation analysis show that the calculated values of correlation coefficients (r_p) exceed the critical value ($r_{\text{т}} = 0.27$) found at $n = 54$, $\alpha = 0.05$. Therefore, it can be stated that pressure affects the formation of adhesive forces on the aggregate surface. However, in Class 1, there is a stronger statistical correlation between the pressure and force of adhesive interaction than in Class 2. It is indicated by higher correlation coefficients: namely, for an aggregate in Class 1, the calculated correlation coefficient between P and F_s stands at 0.95, whereas in Class 2 it is $r_p = 0.58$.

The revealed changes in adhesive forces depending on exerted pressure are due to the structural alterations (defectiveness) of the aggregate, which goes in line with the findings of E. Galan [41].

Therefore, technology-induced treatment of clays has conflicting effects on their composition, structure, and properties [42–46].

Conclusion

1. High pressures have conflicting effects on the formation of defectiveness in structural elements of kaolin, specifically its package, mineral, colloid, and aggregate.

2. The kaolinite mineral package shows higher defectiveness at higher pressures. Defects are formed as a result Al, Fe, Mg, Si ions being displaced from the octahedral and tetrahedral sheets. Al ions are most susceptible to pressure. The removal of ions triggers deformations in the package and formation of "hole"-like energy centers. The pressure within 0–150 MPa has a more significant effect on formation of defectiveness ($r_p = 0.86$) than that within the range of 150–800 MPa ($r_p = 0.82$).

3. The kaolinite mineral pressurized up to 150 MPa shows less defectiveness as a result of its structure alignment ($r_p = 0.67$). At pressures over 150 MPa, the kaolinite mineral shows higher defectiveness ($r_p = –0.72$) as the hydrogen bonds between the packages get disrupted, which forces the structural packages to slip and rotate in relation to one another.

4. The colloid (particle) at pressures going up to 150 MPa shows lower defectiveness due to higher density of the colloid ($r_p = 0.67$). The influence of pressure on formation of defectiveness in the range of 150–800 MPa ($r_p = 0.37$) proved to be hard to reveal.

5. The aggregate under pressure up to 150 MPa shows higher defectiveness as a result of particle fragmentation, as well as slips and displacements of particles in relation to one another ($r_p = 0.95$). The influence of pressure on formation of defectiveness in the range of 150–800 MPa proved to be hard to reveal ($r_p = 0.58$); however, as the pressure increases, it leads to higher defectiveness overall.

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