Alteration of Physical and Chemical Properties of Clays Subjected to Pressure

Valerii V. Seredin, Olga S. Siteva, Karine A. Alvanyan, Andrey V. Andrianov

Perm State National Research University (15 Bukireva st., Perm, 614068, Russian Federation)

Изменение физико-химических свойств глин, подверженных давлению
В.В. Середин, О.С. Ситева, К.А. Алванян, А.В. Андрянов
Пермский государственный национальный исследовательский университет (Россия, 614990, г. Пермь, ул. Букирева, 15)

Keywords: clay, kaolin, bentonite, structure, properties, pressure, sorption, methylene blue, energy potential, IR spectroscopy, defectiveness, temperature, crystal lattice, octahedral sheet, tetrahedral sheet.

Clays represent complex polymeric formations. The properties of clays, including sorption, are largely determined by the structure of their crystal lattice, mineral composition and particle size distribution, as well as by environmental conditions. The mineral composition of clays is represented by the energy on the surface of particles; and the particle size distribution is represented by the active surface area of particles. These two complex parameters mainly determine the sorption activity of clays.

To change the sorption activity of clays, the latter are subjected to mechanical treatments, thermal modifications, and chemical activations with the use of chemical agents such as acids, alkalis, salts at various exposure times. Therefore, a study of patterns of changes in the structure and sorption properties of clays subjected to pressure was conducted.

Experimental studies have shown that if kaolin is subjected to pressure, defects are formed in the structural pack of kaolinite mineral due to the removal of Al$^{3+}$, Fe$^{3+}$, Mg$^2+$, Si$^4+$ ions from it. In this case, pressure has the maximum influence on the removal of Al$^{3+}$ ions from the pack. As a result of the removal of ions, the formation of the defects deforms the crystal lattice of kaolinite. Data obtained through IR spectroscopy confirm the increase of defectiveness (irregularity) of the structure of kaolinite. It has been revealed that when kaolin is subjected to a pressure of 0-150 MPa, the sorption activity mostly depends on pH of the diffuse layer particle solution $Z_{dl} = 73 \%$ and crystallite defectiveness degree $Z_{cr} = 24 \%$. The specific surface area of particles $Z_{s} = 1 \%$ and kaolinite pack defectiveness $Z = 2 \%$ do not have any significant influence on sorption.

If kaolin is subjected to a pressure of 150-800 MPa, kaolin sorption activity mostly depends on kaolinite pack defectiveness $Z = 74 \%$ and crystallite pack defectiveness $Z_{cr} = 19 \%$. The specific surface area of particles $Z_{s} = 3 \%$ and pH of the diffuse layer particle solution $Z_{dl} = 4 \%$ do not have any significant influence on sorption.

Keywords: глина, каолин, бентонит, структура, свойства, давление, сорбция, метилиновый голубой, энергетический потенциал, ИК-спектроскопия, дефектность, температура, кристаллическая решетка, октаэдрический лист, тетраэдрический лист.

Глины являются сложными полиминеральными образованиями. Свойства глин, в том числе и сорбционные, во многом определяются строением их кристаллической решетки, минеральным и гранулометрическим составом, условиями среды. Минеральный состав глин реализуется в виде энергии на поверхности частиц, а гранулометрический – в виде площади активной поверхности частиц. Эти два комплексных показателя в основном и определяют сорбционную активность глин.

Для изменения сорбционной активности глин осуществляют механическую обработку, термическую модификацию и химическую активацию с помощью химических реагентов, таких как кислоты, щелочи, салициловая кислота и различные химические реагенты. Для их реализации необходимо выявить закономерности изменения структуры и сорбционных свойств глин, подверженных давлению.

Экспериментальные исследования показали, что при обработке каолина давлением в структурном пакете минерала каолинита формируются дефекты за счет удаления из него ионов Al$^{3+}$, Fe$^{3+}$, Mg$^2+$, Si$^4+$. При этом давление оказывает максимальное влияние на вынос из пакета ионов Al$^{3+}$. Образование дефектов при удалении вновь влечет за собой деформацию кристаллической решетки каолинита. Полученные данные по ИК-спектроскопии подтверждают увеличение дефектности (неупорядоченности) структуры каолинита. Выявлено, что при давлениях обработки каолина 0-150 МПа наибольшее влияние на сорбционную активность каолина оказывает pH раствора диффузного слоя частиц $Z_{dl} = 73 \%$ и степень дефектности кристаллита $Z_{cr} = 24 \%$. Площадь удельной поверхности частиц $Z_{b} = 1 \%$ и дефектность пакета минерала каолинита $Z = 2 \%$ существенного влияния на сорбцию не оказывают. При давлениях обработки каолина 150-800 МПа наибольшее влияние на сорбционную активность каолина оказывают дефектность пакета минерала каолинита $Z_{cr} = 74 \%$ и кристаллита $Z_{cr} = 19 \%$. Площадь удельной поверхности частиц $Z_{b} = 3 \%$ и pH раствора диффузного слоя частиц $Z_{dl} = 4 \%$ существенного влияния на сорбцию не оказывают.

Инженерная геология и охрана недр. – 2020. Т. 20, № 4. С. 304–316. DOI: 10.15593/2712-8008/2020.4.1

Ключевые слова: глина, каолин, бентонит, структура, свойства, давление, сорбция, метилиновый голубой, энергетический потенциал, ИК-спектроскопия, дефектность, температура, кристаллическая решетка, октаэдрический лист, тетраэдрический лист.

Полученные данные по ИК-спектроскопии подтверждают увеличение дефектности (неупорядоченности) структуры каолинита. Выявлено, что при давлениях обработки каолина 0-150 МПа наибольшее влияние на сорбционную активность каолина оказывает pH раствора диффузного слоя частиц $Z_{dl} = 73 \%$ и степень дефектности кристаллита $Z_{cr} = 24 \%$. Площадь удельной поверхности частиц $Z_{b} = 1 \%$ и дефектность пакета минерала каолинита $Z = 2 \%$ существенного влияния на сорбцию не оказывают. При давлениях обработки каолина 150-800 МПа наибольшее влияние на сорбционную активность каолина оказывают дефектность пакета минерала каолинита $Z_{cr} = 74 \%$ и кристаллита $Z_{cr} = 19 \%$. Площадь удельной поверхности частиц $Z_{b} = 3 \%$ и pH раствора диффузного слоя частиц $Z_{dl} = 4 \%$ существенного влияния на сорбцию не оказывают.
Relevance of the Study

Physical [1–5], mechanical [6–9], and chemical [10–14] properties of clays, including their sorption properties, depend on a number of factors that determine the surface energy potential of particles [15–17], and on factors that form the specific surface of such particles [18].

To obtain a desired clay energy potential, various methods of clay treatment (activation) have been developed: thermal [19, 20], mechanic [21–24], ultraviolet [25], alkaline [26], acid [27] treatment, etc. So, based on information given by Kara-sal et al. [20], when clays are heated up to 400–600 °C, their sorption activity grows as a result of releasing high-energy centres on the mineral surface. According to Sapronov et al. [25], during the ultraviolet activation of clays, ions of metals leave their octahedral positions due to weakening of bonds in the crystal lattice of the minerals. This increases the sorption activity of clays by 1.3 times. Ultrasonic treatments of clays lead to the destruction of aggregates and completion of the crystal lattice, thus, increase the sorption activity of clays [18].

An immense number of scientific papers deals with studying the alteration of physical and chemical properties of clays subjected to pressure. Kosovskaya et al. [28], Goilo et al.[2], Range et al. [29], Frank-Kamenetsky et al. [3], LaIglesia [30], and Galan et al. [24] studied these issues in more detail. For instance, LaIglesia [30] found that exposure of kaolin to pressure (100–2000 MPa) does not lead to significant changes in the coherent scattering area size $d_{001}$ (of energy potential), whereas such changes appear at a pressure exceeding 4000 MPa.

Based on the above, we can come to a conclusion that the influence of pressure on the structure and sorption properties of clays are of significant interest.

Materials and Research Methods

As to methods, the work was done in several ways. At the beginning, samples of clay enriched with clay particles were subjected to compression and shear in the pressure range of 0 to 800 MPa in accordance with method [18]. Then, in one group of the samples, the chemical composition was determined by X-ray fluorescence analysis [1] and, in the other group of samples, the change in deformation vibrations and valence vibrations of bonds and/or groups of bonds in the crystal lattice of the minerals was studied by IR spectroscopy [31, 32].

Infrared spectra were registered with the use of IR Fourier spectrometer (FSM 1202 of Infraspek manufacture) in the range of 400...4000 cm$^{-1}$ at the resolution of 2 cm$^{-1}$ (FT-IR).

The diffractometric analysis of the samples was made with the use of D2 Phaser X-ray powder diffraction instrument according to NSOMMI (Research Council for Mineralogical Methods of Research) of VIMS (Russian National Minerals Research Institute).

The research deals with enriched bentonite and kaolin clays of the Zyryanskoye field (Kurgan Oblast) and Nizhne- Uvelskoye field (Chelyabinsk Oblast), respectively. The particle size distribution and mineral composition of the natural and enriched clays are given in [33].

Formation Principles of Kaolin Structure Defectiveness

The influence of pressure on the change in kaolin structure at the pack level. The structural change at the pack level of kaolinite treated with pressure, can be reached by displacing $\text{Al}^{3+}$, $\text{Fe}^{3+/2+}$, $\text{Mg}^{2+}$, $\text{Si}^{4+}$, which form the octahedral and tetrahedral sheets of kaolinite. To evaluate the defectiveness in the structural pack, the change in the chemical composition of kaolinite subjected to pressure was studied. The defectiveness occurring due to the displacement of atoms that form the octahedral and tetrahedral sheets of kaolinite was studied by the infrared spectroscopy.

The influence of pressure on the change in kaolin chemical composition. The results of the bulk chemical composition of enriched kaolin clay are given in Table 1.

Data in Table 1 show that kaolin composition mainly includes $\text{SiO}_2$ (59.48 %), $\text{Al}_2\text{O}_3$ (25.45 %) and $\text{Fe}_2\text{O}_3$ (2.42 %). Other components are of secondary importance.

Experimental researches of enriched kaolin clay subjected to pressure demonstrate that as the pressure increases up to 800 MPa, the content
of Al$_2$O$_3$ oxides decreases from 25.47 % to 23.49 % respectively, whereas MgO decreases from 0.31 % to 0.24 %. The content of SiO$_2$ increases from 58.95 % to 59.89 %, whereas the content of other oxides (Fe$_2$O$_3$ etc.) changes in different ways.

The reduction in the content of Al$_2$O$_3$ is probably caused by the removal of Al atoms from the octahedral lattice of kaolinite throughout the entire range of applied pressures. The change in the content of Fe$_2$O$_3$ is in agreement with another pattern: as pressure increases up to 150 MPa, the content of ferrous oxides decreases. This can be interpreted as a removal of Fe atoms from kaolinite crystal lattice. During the subsequent pressure increase (from 150 MPa to 800 MPa), Fe content grows, which is probably caused by the incorporation of iron atoms into the mineral's crystal lattice.

The growth in the amount of silicon oxides is probably caused by the increase in the content of quartz [28], the source of which is represented by Si atoms of kaolinite tetrahedral lattice. The formation of quartz can occur in accordance with the following scenario: at the moment of the clay exposure to a pressure up to 150 MPa, Al atoms are removed from the octahedral sheet, whereas Si atoms are removed from the tetrahedral sheet, which is consistent with data in [34]. As soon as vacancies left by Si atoms are energetically strong, Al atoms occupy them, whereas free Si atoms, reacting with oxygen atoms, form new tetrahedrons (quartz). In such a case, the content of quartz increases by one percent.

Therefore, in case of kaolin clay treatment with stress pressure, defects are formed in the structural pack of kaolinite as a result of removal of Al, Fe, Mg, and Si atoms from the octahedral and tetrahedral sheets. Vacancy-type defects are represented by hole-type energy centres, which mainly determine physical and chemical properties of kaolin [15, 22]. The removal of atoms causes deformation of kaolinite crystal lattice.

To evaluate a degree of the pressure influence on the chemical composition change of kaolinite, a correlation analysis was applied. If the stress pressure has a significant influence on the chemical composition, the calculated value of the correlation coefficient ($r_p$) will be higher than critical ($r_t$) obtained at $k = n^2$ degrees of freedom and $\alpha = 0.05$ significance level. The calculation results of paired correlation coefficients are given in Table 2.

Based on Table 2 we can come to a conclusion that in class 1 ($P = 0$–150 MPa) pressure has the most significant influence on the change in Al$_2$O$_3$ ($r_p = -0.84 > r_t = 0.34$), MgO ($r_p = -0.50 > r_t = 0.34$), Fe$_2$O$_3$ ($r_p = -0.53 > r_t = 0.34$) and SiO$_2$ ($r_p = 0.64 > r_t = 0.34$), that is, on the formation of defects in the octahedral and tetrahedral lattices of kaolinite. In class 2 ($P = 150$–800 MPa) we see another behaviour: stress pressure forms defects mainly in the octahedral lattice of kaolinite, which is evidenced by the statistical relation between pressure and aluminium oxide content ($r_p = -0.85 > r_t = 0.34$) and MgO ($r_p = -0.80 > r_t = 0.34$). We did not manage to reveal the tetrahedral lattice defectiveness, which is seen by insignificant statistical relations between $P$ and SiO$_2$ ($r_p = 0.20 < r_t = 0.34$).

Therefore, at the moment of kaolin treatment with the stress pressure, defects are formed in the structural pack of kaolinite as a result of removal of Al, Fe, Mg, Si from it. At the same time, pressure has the most significant influence on the removal of Al atoms from kaolinite.

Physically, the removal of atoms from the octahedral and tetrahedral sheets shall be accompanied by the reduction of bonds till a complete destruction of bonds between
The assessment of structure defectiveness in the octahedral sheet by δAl-OH-Al. The structure of the octahedral sheet is composed of Al ions located in the centre of octahedron OH hydroxyl groups. The experimental results of the bond strength between δAl-OH-Al at ν = 914 cm⁻¹ wave number in kaolinite subjected to stress pressure in the transmission mode showed that as pressure increases up to $P = 150$ MPa, the reflex area ($S$) and wave number decrease significantly, and, at a pressure of 150–800 MPa, it is rather difficult to reveal the influence of $P$ on the change in $S$ and $ν$. This demonstrates that a pressure up to $< 150$ MPa has a more significant influence on the decrease in the bond strength between δAl-OH-Al ions than a pressure $> 150$ MPa.

Therefore, when kaolin clay is subjected to a pressure up to 800 MPa, in the pack, due to removal of Al and Si ions from the octahedral and tetrahedral sheets, local hole-type defects are formed in the amount 2–3 %. Ion displacement (deformation) was seen in kaolin pack, as evidenced by the reduced integral intensity of transmission ($S$) at an increased pressure. The results obtained are consistent with the data [23, 36, 37].

The influence of pressure on the change in kaolinite structure at the mineral level. The influence of pressure on the change in kaolinite structure was studied by the IR spectroscopy methods. The change in crystallite (mineral) structure is understood as rolling, slipping, and rotation of kaolinite packs between themselves. Such changes can be interpreted as kaolinite mineral defectiveness. It is well known that kaolinite packs are linked by the hydrogen bond, that is, ions of surface hydroxyl groups (OH) of the octahedral sheet of one pack are linked to oxygen (O) atoms of the tetrahedral sheet of the other pack. Therefore, if O-H-O bond is destroyed, there is a big probability that rolling, slipping, and rotation of kaolinite packs between themselves occur. The experimental results showed that at a pressure up to 150 MPa we see an increase in the integral intensity of transmission ($S$), and, instead, if pressure grows up to 800 MPa, $S$ decreases. Such trend evidences that, if kaolinite is subjected to a pressure up to 150 MPa, kaolinite structure normalization is observed, i.e. its defectiveness decreases. It can be explained in the following way: at a pressure up to 150 MPa, about 2% of Al ions are removed from kaolinite pack through the destruction of the bonds between Al and OH. Hydroxyl groups dissociate and release hydrogen ions into the space between the packs, thus strengthen the bonds between the packs of kaolinite.

When pressure increases from 150 to 800 MPa, the bonds between H-O-H ions get destroyed, thus, increase defectiveness of kaolinite mineral due to the displacement of the packs between themselves.

Therefore, when pressure increases up to 150 MPa, we observe the normalization of kaolinite structure that leads to the structure defectiveness reduction by 20 %, and, when pressure increases up to 800 MPa, crystallite defectiveness grows by 15–20 %, as compared to the initial defectiveness.

The obtained result is consistent with data in [38, 39, 40], where it is specified that the defectiveness factor of crystallite, $Mk$, (the coherent scattering area) increases when kaolin is subjected to a pressure of up to 150 MPa, that is, kaolinite mineral defectiveness deceases; whereas at a pressure of 150–800 MPa, $Mk$ goes down, i.e. the defectiveness grows.

### Table 2: Correlation matrix

| Parameter | Class 1 | Class 2 |
|-----------|---------|---------|
| $P$, MPa  | $-0.84$ | $0.64$  |
| $0.50$    | $-0.83$ | $-0.70$ |
| $0.20$    | $-0.85$ | $0.20$  |
| $0.52$    | $-0.80$ | $0.52$  |
| $-0.69$   | $-0.80$ | $-0.69$ |
Therefore, when kaolin clay is subjected to a pressure of up to 150 MPa, in the mineral (crystallite) consisting of 20–40 packs, we see the structure normalization, i.e. the defectiveness of the structure decreases. At a pressure exceeding 150 MPa, we observe the increase in the defectiveness of crystallite due to the displacement of the packs between themselves.

The data obtained are consistent with results of studies [41–45].

**pH Alterations in Suspensions of Clays Subjected to High Pressure**

pH alterations in suspensions of clays subjected to pressure in distilled water. The experimental results regarding pH value change in suspensions of kaolin and bentonite clays subjected to pressure in distilled water showed that, if pressure increases up to 150 MPa (class 1), in kaolin clay suspension, we observe the reduction of pH value by 0.383 units at the average value of \[ \text{pH} = 7.14 \] and the standard deviation of \[ \sigma = 0.148 \] (Table 3). When pressure increases from 200 MPa to 800 MPa (class 2), pH almost does not change; its average value decreases by 4 % and equals to 6.84 at \[ \sigma = 0.0372 \].

pH alteration in bentonite clay has another trend. In class 1 it is rather difficult to understand the influence of pressure on pH alterations. The selection range is as follows: \( R = 0.058 \), average pH = 8.25 and \[ \sigma = 0.018 \]. In class 2, when pressure increases, we see the reduction in pH value by 0.181, the average value decreases by 0.5 % and equals to pH = 8.20.

pH alteration in suspensions of clays subjected to pressure in KCl solution. The experimental results regarding pH value change in suspensions consisting of particles of kaolin and bentonite clays subjected to pressure in KCl solution showed that, if pressure grows, pH goes down; at the same time, pH reduction rate at a pressure of up to 150 MPa (class 1) is higher than that at a pressure of 150 MPa – 800 MPa (class 2). The comparison of statistics between the classes demonstrated that the range, the average value, and standard deviation of pH in class 2 is lower than those in class 1 (see Table 3).

Another trend was revealed in bentonite clay: as the pressure increases up to 150 MPa, pH goes down, whereas at \( P = 150–800 \) MPa, it is vice versa, and pH value goes up.

In the aqueous solution, the acidity of kaolin clay is higher than that of bentonite clay. When \( P = 0–150 \) MPa, it is higher by \[ \text{pH} = 1.1 \], and when \( P = 150–800 \) MPa, it is higher by 1.4. In KCl solution we observe a similar trend, i.e. the acidity of kaolin clay is higher than that of bentonite clay. When \( P = 0–150 \) MPa, it is higher by \[ \text{pH} = 0.98 \], and when \( P = 150–800 \) MPa, it is higher by 1.7.

Therefore, when clays are subjected to pressure, pH alters in different ways: at the same time, pressure, in general, increases the acidity of a suspension. The acidity of clay suspensions in the aqueous solutions is lower than that in KCl solution. Based on this we can assume that, when clays are subjected to pressure, their chemical composition changes, and ions, that have left the crystal lattice of kaolinite and montmorillonite minerals, as well as \( K^+ \) ions, act as adsorption centres of hydroxyl groups, thus increasing the acidity of the suspensions.

### Table 3

Statistical characteristics of clay suspensions’ pH

| Clay   | Diluent type   |  \( P = 0 \div 150 \) MPa     |  \( P = 150 \div 800 \) MPa   |
|--------|----------------|-------------------------------|-------------------------------|
|        | range  | average  | standard deviation | range  | average  | standard deviation |
| Kaolin | Distilled water | 0.383 | 7.136 | 0.148 | 0.099 | 6.836 | 0.0372 |
|        | KCl solution | 0.840 | 6.694 | 0.291 | 0.272 | 6.088 | 0.0898 |
| Bentonite | Distilled water | 0.058 | 8.245 | 0.018 | 0.101 | 8.201 | 0.0402 |
|        | KCl solution | 0.129 | 7.877 | 0.037 | 0.181 | 7.778 | 0.0510 |
Table 4

| Clay      | Diluent type | Parameter | Correlation coefficient $r_p$ |
|-----------|--------------|-----------|------------------------------|
|           |              |           | Class 1 $(P = 0–150 \text{ MPa})$ | Class 2 $(P = 150–800 \text{ MPa})$ |
| Bentonite | Distilled water | P         | 0.23                         | 0.41                         | -0.83                        | -0.90                        |
|           |               | Al$^{3+}$ | 1                            | -0.37                        | 1                            | 0.84                         |
|           | KCl solution  | P         | 0.34                         | -0.80                        | -0.86                        | 0.45                         |
|           |               | Al$^{3+}$ | 1                            | -0.40                        | 1                            | -0.27                        |
| Kaolin    | Distilled water | P        | -0.86                        | -0.56                        | -0.85                        | -0.80                        |
|           |               | Al$^{3+}$ | 1                            | 0.79                         | 1                            | 0.49                         |
|           | KCl solution  | P         | -0.86                        | -0.88                        | -0.86                        | -0.82                        |
|           |               | Al$^{3+}$ | 1                            | 0.86                         | 1                            | 0.64                         |

The correlation analysis results show that at a pressure of up to 0–150 MPa, the influence of Al$^{3+}$ ions on the formation of pH is rather high, which is evidenced by the significant correlation coefficient $r_p = 0.79 > r_c = 0.63$ (see Table 4). At a pressure within 150–800 MPa, the influence of Al$^{3+}$ ions on the formation of pH is lower, although the trend remains: $r_p = 0.49 < r_c = 0.63$.

Therefore, as the content of Al$^{3+}$ ions increases in the diffuse layer of a clay particle, the suspension acidity grows. This means that Al$^{3+}$ ions, reacting with hydroxyl groups, bond them ($\text{OH}^-$), and hydrogen ions form an acidic environment.

pH value formation in the distilled water. Let us determine the role of Al$^{3+}$ ions in the pH formation of clay suspension in the distilled water. To do this, we apply the correlation analysis, the idea of which consists in the following: if Al$^{3+}$ ions have an influence on the pH formation of the medium, statistical relations should be observed between them. Then we are going to assess such relations through the correlation between the calculated ($r_p$) and table ($r_c$) correlation coefficients. If $r_p > r_c = 0.63$, we consider that the statistical relations between Al$^{3+}$ and pH are observed.

As the removal of Al$^{3+}$ ions from the octahedral sheet to the diffuse layer increases (with the reduction of Al$^{3+}$ ion content in the octahedral layer), the acidity of bentonite clay suspension increases in the aqueous solution, as well as in KCl solution.

The correlation analysis results show that at a pressure of up to 0–150 MPa, it is rather difficult to reveal the influence of Al$^{3+}$ ions on the formation of pH, which is evidenced by the insignificant correlation coefficient $r_p = -0.37 < r_c = 0.63$ (Table 4). At a pressure within 150–800 MPa, the influence of Al$^{3+}$ ions on the formation of pH is rather strong, which is evidenced by the significant correlation coefficient $r_p = 0.84 > r_c = 0.63$.

Therefore, as the content of Al$^{3+}$ ions increases in the diffuse layer of a clay particle, the acidity of the suspension grows.

As the removal of Al$^{3+}$ ions from the octahedral sheet into the diffuse layer (detached water) increases, the acidity of kaolin clay suspension grows in the aqueous solution, as well as in KCl solution.

pH value formation in KCl solution. The experimental results showed, that pH of the suspension of bentonite clay prepared based on KCl solution, is by 0.3–0.4 units lower (pH = 7.8–7.9) than pH of a suspension prepared based on the aqueous solution (pH = 8.2–8.3) throughout the entire range of Al$^{3+}$ ion content change. This is an evidence of the fact that Al$^{3+}$ ions have an insignificant effect on the formation of pH of the suspension based on KCl, as confirmed by the absence of statistical relations between Al$^{3+}$ and pH, which is seen by insignificant coefficients of the correlation between Al$^{3+}$ and pH (see Table 4).

pH is most influenced by K$^+$ ions which, reacting with hydroxyl groups, bond them (OH). Hydrogen ions remained in the diffuse layer and octahedral sheet of montmorillonite mineral, form the acidic environment of the suspension.

In the suspension of kaolin clay prepared based on KCl solution, there comes another trend.
As the removal of Al$^{3+}$ ions increases up to 24.2 %—which corresponds to 200 MPa—the suspension’s pH changes within a narrow range: $P = 5.95–6.1$. That means that the formation of pH is most influenced by K$^+$ ions.

When the content of Al$^{3+}$ ions decreases from 25.5 to 24.2 % in the octahedral sheet of kaolinite mineral, the influence of Al$^{3+}$ on pH rises sharply: for instance, the acidity of the suspension grows from 7.1 to 6.1, respectively. This is evidenced by statistical relations between Al$^{3+}$ and pH (see Table 4).

Therefore, pH of the suspension is most influenced by K$^+$ ions, Al$^{3+}$ ions have a more significant effect on pH at a pressure exceeding 150–200 MPa.

### Principles of Kaolin Sorption Activity Formation as Seen with the Use of Methylene Blue

Clay sorption activities are much determined by the structure, specific area, and other characteristics of a sorbent [11]. It is well known that these factors have an influence on clay sorption all together, not separately. That is why a research has been conducted to assess the joint influence of the specific surface area ($S_{sa}$), the coherent scattering area ($M_k$), aluminum oxide content in kaolin ($C$), and pH of a suspension of clay (pH) on kaolin sorption.

Methodologically, the problem set was solved in the following way: initially a multiple regression equation was calculated where sorption index $A$ was a dependent variable ($y$), and $S_{sa}$, $M_k$, $C$, pH were independent variables. The equation can be presented in a general view as follows:

$$A = b + k_1 \cdot S_{sa} + k_2 \cdot M_k + k_3 \cdot C + k_4 \cdot \text{pH},$$

where $b$ is the intercept, and $k_1 - k_4$ are coefficients.

Then the selected average values of $A$, $S_{sa}$, $M_k$, $C$, and pH were calculated and inserted in the multiple regression equation, followed by the calculation of the degree of the influence of these figures ($Z_{S_{sa}}$, $Z_{M_k}$, $Z_{C}$, $Z_{\text{pH}}$) on the formation of kaolin sorption activity based on methylene blue. For instance, the degree of influence of the specific surface area ($Z_{S_{sa}}$) of particles on the formation of sorption ($A$) was determined in accordance with the following dependence:

$$Z_{S_{sa}} = k_1 \cdot S_{sa} / A - b.$$

Based on the foregoing and based on the results of previously conducted studies [18], we see that a pressure of 150 MPa is a boundary pressure, at which the composition, structure, and properties of clays are formed in accordance with different scenarios. That is why the degree of influence of $Z_{S_{sa}}$, $Z_{M_k}$, $Z_{C}$, $Z_{\text{pH}}$ on the formation of kaolin sorption was separately evaluated for each class.

For kaolin, which was subjected to a pressure of 0–150 MPa (class 1), the following regression equation was solved:

$$A = -0.178 \cdot C + 16.909 \cdot \text{pH} - 0.161 \cdot M_k + 0.00037 \cdot S_{sa} - 8.575.$$

By using the obtained equation and selected average values ($S_{sa} = 3706 \text{ mm}^2$, $M_k = 229.1 \text{ Å}$, $C = 25.1 \%$, pH = 7.18, and $A = 72.8 \text{ mg/g}$), the degree of influence of these figures on the formation of kaolin sorption activity was calculated based on methylene blue and equaled to the following: $Z_{C} = 73 \%$, $Z_{M_k} = -24 \%$, $Z_{C} = -2 \%$, and $Z_{S_{sa}} = 1 \%$.

Therefore, if kaolin is subjected to a pressure of up to 150 MPa, kaolin’s sorption activity, based on methylene blue, is mainly determined by pH of the solution that makes up a diffuse layer of particles. As pH grows, kaolin sorption increases. The opposite trend has been found for $M_k$; as the thickness of a defect-free crystal grows, kaolin sorption activity decreases ($Z_{M_k} = -24 \%$).

Such conclusion does not contradict the sorption process physics, as the thickness of the defect-free crystal grows, the total defectiveness of kaolin structure decreases and reduces the energy potential on the surface of particles, thus, reduces kaolin sorption activity.

The structure defectiveness at the pack level and the specific surface area have practically no effect on kaolin sorption activity $Z_{C} = -2 \%$, $Z_{S_{sa}} = 1 \%$.

For kaolin, which was subjected to a pressure of 150–800 MPa (class 2), the following regression equation was solved:
\[ A = 9.86 \cdot C + 1.324 \cdot pH + 0.29 \cdot M_k - 0.002 \cdot S_{sa} - 258.3. \]

By using the obtained equation and selected average values \((S_{sa} = 2327 \, \text{mm}^2, \, M_k = 203.4 \, A, \, C = 24.2 \, \%, \, pH = 6.8, \, \text{and} \, A = 44.4 \, \text{mg/g})\), the degree of influence of these figures on the formation of kaolin sorption activity was calculated based on methylene blue and equaled to the following: \(Z_c = 74 \, \%\), \(Z_{M_k} = 19 \, \%\), \(Z_{pH} = 4 \, \%\) and \(Z_{S_{sa}} = 3 \, \%\).

Therefore, if kaolin is subjected to a pressure of up to 150–800 MPa, kaolin's sorption activity, based on methylene blue, is mainly determined by the structures' defectiveness at the level of the pack \(Z_c = 74 \, \%\) and crystallite \(Z_{M_k} = 19 \, \%\). pH of the solution, making up a diffuse layer of particles, and the specific surface area have practically no effect on kaolin sorption activity: \(Z_{pH} = 4 \, \%\) and \(Z_{S_{sa}} = 3 \, \%\).

Conclusions

1. When kaolin is subjected to stress pressure, defects are formed in the structural pack of kaolinite mineral due to the removal of \(\text{Al}^{3+}, \, \text{Fe}^{3+}/2+, \, \text{Mg}^{2+}, \, \text{Si}^{4+}\) ions from it. At the same time, pressure has the maximum influence on the removal of \(\text{Al}^{3+}\) ions from kaolin.

2. When kaolin is subjected to a pressure of up to 150 MPa, kaolinite, consisting of 20–40 packs, demonstrates the normalization of the structure. At a pressure of >150 MPa, the increase in kaolinite defectiveness was observed as a result of the destruction of hydrogen bonds between the packs and, as a consequence, slipping, and rotation of the structural packs between themselves.

3. The experiments demonstrate that at a pressure of 0–150 MPa, to which kaolin was subjected, kaolin sorption activity is most influenced by pH of the solution of a diffuse layer of particles \(Z_{pH} = 73 \, \%\) and by the degree of crystallite defectiveness \(Z_{M_k} = -24 \, \%.\) The specific surface area of particles \(Z_{S_{sa}} = 1 \, \%\) and kaolinite mineral pack defectiveness \(Z_c = 2 \, \%\) do not have any significant effects on sorption. At a pressure of 150–800 MPa, to which kaolin was subjected, kaolin sorption activity is most influenced by the defectiveness of the pack of kaolinite \(Z_c = 74 \, \%\) and crystallite \(Z_{M_k} = 19 \, \%.\) The specific surface area of particles \(Z_{S_{sa}} = 3 \, \%\) and pH of the solution of the diffuse layer of particles \(Z_{pH} = 4 \, \%\) do not have any significant effects on sorption.

References

1. Viakhirev N.P. Promezhutochnye formy v nepryrevnom riadu amorfnoe veshchestvo - kaolinit [Intermediate forms in a continuous row amorphous substance – kaolinite]. Rentgenograpiia mineral'nogo syr'ia. Moscow: Nedra, 1966, vol. 5, pp. 128-131.

2. Goilo E.A., Kotov N.V., Frank-Kamenetskii V.A. Eksperimental'noe issledovanie vliianiia davleniia i temperatury na kristallicheskie struktury kaolinita, illita i montmorillonita [Experimental study of the effect of pressure and temperature on the crystal structures of kaolinite, illite and montmorillonite]. Fizicheskie metody issledovanii osadochnykh porod. Moscow: Nauka, 1966, pp. 123-129.

3. Frank-Kamenetskii V.A., Kotov N.V., Goilo E.A. Izmnenenie struktury glinistikh mineralov v razlichnykh temodinamicheskikh usloviiakh [Changes in the structure of clay minerals under different temodynamic conditions]. Rentgenograpiia mineral'nogo syr'ia. Moscow: Nedra, 1970, no. 7, pp. 166-174.

4. Seredin V.V., Medvedeva N.A., Siteva O.S., Ivanov D.V. Vliianie davleniia na formirovanie defektnosti strukturnogo paketa i minerala kaolinit [Effect of pressure on the formation of defectiveness of the structural package and mineral kaolinite]. Inzhenernaia geologiia, 2019, vol. XIV, no. 4, pp. 44-54.

5. Wu H., Liu P., Wu W., Fan Q., Zhao X., Li P., Liang J., Qiang S. Exploring the relationship between th(iv) adsorption and the structure alteration of phlogopite. Applied Clay Science, 2018, vol. 152, pp. 295-302. DOI: 10.1016/j.clay.2017.11.026

6. Seredin V.V., Andrianov A.V. K voprosu o metodike opredelenia prochnostnykh kharakteristik gruntov [On the question of the method for determining the strength characteristics of soils]. Sovremennye problemy nauki i obrazovaniia, 2013, no. 6, 946 p.
7. Usov P.G., Guber E.A. Izmenenie mekhanicheskoi prochnosti izdelii iz gliny v sviazi so strukturnymi izmeneniiami glinistykh mineralov pri obzhige [Changes in the mechanical strength of clay products due to structural changes in clay minerals during firing]. Izvestiia Tomskogo politekhnicheskogo instituta, 1971, vol. 174, pp. 66-72.

8. Seredin V.V., Krurilev A.S., Andreiko S.S., Galkin V.I. Possibilities for calculating the stress state of rocks during their uniaxial tension and compression. AIP Conference Proceedings, 2020, vol. 2216 (1), p. 020011. DOI: 10.1063/5.0003676

9. Seredin V., Fyodorov M., Lunegov I., Galkin V. Changes in adhesion force on kaolin under pressures. AIP Conference Proceedings, 2020, vol. 2216 (1), p. 040004. DOI: 10.1063/5.0003673

10. Nichiporenko S.P., Kruglitskii N.N., Panasevich A.A., Khil'ko V.V. Fiziko-khimicheskaia mekhanika dispersnykh mineralov [Physicochemical mechanics of dispersed minerals]. Kiev: Naukova dumka, 1974.

11. Tarasevich Iu.I., Ovcharenko F.D. Adsorbtsiia na glinistykh mineralakh [Adsorption on clay minerals]. Kiev: Naukova dumka, 1975.

12. Suraj G., Iyer C.S.P., Rugmini S., Lalithambika M. The effect of micronization on kaolinites and their sorption behavior. Applied Clay Science, 1997, vol. 12, pp. 111-130. DOI: 10.1016/S0169-1317(96)00044-0

13. Kachenov V.I., Seredin V.V., Karmanov S.V. K voprosu o vliianii neftianykh zagriaznenii na svoistva gruntov [On the question of the influence of oil pollution on the properties of soils]. Geologiia i poleznye iskopaemykh Zapadnogo Urala, 2011, no. 11, pp. 164-165.

14. Korolev V.A., Samarin E.N., Panfilov V.A., Romanova I.V. Sorbtionnye svoistva brusita i glinistykh smesei na ego osnove [Sorption Properties of Brucite and Brucite-Based Clay Mixtures]. Ekologiia i promyshlennost' Rossi, 2016, vol. 20, no. 1, pp. 18-24. DOI: 10.18412/1816-0395-2016-1-18-24

15. Seredin V.V., Rastegayev A.V., Panova E.G., Medvedeva N.A. Changes in physical-chemical properties of clay under compression. International Journal of Engineering and Applied Sciences, 2017, vol. 4, no. 3, 22 p.

16. Korolev V.A., Nesterov V.S. Fiziko-khimicheskie zakonomernosti izmenenii elektricheskikh zariadov chastits glinistykh gruntov [Physico-chemical regularities of changes of the clay soil particles electrical charge]. Inzhenernaia geologiia, 2017, no. 4, pp. 50-60. DOI: 10.25296/1993-5056-2017-4-50-60

17. Fil B., Ozmetin C., Korkmaz M. Characterization and electrokinetic properties of montmorillonite. Bulgarian Chemical Communications, 2014, vol. 46, no. 2, pp. 258-263.

18. Seredin V.V., Rastegayev A.V., Medvedeva N.A., Parshina T.Iu. Vliianie davleniia na ploshchad' aktivnoi poverkhnosti chastits glinistykh gruntov [Influence of pressure on the active surface area of clay soil particles]. Inzhenernaia geologiia, 2017, no. 3, pp. 18-27.

19. Pushkareva G.I. Vliianie temperaturnoi obrabotki brusita na ego sorbtionnye svoistva [Influence of temperature treatment of brucite on its sorption properties]. Fiziko-tekhnicheskie problemy razrabotki poleznykh iskopaemykh, 2000, no. 6, pp. 90-93.

20. Kara-Sal B.K., Sapelkina T.V. Povyshenie adsorbtionnykh svoistv glinistykh porod Tuvy v zavisimosti ot metodov aktivatsii [Increasing the adsorption properties of clay rocks of Tuva, depending on the activation methods]. Aktual'nye problemy sovremennoi nauki, 2012, no. 5, pp. 158-162.

21. Boldyrev V.V. Mehanokhimiiia i mekhanicheskaia aktivatsiiia tverdykh veshchestv [Mechanochemistry and mechanical activation of solids]. Uspekhi khimii, 2006, vol. 75, no. 3, pp. 203-216. DOI: 10.1070/RC2006v075n03ABEH001205

22. Medvedeva N.A., Siteva O.S., Seredin V.V. Sorbtionnaya sposobnost' glin, podverzhennykh szhatiiu [Sorption ability of clays exposed to compression]. Vestnik Permskogo natsional'noi issledovatel'skogo politekhnicheskogo universiteta. Geologiia. Neftegazovoe i gornoe delo, 2018, vol. 18, no. 2, pp. 118-128. DOI: 10.15593/2224-9923/2018.4.2

23. Seredin V.V., Medvedeva N.A., Aniukhina A.V., Andrianov A.V. Zakonomernosti izmenenii soderzhania sviazannoi vody v kaolinovoi gline pri ee shhazi vysokymi davleniiami [Regularities of the bound water content variation in kaolin clay under high pressure]. Vestnik Permskogo universiteta, 2018, vol. 17, no. 4, pp. 359-369. DOI: 10.17072/psu.geol.17.4.359

24. Galan E., Aparicio P., Gonzalez Â. The effect of pressure on order/disorder in kaolinite under wet and dry conditions. Clays and Clay
25. Saponova Zh.A., Lesovik V.S., Gomes M.Zh., Shaikhieva K.I. Sorbtsionnye svoistva UF-aktivirovannyh glin Angol'skikh mestorozhdenii [Sorption properties of UV-activated clays of Angola deposits]. Vestnik Kazanskogo natsional’nogo issledovatel’skogo tekhnicheskogo universiteta, 2015, vol. 18, no. 1, pp. 91-93.

26. Sruthi P.I., Reddy P.H.P. Swelling and mineralogical characteristics of alkali-transformed kaolinitic clays. Applied Clay Science, 2019, vol. 183, pp. 353-362. DOI: 10.1016/j.clay.2019.105353

27. Mostalygina L.V., Chernova E.A., Bukhtoiarov O.I. Kislotnaia aktivatsiia bentonitovoi gliny [Acid activation of bentonite clay]. Vestnik Iuzhno-Ural’skogo gosudarstvennogo universiteta, 2012, no. 24, pp. 57-61.

28. Kossovskaya A.G., Shutov V.D., Drits V.A. Glinistye mineraly – indikatory glubinnogo izmeneniia terrigennykh porod [Clay minerals – indicators of deep changes in terrigenous rocks]. Geokhimiia, mineralogiia i petrografiia osadochnykh obrazovanii. Moscow: Akademiia nauk SSSR, 1963, pp. 68-73.

29. Range K.J., Range A., Weiss A. Fire-clay type kaolinite or fire-clay mineral. Experimental classification of kaolinite-halloysite minerals. Proceedings of the International Clay Conference in Tokyo, 1969, pp. 3-13.

30. La Iglesia A. Pressure induced disorder in kaolinite. Clay Minerals, 1993, no. 28, pp. 311-319. DOI: 10.1180/claymin.1993.028.2.11

31. Chukanov N.V. Infrared spectra of mineral species. Springer, 2014. 1726 p. DOI: 10.1007/978-94-007-7128-4

32. Plastininia M.A., Seredin V.V., Karmanov S.V. K voprosu o vliianii neftianykh zagriaznenii na svoistva gruntov [To the question of the oil pollution influence on soils properties]. Geologiia i poleznye iskopaemye Zapadnogo Urala, 2011, no. 11, pp. 164-165.
при разработке мелорозбении полезных ископаемых [Geoinformation technology of engineering-geological forecasting in the development of mineral deposits]. Vestnik Permского университета. Geologiya, 2020, vol. 19, no. 1, pp. 65-72. DOI: 10.17072/psu.geol.19.1.65

45. Rastegaev A.V., Galkin V.I., Kozlova V.L., Voevodkin I.V., Van'tseva I.A. Otsenka tochnosti opredeleniiia prognoznym zapasov nefti v predelakh Solikamskoi vpadiny [Evaluation of expected oil reserves accuracy within Solikamsk basin]. Neftepromyslovoe delo, 2010, no. 7, pp. 8-12.

Библиографический список

1. Вяхирев Н.П. Промежуточные формы в непрерывном ряду аморфное вещество – каолинит // Рентгенография минерального сырья. – М.: Недра, 1966. – Т. 5. – С. 128–131.

2. Гойло Э.А., Котов Н.В., Франк-Каменецкий В.А. Экспериментальное исследование влияния давления и температуры на кристаллические структуры каолинита, иллиита и монтмориллонита // Физические методы исследования осадочных пород. – М.: Наука, 1966. – С. 123–129.

3. Франк-Каменецкий В.А., Котов Н.В., Гойло Э.А. Изменение структуры глинистых минералов в различных температурных условиях // Рентгенография минерального сырья. – М.: Недра, 1970. – № 7. – С. 166–174.

4. Влияние давления на формирование дефектности структурного пакета и минерала каолинит / В.В. Середин, Н.А. Медведева, О.С. Ситева, Д.В. Иванов // Инженерная геология. – 2019. – Т. XIV, № 4. – С. 44–54.

5. Exploring the relationship between th(iv) adsorption and the structure alteration of phlogopite / H. Wu, P. Liu, W. Wu, Q. Fan, X. Zhao, P. Li, J. Liang, S. Qiang // Applied Clay Science. – 2018. – Vol. 152. – P. 295–302. DOI: 10.1016/j.clay.2017.11.026

6. Середин В.В., Андрианов А.В. К вопросу о методике определения прочностных характеристик грунтов // Современные проблемы науки и образования. – 2013. – № 6. – С. 946.

7. Усов П.Г., Губер Э.А. Изменение механической прочности изделий из глины в связи со структурными изменениями глинистых минералов при обжиге // Известия Томского политехнического института. – 1971. – Т. 174. – С. 66–72.

8. Possibilities for calculating the stress state of rocks during their uniaxial tension and compression / V.V. Seredin, A.S. Khrulev, S.S. Andreiko, V.I. Galkin // AIP Conference Proceedings. – 2020. – Vol. 2216 (1). – P. 020011. DOI: 10.1063/5.0003673

9. Changes in adhesion force on kaolin under pressures / V. Seredin, M. Fyodorov, I. Lunegov, V. Galkin // AIP Conference Proceedings. – 2020. – Vol. 2216 (1). – P. 040004. DOI: 10.1063/5.0003673

10. Физико-химическая механика дисперсных минералов / С.П. Ничипоренко, Н.Н. Крутякский, А.А. Панасевич, В.В. Хилько. – Киев: Наукова думка, 1974.

11. Тарасевич Ю.И., Овчаренко Ф.Д. Адсорбция на глинистых минералах. – Киев: Наукова думка, 1975.

12. The effect of micronization on kaolinites and their sorption behavior / G. Suraj, C.S.P. Iyer, S. Rugmini, M. Lalithambika // Applied Clay Science. – 1997. – Vol. 12. – P. 111–130. DOI: 10.1016/S0169-1317(96)00044-0

13. Каченов В.И., Середин В.В., Карманов С.В. К вопросу о влиянии нефтяных загрязнений на свойства грунтов // Геология и полезные ископаемые Западного Урала. – 2011. – № 11. – С. 164–165.

14. Сорбционные свойства бруса и глинистых смесей на его основе / В.А. Королев, Е.Н. Самарин, В.А. Панфилов, И.В. Романова // Экология и промышленность России. – 2016. – Т. 20, № 1. – С. 18–24. DOI: 10.18412/1816-0395-2016-1-8-24

15. Changes in physical-chemical properties of clay under compression / V.V. Seredin, A.V. Rastegaev, E.G. Panova, N.A. Medvedeva // International Journal of Engineering and Applied Sciences. – 2017. – Т. 4, № 3. – С. 22.

16. Королев В.А., Нестеров В.С. Физико-химические закономерности изменения электрических зарядов частиц глинистых грунтов // Инженерная геология. – 2017. – № 4. – С. 50–60. DOI: 10.25296/1993-5056-2017-4-50-60
17. Fil B., Özmetin C., Korkmaz M. Characterization and electrokinetic properties of montmoril // Bulgarian Chemical Communications. – 2014. – Vol. 46, № 2. – Р. 258–263.

18. Влияние давления на площадь активной поверхности частиц глинистых грунтов / В.В. Середин, А.Б. Растегаев, Н.А. Медведева, Т.Ю. Паршина // Инженерная геология. – 2017. – № 3. – С. 18–27.

19. Пушкарев Г.И. Влияние температурной обработки брусита на его сорбционные свойства // Физико-технические проблемы разработки полезных ископаемых. – 2000. – № 6. – С. 90–93.

20. Карасал Б.К., Сапелкина Т.В. Повышение адсорбционных свойств глинистых пород Тувы в зависимости от методов активации // Актуальные проблемы современной науки. – 2012. – № 5. – С. 158–162.

21. Болдырев В.В. Механохимия и механическая активация твердых веществ // Успехи хими. – 2006. – Т. 75, № 3. – С. 203–216. DOI: 10.1070/RC2006v075n03ABEH001205

22. Медведева Н.А., Ситьева О.С., Середин В.В. Сорбционная способность глин, подверженных сжатию // Вестник Пермского национального исследовательского политехнического университета. Геология. Нефтегазовое и горное дело. – 2018. – Т. 18, № 2. – С. 118–128. DOI: 10.15593/2224-9923/2018.4.2

23. Закономерности изменения содержания связанной воды в каолиновой глине при ее сжатии высокими давлениями / В.В. Середин, Н.А. Медведева, А.В. Анюхина, А.В. Андринов // Вестник Пермского университета. – 2018. – Т. 17, № 4. – С. 359–369. DOI: 10.17072/psu.geol.17.4.359

24. Galan E., Aparicio P., Gonzalez Â. The effect of pressure on order/disorder in kaolinite under wet and dry conditions // Clays and Clay Minerals. – 2006. – Vol. 54, № 2. – Р. 230–239. DOI: 10.1346/CCMN.2006.0540208

25. Сорбционные свойства УФ-активированных глин Ангольских месторождений / Ж.А. Сапронова, В.С. Лесовик, М.Ж. Гомес, К.И. Шайхиеева // Вестник Казанского национального исследовательского технического университета. – 2015. – Т. 18, № 1. – С. 91–93.

26. Sruthi P.L., Reddy R.H.P. Swelling and mineralogical characteristics of alkali-transformed kaolinitic clays // Applied Clay Science. – 2019. – Vol. 183. – Р. 353–362. DOI: 10.1016/j.clay.2019.105353

27. Мостальгина Л.В., Чернова Е.А., Бухтояров О.И. Кислотная активация бентонитовой глины // Вестник ЮУрГУ. – 2012. – № 24. – С. 57–61.

28. Коссовская А.Г., Шутов В.Д., Дриц В.А. Глинистые минералы – индикаторы глубинного изменения терригенных пород // Геохимия, минералогия и петрография осадочных образований. – М: Изд-во АН СССР, 1963. – С. 68–73.

29. Range K.J., Range A., Weiss A. Fire-clay type kaolinite or fire-clay mineral Experimental classification of kaolinite-halloysite minerals // Proceedings of the International Clay Conference in Tokyo. – Tokyo, 1969. – Р. 3–13.

30. La Iglesias A. Pressure induced disorder in kaolinite // Clay Minerals. – 1993. – № 28. – Р. 311–319. DOI: 10.1180/claymin.1993.028.2.11

31. Дятлова Е.М., Бобкова Н.М., Сергиевич О.А. ИК-спектроскопическое исследование каолинового сырья белорусских месторождений // Проблемы недропользования. – 2019. – № 2. – С. 143–149. DOI: 10.25635/2313-1586.2019.02.143

32. Плюснина И.И. Инфракрасные спектры минералов. – М.: Изд-во Моск. ун-та, 1976.

33. Changes of energy potential on clay particle surfaces at high pressures / V.V. Seredin, T.Y. Parshina, A.V. Rastegaev, V.I. Galkin, G.A. Isaeva // Applied Clay Science. – 2018. – Vol. 155. – Р. 8–14. DOI: 10.1016/j.clay.2017.12.042

34. Котельников Д.Д., Конохов А.И. Глинистые минералы осадочных пород. – М.: Недра, 1986.

35. Chukanov N.V. Infrared spectra of mineral species. – Springer, 2014. DOI: 10.1007/978-94-007-7128-4

36. ПластиникаМ.А., Куковский Е.Г. Степень совершенства каолинитов по данным рентгенографии и ИК-спектроскопии // Минералогический журнал. – 1979. – Т. 1, № 2. – С. 67–72.

37. Depth-dependent transformation of kaolinite to dickite in sandstones of the
Norwegian continental shelf / S.N. Ehrenberg, P. Aagaard, M.J. Wilson, A.R. Fraser, D.M.L. Duthie // Clay Minerals. – 1993. – № 28. – P. 325–352. DOI: 10.1180/claymin.1993.028.3.01

38. Франк-Каменецкий В.А. Рентгенография основных типов породообразующих минералов (слоистые и каркасные силикаты). – Л.: Недра, 1983.

39. Шлыков В.Г. Рентгеновский анализ минерального состава дисперсных грунтов. – М.: ГЕОС, 2006.

40. Infrared and Raman Spectroscopies of Clay Minerals / W.P. Gates, J.T. Kloprogge, J. Madejova, F. Bergaya, W.P. Gates, S. Petit // Elsevier. – 2017. – Vol. 8. – P. 620.

41. Characterization and differentiation of kaolinites from selected czech deposits using infrared spectroscopy and differential thermal analysis / L. Vaculíkova, E. Plevová, S. Vallová, I. Koutník // Acta Geodynamica et Geomaterialia. – 2011. – Vol. 8, № 1 (161). – Р. 59–67.

Please cite this article in English as:
Seredin V.V., Siteva O.S., Alvanyan K.A., Andrianov A.V. Change in the Physico-Chemical Properties of Clays Subjected to Pressure. Perm Journal of Petroleum and Mining Engineering, 2020, vol.20, no.4, рр.304-316. DOI: 10.15593/2712-8008/2020.4.1

Просьба ссылаться на эту статью в русскоязычных источниках следующим образом:
Изменение физико-химических свойств глин, подверженных давлению / В.В. Середин, О.С. Ситева, К.А. Аванян, А.В. Андрианов // Недропользование. – 2020. – Т.20, №4. – С.304–316. DOI: 10.15593/2712-8008/2020.4.1