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SORPTION ABILITY OF CLAYS EXPOSED TO COMPRESSION

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СОРБЦИОННАЯ СПОСОБНОСТЬ ГЛИН, ПОДВЕРЖЕННЫХ СЖАТИЮ

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clay, montmorillonite, kaolinite, pressure, specific surface, sorbent, petroleum products, fractional analysis, ion exchange capacity, methylene blue, adsorption, diesel fuel, engine oil, transmission oil, thermogravimetry.

The paper discusses the effect of high pressures on adsorption of inorganic ions (KCl), methylene blue and petroleum products (engine oil, transmission fluid, diesel fuel) by samples of montmorillonite and kaolinite. The relationship between the value of the applied pressure (in the range from 0 to 700 MPa), fractional composition, specific surface and the microstructure of mineral particles was revealed. During the study, dynamics of changes in the content of the clay, dust and sand fractions in the clays under study was noted. It is established that an increase in clay compression to 700 MPa leads to a decrease in the content of clay fractions and an increase in the fraction of the dust fraction. Changes in the fractional composition occur more intensively in kaolinite clay than in montmorillonite clay. The pressure intervals were determined according to the intensity of the formation of the fractional composition of clays 0-200 and 200-700 MPa. Adsorption parameters of clays are determined. According to potentiometric measurements, it has been established that the ion-exchange capacity is higher in montmorillonite than in kaolinite with respect to cations. The magnitude of kaolinite adsorption with respect to methylene blue decreases to a pressure of 200 MPa, which is caused by the content of the clay fraction, does not change significantly at pressures of 200-700 MPa. The adsorption rate of montmorillonite has a general tendency to increase. Adsorption indicators of clays with respect to methylene blue allow predicting the sorption capacity of the studied materials to petroleum products.

Ключевые слова:

глина, монтмориллонит, каолинит, давление, удельная поверхность, сорбент, нефтепродукты, фракционный анализ, ионообменная емкость, метиленовый голубой, адсорбция, дизельное топливо, моторное масло, трансмиссионное масло, термогравиметрия.

Изучено влияние высоких давлений на адсорбцию неорганических ионов (KCl), метиленового голубого и нефтепродуктов (моторное масло, трансмиссионная жидкость, дизельное топливо) образцами монтмориллонита и каолинита. Выявлена взаимосвязь между величиной прикладываемого давления (в интервале от 0 до 700 МПа), фракционным составом, удельной поверхностью и микроструктурой минеральных частиц. В ходе проведенного исследования была отмечена динамика изменения содержания глинистой, пылевой и песчаной фракций в исследуемых глинах. Установлено, что увеличение сжатия глины до 700 МПа приводит к уменьшению содержания глинистых фракций и увеличению доли пылевой фракции. В каолиновой глине изменения фракционного состава протекают более интенсивно, чем в монтмориллонитовой глине. Определены интервалы давлений по интенсивности формирования фракционного состава глин 0–200 и 200–700 МПа. Определены адсорбционные параметры глин. Согласно потенциометрическим измерениям установлено, что показатели ионообменной емкости в отношении катионов выше у монтмориллонита, чем у каолинита. Величина адсорбции каолинита по отношению к метиленовому голубому уменьшается до давления 200 МПа, что обусловлено содержанием глинистой фракции, при давлениях 200–700 МПа существенно не изменяется. Показатель адсорбции монтмориллонита имеет общую тенденцию к возрастанию. Адсорбционные показатели глин по отношению к метиленовому голубому позволяют спрогнозировать сорбционную способность исследуемых материалов к нефтепродуктам.

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Introduction

Clays represent complex polymineral formations [1-3]. Their properties, including sorption, mainly depend on the lattice structure, mineral composition [4, 5], particle size distribution, [6], and environmental conditions [3, 5]. The mineral composition of clays manifests itself as energy on the surface of particles, whereas the particle size distribution manifests itself as the active surface area of particles [6]. These are exactly the two complex parameters which determine sorption activity of clays [4, 7].

Adsorption of substances from solutions at the "hard surface – water" phase boundary depends on the surface boundary electrical characteristics. Clay minerals are sources of constant and alternating surface charge [8]. Layered structures bear constant electric charge which is associated with the manifestation of heterovalent isomorphism in the lattice i.e. isomorphous replacement of Si with Al in a tetrahedral lattice and isomorphous replacement of Al with Mg in octahedrons. It does not depend on pH of the environment. Alternating charge, depending on pH of the environment, is located on lateral fractures of clayey crystallite, where hydroxyl groups are capable of proton adsorption-desorption processes.

Thanks to their properties, clays can absorb inorganic ions, organic molecules, including dyes and petroleum products [9, 10], on the surface of a particle and in the interlayer space; thus, strong associations are formed which are kept on the surface by electrostatic force, as well as by Van der Waals forces [4].

In case of inorganic ions, the sorption capacity is expressed by determining the ion-exchange capacity and cation-exchange capacity. These values are not constant and depend on pH, ionic force of the solution, and eluting ion. The highest values are common for montmorillonoids and the lowest values are common for kaolinites [8].

Determining clay-adsorption with the use of methylene blue (MB) dye is a wide-spread method that does not require special equipment [11-16]. In accordance with the chemical classification, MB is a dye belonging to the thiazine group. Its empirical formula is as follows: $C_{16}H_{18}N_3S$ (its molecular weight is 319.85 g/mol) [17]. It is a cation type

dye, which can be absorbed on a negatively charged surface of clay particles [18]. A MB molecule is rectangular in shape and its dimensions are as follows: $17.0\text{\AA} \times 7.6\text{\AA} \times 3.25\text{\AA}$. Dye absorption on the surface of clay occurs in two ways: 1) cation exchange on the surface of aluminosilicate lattice; 2) attraction of dye molecules by Van der Waals forces or chemisorption (hydrogen bond) with the surface of Si-OH and Al-OH of the aluminosilicate lattice. [19]. In aqueous solutions organic dyes form associates of various complexities. This property allows us to use dye solutions to evaluate quality of sorbents with respect to various petroleum products.

In order to evaluate sorption activity of clays the following is performed: mechanical treatment, thermal modification [20-23], and chemical activation with the use of chemical agents such as acids [24-27], alkali [28], and salts combined with different exposure duration [29].

Compression under pressure is one of the mechanical methods [6, 30] of clay activation. As soon as clayey soils represent porous objects, their compression under pressure leads to changes in the structure. At low pressure clays are compacted as a result of reorientation of particles and reduction of pore volume [1]. The degree of orientation of particles of clays of different mineral composition differs at growing pressure. Kaolinite particles obtain more perfect orientation at a small pressure as compared to montmorillonite clay. The degree of perfection of particle orientation under pressure depends on the particle size, shape, friction rate on the surface, and hydrophilic behaviour. Bigger and asymmetrical particles are more oriented (kaolinite), than isodiametric (symmetric) and small (montmorillonite) particles.

At a compacting pressure of up to 100 MPa there is an optimum amount of water and, respectively, a definite thickness of a hydrate film which correspond to building of a structure of the maximum strength. At the threshold pressure, squeezing-out of hydrate films and formation of point contacts start. Such threshold value for montmorillonite is 35 MPa and that for kaolinite is 25 MPa [31]. Compacting pressure increased up to 100 MPa first leads to dispergation of structure forming aggregates and then to

deformation of contact surfaces through some compaction of structure elements and squeezing-out of hydrate films.

Based on the foregoing we may say that issues concerning evaluation of sorption properties of clays, subjected to mechanical activation by high pressure, are not studied enough. So, the purpose of the work is to determine sorption capacity of clayey soils exposed to high pressure when they encounter inorganic ions, methylene blue dye, and petroleum products.

Objects of the research and research methods

The objects of the research included the following clays of various crystalline structures: Lobanovsky montmorillonite and Chelyabinsk kaolin clays. Based on results of X-ray structure analysis [30] the montmorillonite clay consists of montmorillonite (75 %), kaolinite (3.6 %), quartz (11.4 %), albite (6.7 %), and calc spar (3.3 %). The kaolin clay contains kaolinite (76.7 %), montmorillonite (15.6 %), and quartz (7.7 %).

A high-pressure device [30] was used to transfer pressure to clay samples. Its working surfaces are made of hard-alloy material. The PLG-20 press was used as a loading device. Clay samples of 0.75 cm² area were produced at the device in the pressure range of 0 to 700 MPa.

To determine sorption properties of clays the following products were used as sorbates: methylene blue dye, diesel fuel of L grade (diesel), engine oil MOTO 2T (EO), and gearbox oil TEP-15 (GO).

Results of the research and discussion

Change of particle size distribution in clays when clays are compressed. Particle size distribution of clays was determined by a laser diffraction analyzer ANALYSETTE 22 MicroTecplus [6, 32]. In the process of size analysis the following fractions were found: $F_{<0.1}$, $F_{0.1-0.2}$, $F_{0.2-0.5}$, $F_{0.5-1}$, F_{1-2} , F_{2-5} , F_{5-50} , F_{50-100} , and $F_{>100}$ (the index is a fraction particles size, μm). It should be noted that according to GOST 25100-2011 [33], $F_{<0.1}-F_2$ correspond to clay fraction, F_{2-50} correspond to pulverous fraction, F_{50-100} and $F_{>100}$ correspond to sand fraction.

For the original samples not subjected to compression the following values were obtained:

– kaolinite: clay fraction ($F_{<0.1}-F_2$) 52.36 %, pulverous fraction (F_{2-50}) 47.62 %, and sand fraction (F_{50-100} and $F_{>100}$) 0.02 %;

– montmorillonite: 29.94; 70.06, and 0 % respectively. Change in the particle size distribution after compression under pressure of 0 to 700 MPa is shown in Fig. 1.

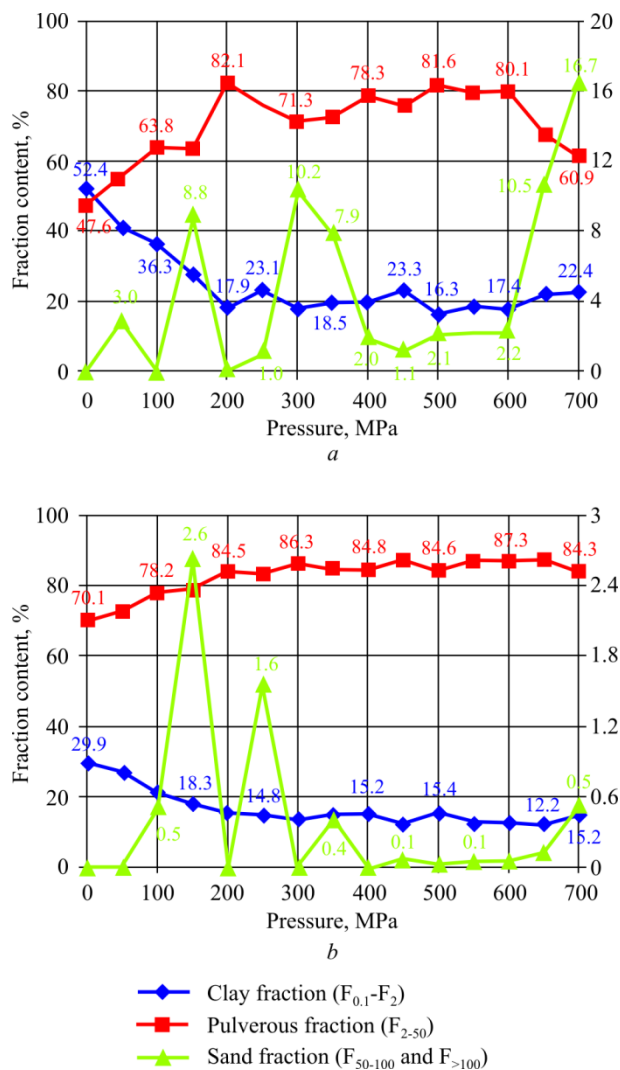


Fig. 1. Dynamics of changes in clay, pulverous, and sand fractions in the following tested clays: a – kaolinite; b – montmorillonite

The research conducted with clay samples after their compaction by pressure allowed us to find the following trends.

First, as clay compaction grows, the overall trend to the decrease of clay fractions and increase of pulverous fraction is observed. This is due to the formation of aggregates from the clay fraction of the soil. Assembling of fine colloids, resulting in

aggregation, after exposure to pressure, is probably due to change in the interaction forces between particles. Coagulative contacts were formed between particles in original samples of clays at a pressure of 0 MPa. When pressure increases up to 150-200 MPa, transient contacts are formed. Coagulative forces, as well as chemical nature forces, which appear due to weakening and breaking of the hydrate film and formation of point contact, participate in their formation. When pressure exceeds 200 MPa strong phase contacts of chemical and ionic-and-electrostatic nature are formed.

Second, in kaolin clay, changes in particle size distribution are more intense than in montmorillonite clay. This can be explained by the following: in kaolin clay the clay fraction content is higher than in argillite-like montmorillonite clay, so the specific surface in kaolin clay is bigger than that in montmorillonite clay. The bigger the specific surface is, the more contacts we have between particles. Hence, the process of aggregation of particles in kaolin clay is more intense than in montmorillonite clay.

Third, $P = 150-200$ MPa pressure threshold interval was found based on the intensity of clay fractional formation. This can be explained by the fact that, in case of increase of pressure from 0 to 150-200 MPa acting on clay samples, the clay samples' microstructure changes occur through change in types of contacts between particles: from coagulative to transient and phase. If the pressure exceeds 150-200 MPa, soil microstructure changes insignificantly, as soon as phase type of contacts is formed between particles.

Changes in clay particle size distribution lead to changes in the specific surface area of particles (S_s). It has been found that, if the pressure increases, the area of active surface of kaolin and montmorillonite clays decreases. In such case the biggest rate of the surface reduction is seen at a pressure under 150 MPa. If the pressure exceeds 150 MPa, the influence of the pressure on S is less significant.

Clay sorption capacity research. Clay sorption capacity research was conducted in respect of the following: inorganic ions, organic ions, and petroleum products.

Determining clay sorption capacity. Inorganic ions. Clay sorption capacity was determined based

on the fact that clays are H-cation exchangers, and so a hydrogen ion on the surface of clayey minerals may participate in exchange reaction with other cations. Adsorption of anions is weaker than adsorption of cations and it occurs on lateral fractures of clay particles. The area of fractures represents an insignificantly small area of the total surface area of particles in general [1]. That is why the sorption analysis was run only in respect of cations.

An important detail in the process of ion exchange of alkali metals is a significant influence of acidity of the environment (pH). On this basis, adsorption of potassium chloride ($C_{KCl} = 0.1$ mol/l) was determined by potentiometric titration method [34, 35]. It is known that the ion exchange process on clayey minerals is thermodynamically-reversible [34, 36]. That is why in the process of studying the ion exchange on the surface of clays the time of ion exchange balance achievement is important. Values of the balanced condition in case of different cation exchange in different types of clayey minerals are not the same [37]. In some cases the balance is reached after some days (usually 2-3). Taking into account that fact, the time, needed for reaching the balance in kaolinite and montmorillonite in the presence of potassium chloride, was found and it amounted to 24 h; the process of ion exchange was considered balanced when pH value did not change any more.

Based on titration experimental curves (Fig. 2) ion-exchange capacity was calculated (Q_{H^+/OH^-}) (mmol/g) using the following formula:

$$Q_{H^+/OH^-} = \frac{C(V - V_0)}{m},$$

where C is a titrant concentration (C_{HCl} or C_{NaOH}) 0.1 mol/l; V and V_0 are titrant volumes in the presence of clay and without clay, ml; m is a clay weight, g.

There are titration curves and ion-exchange capacity dependences on the solution pH in Fig. 2 and 3 for clays of different nature when they come in contact with dispersive medium.

Based on the obtained experimental results we can single out the following aspects characterizing exchange adsorption of clays depending on pH value. First, the type of ion exchange curves ($Q_{H^+/OH^-} = f(pH)$) is determined by properties of functional (ionogenic) groups of clay minerals and

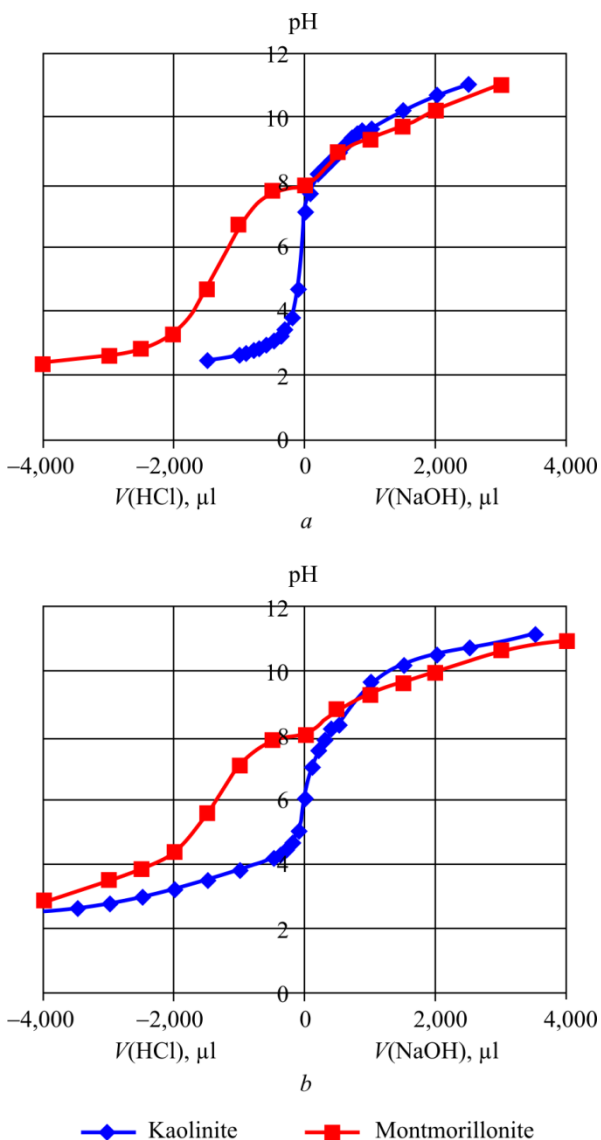


Fig. 2. Titration curves of kaolinite and montmorillonite dispersion at a pressure of 0 (a) and 700 MPa (b)

it is specific to bi-functional ion-exchangers with a strong and weak acid group. Second, sorption behaviour of clays exposed to pressure significantly depends on the nature of a mineral (structure, composition). Thus, ion exchange capacity in respect of cations is higher for montmorillonite than that for kaolinite. This is explained by the fact that kaolinite interlaminar bonding is provided by molecular and hydrogenic forces the energy of which exceeds the hydration energy of interlaminar space, whereas bonding in montmorillonite is provided by molecular forces and cations located in the interlaminar space and this bonding is not sufficient to resist hydration, so the interlaminar space expands. Moreover, ion-exchange capacity rate of kaolinite is higher than that of montmorillonite.

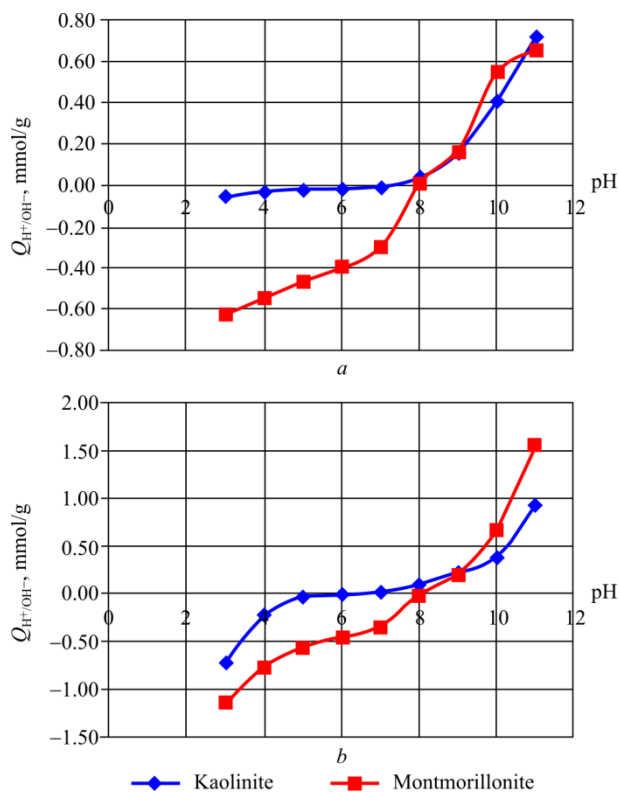


Fig. 3. Dependence of kaolinite and montmorillonite ion-exchange capacity on pH; applied pressure: 0 (a) and 700 MPa (b)

Third, when the content of clay fraction in samples decreases and the pressure increases, the degree of dispersion of clays decreases, therefore, the ion-exchange capacity should decrease as well, but the test showed the contrary: when pressure increased, the degree of ion-exchange capacity grew in montmorillonite, as well as in kaolinite. This is explained by growing defects in the crystalline structure of clays and by appearance of new functional groups (“active centers”). Exchange processes in kaolinite take place mainly on lateral fractures of particles and they occur due to the presence of uncompensated valence links. Therefore, growing ion-exchange capacity can be explained by growing of the surface area of fractures of kaolinite as well.

Nevertheless, the content of clay fraction goes down, and the growing area of lateral faces of kaolinite can be explained only by simultaneous processes of fragmentation and aggregation of particles. In such case the area of basal faces goes down, whereas the area of lateral fractures goes up.

Determination of sorption capacity of clays. Methylene blue dye. Methylene blue dye was adsorbed in accordance with a method as per

GOST 21283-93 [38]. Clay-adsorption value (mg/g) was determined based on the following formula:

$$A = \frac{C \cdot V}{m},$$

where C is a MB dye solution concentration, mg/cm³; V is a MB dye solution volume used for titration, cm³; m is a weight of a tested clay sample, g.

Change of montmorillonite and kaolinite sorption capacity in respect of MB dye depending on the pressure applied to samples is shown in Fig. 4.

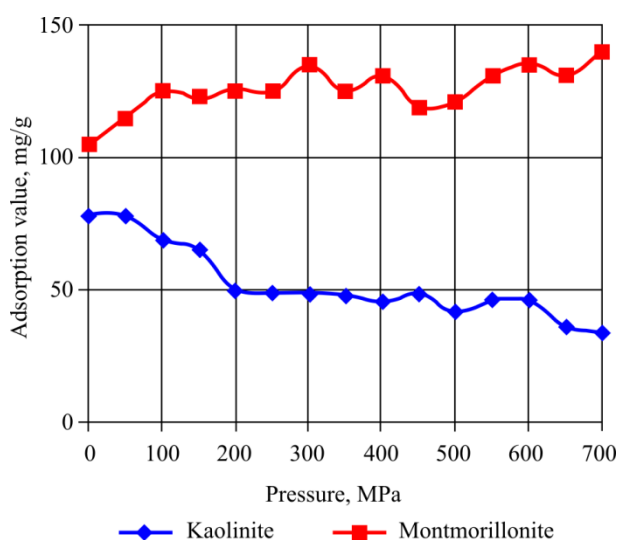


Fig. 4. Kaolinite and montmorillonite adsorption value change dynamics for methylene blue dye depending on the pressure applied

Adsorption value of kaolinite is significantly lower than that of montmorillonite, which is due to the sorption capacity of the latter in the interlaminar space [39]. At a pressure of 0-200 MPa kaolinite demonstrates general drop of adsorption value from 80 to 50 mg/g; after 200 MPa this parameter does not change significantly. The content of clay fraction is directly related to kaolinite adsorption value at applied pressures.

Kaolinite adsorption value manifested in respect of MB dye decreases if pressure increases; at the same time its ion-exchange capacity grows. This is explained by the fact that, when pressure is applied, the charge value increases on the surface of kaolinite particles and this value is sufficient for the growth of sorption of inorganic ions, but insufficient to keep MB dye molecules on the surface of clay particles.

Original montmorillonite has higher sorption capacity which is due to expansion of the interlaminar space up to the dimension of intruding molecules [40, 41]. If pressure increases, the adsorption value of montmorillonite grows from 105 to 140 mg/g and it is inversely related to the content of clay fraction. Based on that we come to a conclusion that when the samples of clay are compacted under pressure, the area of defects on the surface of minerals increases and, consequently, new “active centers” appear on the surface of clay particles which are ready to adsorb MB dye.

Adsorption of petroleum products by clays. Samples of clays preliminary saturated with diesel fuel, engine oil, and gearbox oil for three days, were dried in an infrared thermogravimetric moisture meter MA35 at a temperature of 160 °C. First, in the drying chamber the samples were weighed, and then the loss of weight was determined automatically by means of infrared rays, and, afterwards, the result was converted into moisture (petroleum product) content units with regard to the initial weight of each sample. The adsorption value A , mg/g, was calculated based on the following formula:

$$A = \frac{(m_1 - m_2)1,000}{m_2},$$

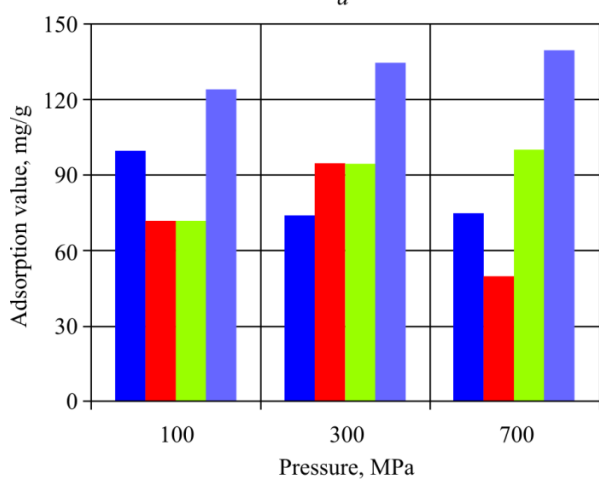
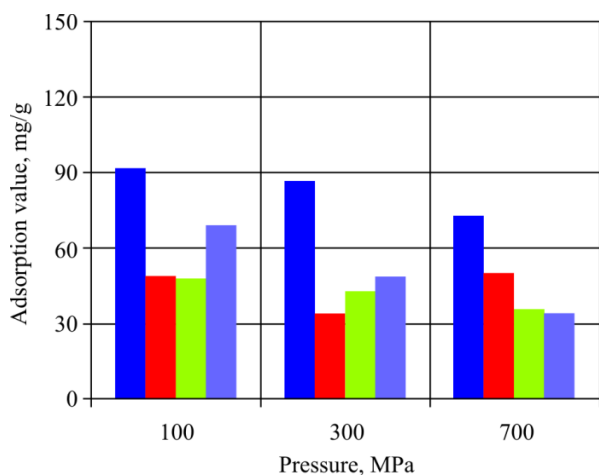
where m_1 is a weight of a clay sample saturated with a petroleum product before the beginning of drying, g; m_2 is a weight of a clay sample after the test in the moisture meter, g.

Change in montmorillonite and kaolinite sorption capacity manifested in respect of diesel fuel, engine oil, and gearbox oil depending on pressure is shown in Fig. 5. As an example the charts show the results obtained at the following pressures: 100, 300, and 700 MPa.

Based on the adsorption value change dynamics we see that kaolinite and montmorillonite demonstrate the maximum sorption capacity values in respect of diesel fuels in original samples (not exposed to pressure). Then adsorption drops sharply to 92-99 mg/g at a pressure of 100 MPa, and after that pressure there are no significant changes in adsorption.

During sorption of engine oil and gearbox oil by kaolinite, the biggest fluctuations of adsorption value are seen in the range before 200 MPa; at

higher pressures the adsorption value changes within 40–60 mg/g.



a

b

■ Diesel fuel ■ Gearbox oil
 ■ Engine oil ■ Methylene blue dye

Fig. 5. Kaolinite (a) and montmorillonite (b) adsorption value change dynamics shown for petroleum products and MB dye at the following pressures: 100, 300, and 700 MPa

During sorption of engine oil by montmorillonite until a pressure of 400 MPa the adsorption value increases up to 100 mg/g is observed; at higher

pressures no trends are observed. During adsorption of gearbox oil by montmorillonite a general trend is seen manifesting itself in the growth of values from 70 to 120 mg/g.

It should be noted that adsorption capacity has been studied with the use of a moisture meter the operating temperature of which does not exceed 160 °C; at such temperature only fractions that boil at a temperature not exceeding 160 °C are evaporated from clay. Therefore, the chart does not show a complete picture due to the fact that samples still contain high-boiling components of petroleum products.

When we compared the test data for petroleum products and methylene blue dye (please see Fig. 5), we found the adsorption processes seen in the clay minerals to be similar.

Conclusion

1. The experiments show that, if the pressure applied to kaolinite and montmorillonite grows up to 700 MPa, there is a general trend towards decrease of the clay fraction content and increase of the pulverous fraction content.

2. Adsorption behaviour of clays exposed to pressure significantly depends on the mineral composition, particle size distribution, and crystalline structure defects. Kaolinite and montmorillonite ion-exchange capacity depends on the environmental acidity.

3. Kaolinite adsorption value for methylene blue dye goes down until a pressure of 200 MPa, which is explained by the clay fraction content, and it does not significantly change at a pressure of 200-700 MPa. Montmorillonite adsorption value shows a general trend to growth.

4. Adsorption of petroleum products by kaolinite and montmorillonite is at the threshold level at a pressure of 100 and 400 MPa.

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