PHYSICOCHEMICAL MECHANICS OF MICROSTRUCTURAL TRANSFORMATIONS OF SWELLING CLAY MINERALS

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An original model of microstructural transformations during swelling of clays is considered, and a thermodynamic and physical-mechanical description of the specific features of clays in the process of swelling in vapors and aqueous solutions is given. The model proposed to explain these properties is based on the idea of mutual movement of clay particles in clay rock aggregates during swelling with the formation of new pores between clay particles forming crystallites and aggregates. The model is based on a mechanism of utilizing excess surface energy of clay particles with account for the influence of certain parameters of the medium, for example, solution concentration, through a change in the mutual orientation of clay particles, mainly due to rotations or shifts relative to each other with the formation of a free surface available for further wetting. In a thermodynamic description, such a process will manifest itself in a change in the energy of surface interaction on the wetted areas of particles when moving during mutual shifts and rotations. Changing in this case is also one of the most important parameters of the clay rock — microporosity. In this work, this phenomenon was studied experimentally using the methods of static moisture capacity and Mössbauer (gamma-resonance) spectroscopy. The proposed model makes it possible to explain the features of the clay swelling process and compare the observed experimental data with the theoretical description of the clay swelling process.

Keywords: clay rocks, crystallites and aggregates, microporosity, clay swelling, low permeability.

Introduction. Clays have long been the object of intensive study for various branches of geology, sciences and industries related to the extraction of hydrocarbons, and various branches of technology due to the functions that clays perform and, above all, the presence of a number of specific properties of clays (low permeability, ability to swell, plasticity when wet, and a number of others). Thus, low-permeability clay rocks usually play the role of water confining strata (fluid seals for inorganic liquids) for water-bearing or oil-bearing beds. They act as a natural buffer against surface contamination of groundwater [1] and are raw materials for construction and other industries (ceramics, building products, drilling fluids).

The term "clays" most often refers to fine-grained sedimentary rocks usually silty when dry and acquiring plasticity when moistened. Clays owe their specific properties to the presence of clay minerals in their composition. Most often, clay minerals are the product of chemical weathering of silicates, mainly feldspars. They can also form in places of hydrothermal activity [2]. Chemical weathering occurs mainly through carbon dioxide hydrolysis with the participation of weakly concentrated natural solutions of carbon dioxide mobilized by rainwater from the atmospheric air, as well as released by plant roots, soils or soil biota [3]. Carbonic acid breaks the bonds between aluminum and oxygen in the feldspar crystal lattice, releasing other metal ions and orthosilicic acid (silica gel). The specific type of clay minerals formed depends on the conditions of formation, mainly on the composition of the original rock and climate. Acid weathering of feldspar-rich rock such as granite in warm, humid climate results in the formation of kaolinite. Weathering of the same rock under alkaline conditions leads to the formation of illite. Weathering of magmatic rocks under alkaline conditions results in the formation of smectite; subsequent intensive weathering of newly formed clay minerals leads to the formation of other clay minerals (for example, this is how gibbsite is formed). Depending on the formation, two types of clay deposits are distinguished — primary and secondary. The primary clays are formed as residual deposits in the soil and remain at the site of formation. The secondary clays are the clays that have been transported from their original site by water erosion and subsequently formed

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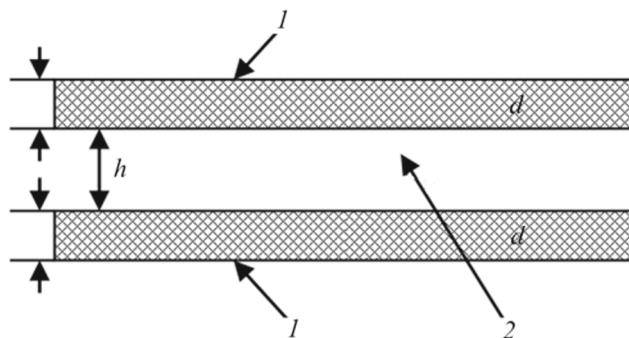
Fig. 1. Montmorillonite particles (elementary silicate layers) with a film of interlayer water between them: 1) clay particle; 2) interlayer solution; h, thickness of interlayer water with adsorbed cations.

new sedimentary deposits. The secondary clay deposits are usually localized in sedimentary basins such as lakes and seas [4, 5]. In what follows, we will be interested in swelling clay minerals and mainly montmorillonite [2, 6].

Montmorillonite is a hydrous aluminum–magnesium silicate of sodium, potassium, calcium, and magnesium. The mineral species montmorillonite is included, as already noted, in the group of smectites, i.e., minerals with intracrystalline swelling. These minerals are diagnosed by changes in the parameters of the crystal lattice determined by x-ray analysis on moistening clay preparations [7]. Montmorillonite is the most highly dispersed mineral in the smectite group and among clay minerals. The internal surface of particles of 1 g of montmorillonite reaches a value of 750 m^2. In contact with water and some organic liquids, it swells osmotically. In aqueous pastes and suspensions, chemical reactions of cation exchange occur. The specific properties of the montmorillonite are due to the specific features of its crystal chemistry and the structure of the particles formed by elementary silicate layers of montmorillonite — crystallites and microaggregates. The crystal chemical structure of montmorillonite was studied using x-ray analysis, electrography, electron microscopy, and microdiffraction, as well as resonance spectroscopy methods — proton magnetic resonance (PMR) or electron paramagnetic resonance (EPR) and nuclear gamma resonance (NGR) [8, 9]. In accordance with known concepts, the elementary structural unit of the mineral montmorillonite is a "three-storey" dioctahedral silicate layer built by joining three networks: one internal octahedral and two external tetrahedral. A negative electric charge arises in the silicate layer primarily due to heterovalent isomorphism in octahedra (replacement of trivalent aluminum with divalent magnesium). Isomorphism in tetrahedra is also possible (beideliticity, replacement of tetravalent silicon by trivalent aluminum). An excess negative charge can additionally arise due to deprotonation of hydroxyl groups of the basal surfaces of elementary silicate layers. The negative charge of silicate layers compensates for the so-called extralayer cations of sodium, potassium, calcium, and magnesium (Fig. 1). The total content of extralayer cations that have the ability to enter into exchange reactions in aqueous clay pastes and suspensions is characterized by the exchange capacity (EC) of the clay. The value of the exchange capacity calculated for air-dry clay for most of the studied montmorillonite clays is 1.0 ± 0.1 mg-eq/g. The NGR and EPR spectroscopy methods provide important information about the intracrystalline position and state of iron ions, which act as redistributors of excess negative charges in the octahedral network of the silicate layer, which is necessary to identify the structural-crystal chemical varieties of montmorillonite. Crystallization of silicate layers, the formation of crystallites and microaggregates of the mineral occur in contact with water vapor and aqueous solutions. In this case, there are three types (three forms) of connections between water molecules and the active centers of montmorillonite.

The first type is a donor–acceptor bond between one proton of a water molecule and oxygen of the octahedral network, which carries an excess negative charge. This is the strongest bond, serving as a bridge between the silicate layer and the water molecules of the hydration layers on the basal surfaces of montmorillonite particles.

The second type is coordination bonds between water molecules and extralayer cations leading to screening and weakening the bonds of cations with the surface of the silicate layer.

The third type is intermolecular hydrogen bonds, which ensure the formation of a single network of water molecules in the plane of the basal surfaces and between layers along the crystal axis C, ultimately leading to the formation of an aggregate structure of montmorillonite (Fig. 2).
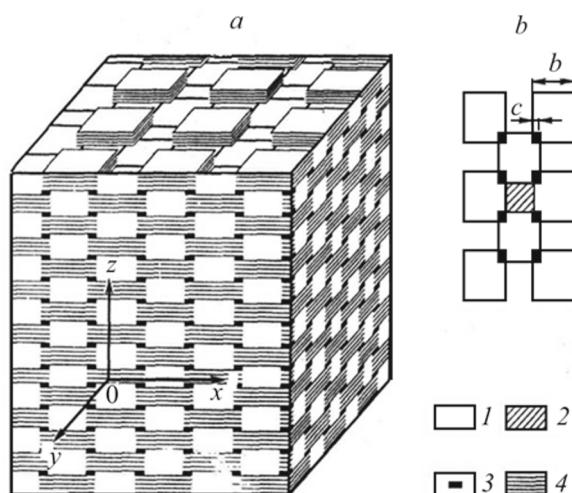
Fig. 2. Aggregate structure of clay rock: 1) interaggregate (transport) pores; 2) non-transport pores; 3) intra-aggregate pores; 4) units [10]. Orientation of crystal axes A, B, C coincides with the orientation of Cartesian axes x, y, z (given in the figure), respectively; a, microaggregate structure of montmorillonite as a whole; b, basal surfaces of clay particles (unhatched squares with side b), filled squares with side c correspond to ultramicroaggregate pores (areas of overlap of microaggregates during the formation of microaggregate structure).

It has been established that at a relative air vapor pressure of about 92%, the formation of monomolecular networks (layers) of water on the basal surfaces of all silicate layers is completed [6]. The amount of water at this air humidity for the monomineral fraction of montmorillonite, regardless of the nature of the extralayer cations, is about 32% based on dry clay (or about 13 water molecules per formal unit of surface area of the unit cell of montmorillonite). Judging by the mechanism of rotation of tetrahedra, it was revealed that the crystalline structure of silicate layers passes into a stressed state with a decrease in air humidity. This allows one to explain the nonlinear increase in the volume of clay upon absorption of water.

The specific properties of the crystal chemistry of montmorillonite predetermine very small sizes of clay particles (approximately 50 by 200 nm). Silicate layers of thickness 0.95 nm along the C axis are separated from each other by hydration-ion layers, and together they form larger layered three-dimensional particles — crystallites and microaggregates. Using the Mössbauer (NGR) spectroscopy method, the mobility of microparticles in the form of oscillatory movements and their relative proportion depending on the degree of moistening, freezing, and pressing pressure were revealed [8, 9]. The Mössbauer effect of recoilless absorption of gamma rays by iron-57 nuclei manifests itself only in solids, in systems of interconnected particles with a critical mass of $3 \cdot 10^{-17}$ g. The mass of a single silicate layer is $3 \cdot 10^{-18}$ g. Consequently, if there are microparticles in clay with a mass greater and less than the critical one, only large particles make a contribution to the value of the Mössbauer effect. With an increase in air humidity, a decrease in the intensity of the gamma signal begins, and after mechanical pressing of clay powder at a pressing pressure of 280 kg/cm^2 the signal intensity value was restored and maintained even at higher air and clay moisture contents than in powders of the same moisture content, but without pressing. Saturation of clay powders with ethylene glycol gives only the maximum Mössbauer effect. In our opinion, the mechanism that explains the specific manifestation of the Mössbauer effect in montmorillonite clay powders of different moisture contents lies in the influence of thermal fluctuations of the charge density of the pore solution of ultramicropores, formed due to the dissociation of part of the extralayer cations during the hydration of clay in water vapor, on the vibrations of iron-57 nuclei in the composition of clay microparticles that carry an excess negative charge and thus represent macroanions. At moisture contents exceeding the intracrystalline swelling region, multilayer hydrate shells are formed on the surface of clay microparticles. Plastic clay masses and pastes are formed. It is very important that in the swollen state, interlayer cations can enter into exchange reactions [10].

Experimental Studies. Below we present the results of the experiments of [9], in which some properties of montmorillonite clays were studied. The sample was polymineral clay containing 32% MC (a mixture of montmorillonite

TABLE 1. Results of Measurement of Water Content (in grams per 100 g of dry sample) in Clay Samples for Different Moisture Content Values (Mindyushsk deposit of the Republic of Tatarstan, Russia)

Samples	Moisture content		
	43%	92%	93%
Sample 1	5.21	19.90	36.44
Sample 2	6.05	18.30	26.85
Sample 3	6.32	18.37	36.40
Original	6.47	9.69	13.16

(MM) and mixed-layer montmorillonite-hydromica (MH) formation with a predominance of MM). An analysis performed on the initial air-dry clay powder using the static moisture capacity method at a certain air humidity showed that in water vapor the hydration of MC crystallites occurs predominately on the basal surfaces in the form of intracrystalline swelling (Table 1, coefficient $K = 1.49$, $K = w(0.92\%)/w(0.43\%)$, w is the air humidity. After treating this clay with a solution of a sodium chloride and then washing it with water, the clay swelling in a special cell with rigid walls, i.e., under conditions of limited volume. After filling the entire volume of the cell, the clay was removed, dried in air, ground to powder, and the samples were placed in desiccators, where a given water vapor pressure was maintained. After reaching equilibrium, it turned out that the hydration of the clay powder of this sample in comparison with the original clay at the same water vapor pressure increased by 2.8–2.9 times. In this case, the bulk of water was absorbed in microcapillaries (coefficient $K = 3.82$) and only one third of the water was adsorbed to form a hydration layer on the basal surfaces of the crystallites. Thus, salt treatment with a sodium chloride solution followed by washing of free salts led to a sharp change in the structure of clay particles. This structure turned out to be fixed in dried clay even after it was ground to powder, that is, in grains less than 0.1 mm in size.

The second experiment was carried out in a cell with a "free" volume under conditions of constant pressure applied to the clay, and no change in the total volume was detected. The formation of "open fan"-type structures occurred to a lesser extent, since, in this case, the capillary absorption of water in the powders noticeably decreased (coefficient $K = 3.02$). It is obvious that in the first experiment, osmotic intercrystalline water "captured" the entire free surface of the macropores, while in the second experiment this was somewhat hindered by external pressure.

The third experiment was also carried out in a cuvette with a variable volume, but the washing sequence was changed — initially water was introduced into the clay and then a sodium chloride solution, as in the first experiment. No change in the total volume was detected. In this case, microporosity in the dried clay powder, as expected, manifested itself to an even lesser extent. Capillary-absorbed water accounted for about 70% of the water absorbed in the form of hydrate layers.

A special experiment was also carried out using the Mössbauer (NGR) spectroscopy method (Fig. 3), which also revealed structural and phase differences in the descriptions of the three samples and in comparison with the original clay. In the sample of the original clay, during its hydration in water vapor, the proportion of particles in the form of a condensation (solid-phase) structure decreased quickly. Already when the clay contained 13% water, the share of particles in the solid-phase structure decreased to 23% (the share of the coagulation one increased accordingly to 77%). In the sample of the first experiment, 23% of solid-phase particles were recorded at a moisture content of clay powder of 29%, and at a moisture content of 36% there were practically no solid-phase particles, the clay completely passed into the phase of a coagulation structure, which, obviously, was facilitated by microporosity and capillary condensation of water. In the sample of the second experiment, intermediate relationships were observed between the original clay and the sample of the first experiment, but closer to the latter. The complete transformation of the structure into coagulation was completed at a clay moisture content of 27%. In the clay of the third experiment, even after adding water, a small proportion (7%) of solid particles remained. Thus, the effect of salt solutions on clays causes very significant and diverse changes at all structural levels of clay particles and in the rock as a whole. The mechanism of this effect was outlined in [9] and is as follows: during the hydration of the basal surfaces of the silicate layers of montmorillonite, compensatory cations are separated from the basal surface and together form a positive electric charge of the ion-hydrate layer. Since compensator have the opportunity
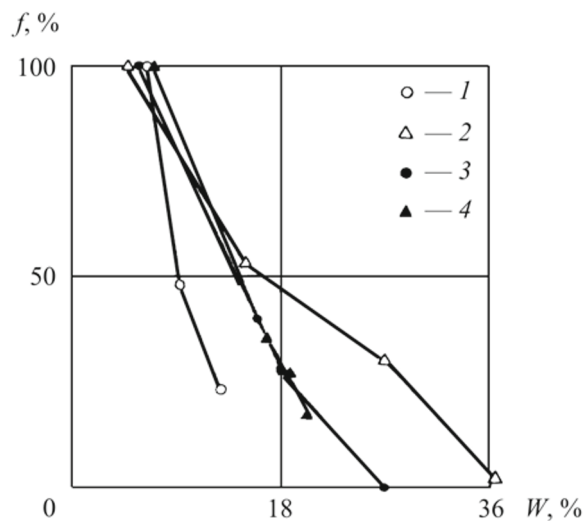
Fig. 3. Decay of the relative intensity of the Mössbauer signal in clay samples at different moisture contents: 1) initial sample; 2) first sample; 3) second sample; 4) third sample.

to participate in the thermal fluctuations cations during the formation of the ion-hydrate layer, we can say that the center of the electric charge of the ion-hydrate layer also experiences thermal fluctuations, forcing the clay microparticles themselves, which are macroanions, to "respond" to thermal fluctuations of the charge of the ion-hydrate layer. Iron ions in the structure of the clay particles also participate in these induced fluctuations of the clay particles, thereby ensuring a decrease in the gamma resonance response as the basal surfaces of the clay particles are hydrated. The question arises: what process ensures an increase in the proportion of solid-phase structure in samples of clay treated with a saline solution. With account for the data in Table 1, the answer is obvious — the silicate layers in the crystallites move apart according to a "fan" mechanism with the formation of micropores and weakening of the influence of compensatory cations trapped in the pore solution in these micropores, on the vibrations of iron ions in the layer itself. In addition, the amount of moisture absorbed by the clay during the experiments was recalculated with account for the complete exchange of calcium cations for sodium. It was shown that the appearance of additional moisture can only be explained by the presence of capillary condensation in newly formed micropores, since it is difficult to attribute the increase in the amount of water at the same moisture content to the hydration of additional sodium ions [11], especially taking into account the NGR data. It should also be emphasized that there are other ideas about the spatial distribution of clay particles during the formation of clay rocks. Using the concept of the interaction of clay particles according to the "basis–cleavage" principle, it is possible to obtain structures that, when being swelled, behave like a kind of "accordion:" the change in the volume of the rock during swelling is due to a change in the contact angle in the "basis–cleavage" node [12, 13]. Another pattern of packing of clay particles during the formation of clay rocks is also possible — according to the "basis–basis" principle, when the particles are arranged and form an aggregate structure similar to that shown in Fig. 2. Note that with such structures, swelling in both the first and second cases should occur with a change in volume, and after the end of swelling the structure should return to its original state. To check this, we carried out an additional experiment on the swelling of montmorillonite clays. Two samples of the same clay were taken. The first sample was at a fixed humidity, the second was subjected to swelling by changing the humidity in the desiccator. The second sample was then brought to the same moisture content as the first. At the end of the experiment, the specific surface areas of two initially identical samples were compared.

For this purpose, we used the adsorption-luminescence method [6, 8], which consists of the adsorption of large organic cations on the basal surfaces of crystallites and makes it possible to determine the proportion of the surface of particles with multilayer hydration shells. In this case, no changes in the total volume were recorded. The results are given in Table 2. Thus, when clay rocks swell, a redistribution of pore space occurs due to the formation of new pores that appear when clay particles move apart, forming clay microaggregates and aggregates. In Fig. 2 this looks like a destruction of the original order in the arrangement of particles accompanied by the transition of each neat pack of particles due to the rotation of each particle in its own direction and filling the transport pores with new micropores. However, the experiment also showed more interesting aspects of swelling. For example, samples from two deposits [Oglanli deposit (Turkmenistan)

319

TABLE 2. Change in Exchange Capacity and Clay Numbers of Clay Samples before (initial) and after (final) Their Hydration

Field	State	EC	CN
Oglanly	initial	67	291
Oglanly	final	62	242
Sarigyukh	initial	77	462
Sarigyukh	final	72	410
Berezovskoe	initial	47	43
Berezovskoe	final	52	78

and Sarigyukh deposit (Armenia)] had a high content of the montmorillonite component, but experiments showed that their free surface area decreased after the experiment. This can be explained by the fact that the process of particle rotation due to the predominantly montmorillonite composition of the clay component was maximally intensified on destruction of the original crystallites and the formation of new micropores in those areas that, before swelling, were the outer surfaces of the crystallites and were capable of adsorbing large organic cations (Table 2). This is evidenced by changes in such parameters as exchange capacity (EC) and clay number (CN). Let us consider some thermodynamic and rheological features of the description of such a process.

Physicochemical Mechanics of Swelling Clays. Let us construct, in accordance with the foregoing, a theory that would describe the process we observe. We will build this theory within the framework of the classical thermodynamics of multiphase multicomponent systems, i.e., within the framework of the osmotic equilibrium approximation. Next, we will generalize the obtained relations to the general case of physicochemical mechanics of heterogeneous systems. We will check the reliability of the theory by its correspondence, first of all, with the known data on the intracrystalline swelling of montmorillonite [14] and data on the dependence of the charge of the Stern layer on the concentration of the pore solution [15]. Based on the balance equations of water and solution components (cations and anions of the solute), as well as the first Lippmann equation [15]

$$d\gamma/d\varphi = q \tag{1}$$

it is possible to obtain the needed relation for the interlayer distances between clay particles depending on the concentration of the solution and the basic physical and chemical parameters of the clay. The condition for the equality of equilibrium is the zero change in the Gibbs free energy of the entire system at constant pressure and temperature:

$$\sum_{i=0,1,2} (\mu_i \delta n_i + \bar{\mu}_i \delta \bar{n}_i) + \gamma \delta A + \mu_1^s \delta n_1^s = 0 . \tag{2}$$

The corollary of (2) is the equality of the chemical potentials of the corresponding components:

$$\bar{\mu}_1 = \mu_1 , \quad \bar{\mu}_2 = \mu_2 , \tag{3}$$

where for the chemical potentials of cations and anions we have

$$\bar{\mu}_1 = \mu_1^0 + RT \ln \bar{C}_1 + ez_1\bar{\varphi} , \quad \bar{\mu}_2 = \mu_2^0 + RT \ln \bar{C}_2 + ez_2\bar{\varphi} ,$$
$$\mu_1 = \mu_1^0 + RT \ln C_1 + ez_1\varphi , \quad \mu_2 = \mu_2^0 + RT \ln C_2 + ez_2\varphi . \tag{4}$$

We assume that in interaggregate pores $\varphi = 0$, and in intraaggregate pores $\varphi \neq 0$, since it is created by exchangeable cations of clay particles. We also assume for simplicity that $z_1 = 1$, $z_2 = -1$ (corresponds to a binary 1–1 electrolyte). Adding Eqs. (4), we obtain, in accordance with the standard procedure, the so-called Donnan equilibrium equation [15]:

$$\overline{C}_1\overline{C}_2 \ = \ C_1 C_2 \ = \ C_0^2 \ . \tag{5}$$

From the condition of general electrical neutrality in the "basal surface–pore solution" system, we have

$$\overline{C}_1 - \overline{C}_2 \ = \ 2q/H \ . \tag{6}$$

Then, from (5) and (6) we obtain

$$\overline{C}_1 \ = \ (q/H) + \sqrt{(q^2/H^2) + C_0^2} \ , \quad \overline{C}_2 \ = \ -(q/H) + \sqrt{(q^2/H^2) + C_0^2} \ . \tag{7}$$

From (2)–(4) we write the relation

$$2\gamma/H \ = \ RT(\overline{C}_1 + \overline{C}_2 - 2C_0) \ . \tag{8}$$

Taking (7) into account, we obtain

$$2\gamma/H \ = \ 2RT(\sqrt{q^2/H^2 + C_0^2} - C_0) \ . \tag{9}$$

This approach resembles the approach in [16]. Equation (9) can be resolved for H:

$$H \ = \ A/C_0 \ , \tag{10}$$

$$A \ = \ [q^2 - \gamma^2/(R^2 T^2)]/[2\gamma/(RT)] \ . \tag{11}$$

There are two possible situations here. When the concentration of the interaggregate solution is low, then, as is known from the colloid chemistry [15], the charge of the Stern layer becomes proportional to the square root of the solution concentration, and from Eqs. (1), (10), and (11) we obtain

$$q \cong \sqrt{C_0} \ \Rightarrow \ H \cong 1/\sqrt{C_0} \ . \tag{12}$$

When the concentration of the interaggregate solution is high, the charge of the Stern layer becomes proportional to the first power of the solution concentration, and from Eqs. (1), (10), and (11) we obtain

$$q \cong C_0 \ \Rightarrow \ H \cong \text{const} \ . \tag{13}$$

This behavior corresponds to well-known data on the intracrystalline swelling of montmorillonite [14].

If clay microaggregates are subjected to a mechanical load σ, Eq. (9) can be easily generalized to this case:

$$(\sigma - p) + 2\gamma/H \ = \ 2RT(\sqrt{q^2/H^2 + C_0^2} - C_0) \ . \tag{14}$$

Taking into account the definition of effective stresses σ^f [17], we rewrite Eq. (14) in the form

$$\sigma^f/(1 - m) + 2\gamma/H \ = \ 2RT(\sqrt{q^2/H^2 + C_0^2} - C_0) \ . \tag{15}$$

Equation (15) can be rewritten in a more familiar form. By replacing the osmotic pressure $2RT(\sqrt{q^2/H^2 + C_0^2} - C_0)$ by its generalization — the disjoining pressure $\Pi(H)$ and the term $2\gamma/H$ by its analog — the capillary pressure p_c, we will write

$$\sigma^f/(1 - m) + p_c \ = \ \Pi(H) \ . \tag{16}$$

Note that Eq. (16) was used in this form by the authors of [18] and gave good agreement with the results of the corresponding experiments. The quantity $\sigma^f/(1 - m)$ will be called the swelling function. Let us find the extremum of the swelling function.
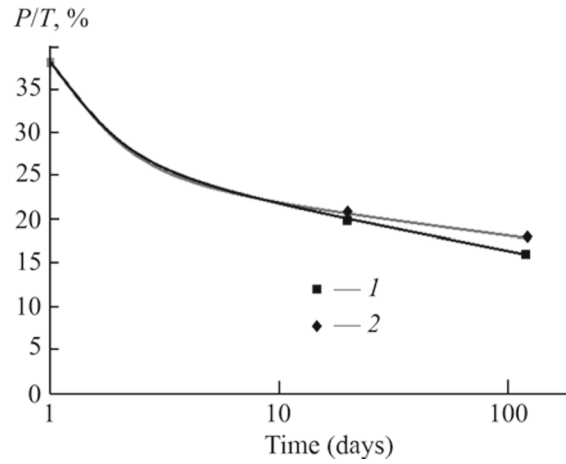
Fig. 4. Dependence of microstructural porosity of clays on time: 1) experimental curve;
2) theoretical curve [18].

To do this, we differentiate the left and right sides of (15) with respect to q and equate the derivative of the swelling function to zero. Then we will have

$$\varphi/H \;=\; RTq/(H^2\sqrt{q^2/H^2 + C_0^2})\,. \tag{17}$$

It can be seen that by the nature of the change in the sign of this function at the extremum point, the swelling pressure corresponds to a minimum. Then, for the charge at this point we finally get

$$q \;=\; \varphi C_0 H \Big/\!\left(RT\sqrt{1 - \varphi^2/(RT)^2}\right). \tag{18}$$

It is interesting that if for the dependence of the interlayer distance on the concentration of the solution in the macropores C_0 for low concentrations we accept the Norrish dependence [14] $H \cong 1/\sqrt{C_0}$ (the proportionality of the interlayer distance to the inverse square root of the concentration), then for the charge of the Stern layer we obtain the relation $q \cong \sqrt{C_0}$, which fully corresponds to the conclusions on the behavior of the charge of the Stern layer of colloidal particles in electrolyte solution [15]. For the case $H \cong$ const we have $q \cong C_0$, which also corresponds to [15].

Let us now examine the question of the rate of swelling. To do this, let us turn again to Eq. (14). However, in this case, the equality in Eq. (14) cannot be required, since it meets the equilibrium conditions. Let us introduce a new variable π and call it the swelling pressure in accordance with the equation

$$\pi \;=\; 2RT(\sqrt{q^2/H^2 + C_0^2} - C_0) - (\sigma - p) - 2\gamma/H\,. \tag{19}$$

Then the equation for the swelling rate in the case of maintaining the total volume in accordance with L. Onsager′s principle on the proportionality of thermodynamic forces and flows [19] can be written in the form

$$-\frac{dm}{dt} \;=\; \alpha\pi\,, \qquad \alpha \;=\; \text{const}\,. \tag{20}$$

Work [20] provides a description of an experiment that allows one to use Eq. (20) under the conditions $C_0 = 0$, $\sigma = p = 0$ in which the experiment was carried out. Then Eq. (20) can be written in the form

$$-\frac{dm}{dt} \;=\; \frac{2\alpha RTq(1 - \varphi)}{H}\,. \tag{21}$$

322

By introducing the conventional volumetric exchange capacity Q instead of surface exchange capacity q (the number of exchange centers per unit surface of clay particles), we obtain the following version of Eq. (21):

$$\partial m / \partial t = -2\alpha RTQ(1 - \varphi) / [V_0(1 - m) - V_s] ; \quad V_0, V_s = \text{const} . \tag{22}$$

The last equation is easy to integrate. Finally we have

$$(1 - m - V_s/V_0)^2 = (1 - m_0 - V_s/V_0)^2 + 4\alpha RTQ(1 - \varphi)t/V_0 . \tag{23}$$

Using the data from the description of the experiment, it is possible to determine the parameters of Eq. (23), plot the dependence of the change in porosity on time, and compare it with the theoretical dependence obtained by the authors of [18]. The results are shown in Fig. 4.

Research Results. *Experimental studies of swelling of montmorillonite.* Thanks to the experiments on swelling of montmorillonite, it was possible to unambiguously establish that the swelling process is accompanied by the moving apart of elementary silicate layers that form the microaggregate structure of montmorillonite relative to each other. This leads to the formation of additional micropores, in which condensation of additional moisture occurs observed experimentally. Physically, this reaction of montmorillonite clay to an increase in moisture content is understandable — the formation of additional micropores leads to the appearance of additional capillary pressure, counteracting the swelling pressure, which ultimately leads to minimization of the swelling pressure in montmorillonite.

Thermodynamics and physicochemical mechanics of swelling of montmorillonite. According to the data obtained during experimental studies, a thermodynamic model of the swelling process was developed taking into account the effect of the moving apart of silicate layers of montmorillonite clay. It was shown that the consistent construction of a thermodynamic model not only takes into account the physical effects of the separation of silicate layers and the formation of micropores, manifested in the appearance of additional capillary pressure, but also makes it possible to explain the classical results of [14] on the dependence of the interlayer distance on the solution concentration.

CONCLUSIONS

This work presents an experimental and theoretical study of the process of swelling of montmorillonite clays in contact with water vapor and aqueous solutions. The following results were obtained:

1) the fact of the moving apart of the silicate layers of montmorillonite that form the microaggregate structure of clay with the formation of additional micropores has been established;

2) this effect is observed at all times, thus it does not depend on the structure that is formed by microaggregates themselves;

3) a thermodynamic model of the process of swelling of montmorillonite clay was developed that explains the characteristic features of the physicochemical mechanics of montmorillonite and describes the fact of the separation of silicate layers by the appearance of additional capillary pressure in the micropores formed during the separation of the silicate layers of montmorillonite.

NOTATION

A, surface area of clay particles; C_i, concentration of the corresponding component; C_0, concentration of the interaggregate solution; e, electron charge, the line marks the corresponding values of the osmotic cell (microaggregate) of clay; H, interlayer distance (distance between two adjacent clay particles); p, pressure in the solution; p_c, capillary pressure; Q, volumetric exchange capacity of clay; q, surface charge of clay particles expressed in concentration units (a unit of charge corresponds to one particle); R, universal gas constant; V_0, volume of a representative element of the porous medium; V_s, volume of the solid phase itself in the composition of a representative volume element; z_1 and z_2, valences (charges) of cations and anions, respectively; α, swelling rate constant; γ, surface tension of clay microaggregates

($\gamma = \gamma_{ml} - \gamma_{sl}$, where γ_{ml} is the specific surface energy (surface tension) at the boundary between the surface of a clay particle and a multilayer film of water, γ_{sl}, specific surface energy (surface tension) at the boundary between the surface of a clay particle and a monolayer film of water); δ, means variation of the corresponding value; μ_i, chemical potential of the corresponding component, symbol; μ_i^0 means standard chemical potential of cations and anions; $\Pi(H)$, disjoining pressure; π, swelling pressure; σ, stress in the solid phase; σ^f, effective stress; φ, electric potential. Indices: 0 corresponds to water; 1 corresponds to cations of the pore solution; 2 corresponds to anions of the pore solution; s means a component that is adsorbed on the basal surfaces of clay particles (silicate layers).

REFERENCES

1. V. A. Mironenko and V. G. Rumynin, *Problems of Geoecology* [in Russian], in 3 vols., Izd. Moskovsk. Gos. Gorn. Univ., Moscow (1998).
2. R. E. Grim, *Clay Mineralogy*, McGraw-Hill, New York (1953).
3. Nora K. Foley, *Environmental Characteristics of Clays and Clay Mineral Deposits*, Texas Sodium Bentonite, Inc. (1999).
4. O. V. Yapaskurt, *Lithology* [in Russian], Infra-M, Moscow (2016).
5. J. K. Mitchell, *Fundamentals of Soil Behavior*, John Wiley & Sons, Inc., New York (1976).
6. M. V. Eirish, On the nature of the sorption state of cations and water in montmorillonite, *Kolloid. Zh.*, **26**, No. 5, 633–639 (1964).
7. K. Norrish and I. A. Raussel-Colom, Low-angle X-ray diffraction studies of the swelling of montmorillonite and vermiculite, *An. Tenth Natl. Conf. on Clays and Clay Minerals* (1957), pp. 123–149.
8. M. V. Eirish and L. I. Tret′yakova, The role of sorptive layers in the formation and change of the crystal structure of montmorillonite, *Clay Minerals*, No. 8, 255–266 (1970).
9. M. G. Khramchenkov, M. V. Eirish, and Yu. A. Kornil′tsev, Study of structural changes and thermodynamic model of filtration properties of clay rocks, *Geoékologiya*, No. 5, 65–73 (1996).
10. L. I. Kul′chitskii and O. G. Us′yarov, *Physicochemical Basis for the Formation of the Properties of Clay Rocks* [in Russian], Nedra, Moscow (1981).
11. A. F. Wells, *Structural Inorganic Chemistry*, OUP Oxford, USA (2012).
12. M. Tuller and D. Or, Hydraulic functions for swelling soils: Pore scale consideration, *J. Hydrol.*, **272**, 50–71 (2003).
13. L. Dormieux, E. Lemarchand, and O. Coussy, Macroscopic and micromechanical approaches to the modelling of the osmotic swelling in clays, *Transp. Porous Media*, **50**, 75–91 (2003).
14. K. Norrish, Swelling of montmorillonite, *Disc. Faraday Soc.*, **18**, 120–134 (1954).
15. A. W. Adamson, *Physical Chemistry of Surfaces*, Wiley-Interscience, New York (1976).
16. A. V. Smagin, Ionic-electrostatic model of the wedge pressure and specific surface area in colloidal systems, *J. Eng. Phys. Thermophys.*, **92**, No. 3, 744–755 (2019).
17. V. N. Nikolaevskiy, *Geomechanics and Fluid Dynamics*, Kluwer Academic Publishers, Dordrecht (1996).
18. N. E. Galiullina, M. G. Khramchekov, and R. M. Usmanov, Mathematical modeling of unsaturated filtration in swelling soils using the capillary-rise problem as an example, *J. Eng. Phys. Thermophys.*, **94**, No. 6, 1519–1525 (2021).
19. I. Gyarmati, *Non-Equilibrium Thermodynamics. Field Theory and Variational Principle* [Russian translation], Mir, Moscow (1974).
20. A. Yakobson, Phenomena of thixotropy in crumpled soft clays, in: *Engineering-Geological Properties of Clayey Rocks and Processes in Them*, Publishing House of Moscow State University, Moscow (1972), pp. 25–34.