

Some features of clay structure transformation in course of clayey swelling process

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Abstract

The original model of structural transformation in course of clay swelling, thermodynamical and physicochemical features of clayey swelling properties are examined. The model is based on the concept of mutual movement of clayey particles in aggregates of clayey rock at swelling with the formation of new pores between the clay particles that form the aggregates. The obvious mechanism of recycling of superfluous surface energy of clay particles is put in a basis of a model with modification of some parameters of the environment, for example, the concentration of a solution, through the change of relative orientation of clay particles, mainly, through turns from each other [1]. In the thermodynamic description, such a process will be shown in the change of a superficial tension on moistened sites of particles at movement during mutual turns. One of the major parameters of clay rock – micro-porosity in this case varies. In work [2] this phenomenon has been experimentally investigated with the use of methods of a static moisture capacity and Messbauer spectroscopy. The proposed model permits to explain the features of the clayey swelling process and to match the observed experimental data with the theoretical description of the clay swelling process.

Keywords: clay, moisture, swelling, Messbauer spectroscopy
 Kulcsszavak: agyag, nedvesség, duzzadás, Messbauer-spektroszkópia

1. Introduction

It's well known [3], that the specific properties of clays are caused by the existence of clay minerals, structurally arranged like thin sheet particles (about 50 – 100 nm in diameter and about 1 nm in height, as it is shown on Fig. 1).

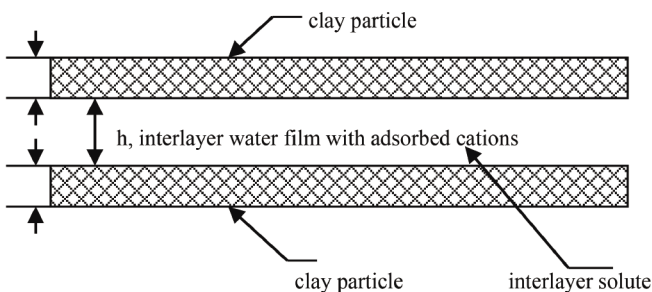


Fig. 1 Clay particles (aluminosilicate layers) and interlayer film between them
 1. ábra Agyagszemcsék (alumínium-szilikát rétegek) és a köztük lévő rétegeközi film

Also, it is common knowledge [4], that there are two main types of clay minerals – with mobile and fixed crystal lattices. Clay minerals of the first type (for example, montmorillonite) are able to swell. We dwell on this moment in more detail.

One of because the isomorphic substitutions in crystal lattice particles of clay minerals usually carry an electrical charge (usually negative), which is compensated by cations. These cations are called cations neutralizers. Cations-neutralizers are adsorbed onto the surface of particles and at hydration, they are able to dissociate (totally or partly) and make the double diffusion layer [3]. At this montmorillonite takes place, a certain amount of liquid enters between clay particles, and we can observe the swelling (Fig. 1).

From experimental data it follows, that isomorphic substitutions in aluminosilicate layers determine not only the presence of a certain amount of cations neutralizers but predetermine the possibility water molecule entry into the crystal structure of montmorillonite and the formation of so-called hydrate-ionic layers [5]. The specific course of the hydration process, cation displacement, and some elements of clay crystal lattice deformation and rotation, shows a competition between adsorbed cations and polar water molecules for neutralization of the negative valency charge on the corresponding sites in aluminosilicate layers. This specific community of adsorbed cations and polar water molecules is called hydrate-ionic layer.

Hydrate-ionic layers which give rise to the most important properties of montmorillonite, are also the most flowing link in the structure, since bonds between molecules and ions within these layers are much weaker than those in aluminosilicate layers. Thus, the condition necessary for forming the crystal structure, that is, the fixation of all particles, would be possible only over a some-what small range of hydrate-ionic layer size. This fact makes the crystal lattice of montmorillonite mobile and able to swell.

It is also significant that the hydrate-ionic layers while forming between aluminosilicate layers, not only separate silicate layers but also combine them into structures of secondary particles (crystallites). The main bonding elements in these structures are adsorbed cations. Sorption of cations of any type or size results from their ability to change position within the hydrate-ionic layers and is also due to the fact that multivalent cations simultaneously belong to two aluminosilicate layers (except the other surfaces of crystallites).

The number of interconnected hydrated aluminosilicate layers in the structure of crystallites along the crystalline axis “c” changes according to the composition of adsorbed cations and the ambient conditions (concentration of admixture in inter-particle solute or moisture). It’s clear that mono-valence cations hydrate-ionic layers are the mostly weak links, bonding aluminosilicate layers. So, the difference between clay types in the ability to swell appears in competition between the areas of clay particle surfaces, where the hydrate-ionic layer was formed, and areas, where the hydrate-ionic layer was formed only partially or absent.

The original experimental results about features of interaction in a system “water – adsorbed cations – admixture of inter-layer solute” were obtained in [2]. These results permitted to formulate the model of structural change in course of clay swelling. The model is based on the concept of “fan” movement of clayey particles in aggregates of clay rock at swelling. It is best to use the swelling clay structure model proposed by [6] and shown in Fig. 2.

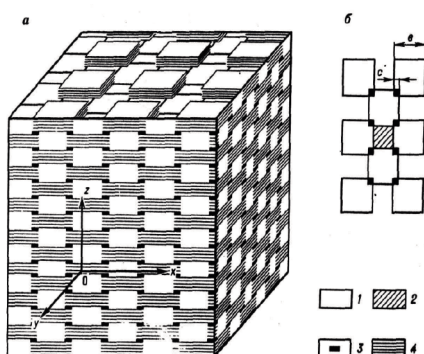


Fig. 2. Clayey rock aggregated structure. 1 – inter-aggregate (transport) pores, 2 – non-transport pores, 3 – intra-aggregate pores, 4 – aggregates

2. ábra Agyagos kőzet aggregált szerkezet. 1 – aggregátumok közötti (transzport) pórusok, 2 – nem transzport pórusok, 3 – aggregátumon belüli pórusok, 4 – aggregátumok

This model will be used by us as a basic one in further analysis of own experimental data. Comparison with other types of arrangement of clay particles in clay rock will be discussed below.

2. Experimental research

One of the major parameters of clay rock – micro-porosity in this case varies. In work [2] this phenomenon has been experimentally investigated with the use of methods of static moisture capacity and Messbauer spectroscopy.

The mechanism of this process is based on the obvious notion that clayey particles will primary move in a lateral direction then in normal (relatively basal surface of aluminosilicate layers) to utilize the superfluous surface energy of clay particles that is appeared in course of swelling. “Normal” movement is adjusted to changes in volume, and it is often limited or not possible in real underground conditions. “Lateral” movement is not connected with the volume change, but only with mutual clay particle displacement. It leads to a change of mutual orientation of clay particles, mainly, through turns from each other like elements of fan [2]. Such process has to be exhibited

in change of such parameters of clay like its micro-porosity.

Moisture	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
Initial	6,47	9,69	13,16

Table 1 The results of water content (in gramm on 100 gramm of dry sample) measurements in clay samples for differ meaning of moister

1. táblázat Az agyagminták víztartalmának mérési eredményei (grammban, 100 gramm száraz mintán) az eltérő nedvességtartalomra vonatkozóan

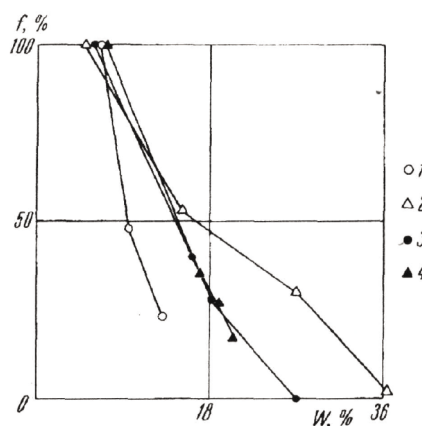


Fig. 3 Messbauer signal attenuation in clay samples for different moister 1 – initial sample, 2 – first sample, 3 – second sample, 4 – third sample

3. ábra Messbauer-jelek gyengülése agyagmintákban különböző nedvességtartalom esetén. 1 - kiindulási minta, 2 - első minta, 3 - második minta, 4 - harmadik minta.

Naturally, we obtained in course of experiments on the static moisture capacity of clayey samples, that when we change the inter-particle solute concentration, the quantity of adsorbed water for some fixed meanings of moister changes too (Table 1).

This was at once a measurement of Messbauer effect (Messbauer signal attenuation, *f*) in the same clay samples for same moister. Results are demonstrated in Fig. 3.

Good agreement between two series of experimental results can be seen in comparison of Table 1 and Fig. 3.

Physically such a process appears in change of a superficial tension on moistened sites of particles at movement during mutual turns. It should be noted that no overall change in volume was observed during the experiments. Also, it should be noted 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 principle “basis - chip”, it is possible to obtain structures that, when swelling, behave like a kind of “accordion”: a change in the rock volume during swelling is caused by a change in the contact angle at the “basis - chip” node [8, 9]. There is another possible way of packing clay particles during the formation of clay rocks - according to the “basis - basis” principle, when the particles are located, similar to how it is shown in Fig. 2. Note that when such structures swell in both the first and second cases, there is a change in volume, and after the end of swelling, the structure should return to its original state. To verify this, we conducted 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 due to a change (growth) in the humidity in the desiccator. Then the second sample was brought to the same humidity value as the first one. At the end of the experiment, the specific surfaces of two initially identical samples were compared. For this, the method of adsorption-luminescence analysis (Airish et al.) was used, which makes it possible to fix the fraction of the particle surface available for swelling in montmorillonite. It was shown that the free specific surface of clay particles of montmorillonite clay in two samples after the experiment is different (Table 2). At the same time, no change in the total volume was also recorded. This can only mean one thing – when the clay swells, the clay particles move apart according to the mechanism of a fan or a deck of cards with the formation of new micropores, as in the first experiment. Thus, when clay rocks swell, the pore space is redistributed due to the formation of new pores that appear when clay particles move apart, forming clay micro aggregates and aggregates. On Fig. 2, this would look like the destruction of the original order in the arrangement of particles, accompanied by the transition of each neat stack of particles due to the rotation of each particle in its direction and the filling of transport pores with new micropores. Let us consider some thermodynamic features of the description of such a process.

It should be noted that no overall change in volume was observed during the experiments.

Also, it should be noted that the conclusion about the appearance of micropores due to the fan mechanism of the expansion of clay particles during ion exchange is not indisputable. Attention is drawn to the fact that during the ion exchange of calcium for sodium, the number of ions capable of being hydrated in water vapor doubles. At the same time, the hydration energy of calcium is 3.5 times higher than that of the sodium ion, the same applies to the size of stable aqua complexes of calcium and sodium [7], so that unambiguous conclusions can only be drawn from the change in the amount of water bound by sodium ions and the equivalent (by charge) the amount of calcium ions is difficult to do. 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 swelling, behave like a kind of “accordion”: the change in rock volume during swelling is caused by a change in the contact angle at the “basis–cleavage” node [8, 9]. There is another possible way of packing clay particles during the formation of clay rocks - according to the “basis - basis” principle when the particles are located and form an aggregate structure similar to the one shown in Fig. 2. Note that when such structures swell in both the first and the in second case, there should be a change in volume, and after the end of swelling, the structure should return to its original state. To verify this or to obtain experimental data refuting this fact, 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 due to a change (growth) in the humidity in the desiccator. Then the second sample was brought to the same humidity value as the first one. At the end of the experiment, the specific surfaces of two initially identical samples were compared. For this, the method of adsorption-luminescence analysis [2, 5] was used, which makes it possible to fix the fraction of the particle surface available for swelling in montmorillonite. It was shown that the free specific surface of clay particles of montmorillonite clay in two samples after the experiment is different (Table 2). At the same time, no change in the total volume was also recorded. This can only mean one thing – when the clay swells, the clay particles move apart according to the mechanism of a fan or a deck of cards with the formation of new micropores, as in the first experiment. Thus, when clay rocks swell, the pore space is redistributed due to the formation of new pores that appear when clay particles move apart, forming clay micro aggregates and aggregates. In Fig. 2, this would look like the destruction of the initial order in the arrangement of particles, accompanied by the transition of each neat stack of particles due to the rotation of each particle in its direction and the filling of transport pores with new micropores.

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

Table 2 Changes in the exchange capacity and clay numbers of clay samples before (initial) and after (final) their moistening

2. táblázat Az agyagminták cserekapacitásának és agyagszámának változása a nedvesítés előtt (kezdeti) és után (végső)

However, the experiment also showed more interesting aspects of swelling. Samples from two deposits (Oglanlinskoe deposit (Turkmenistan) and Sarigyukhscoe deposit (Armenia), with a high content of the montmorillonite component. Experiments showed that their free surface decreased after the experiment. This can be explained by the fact that the process of turning particles due to the predominantly montmorillonite composition of the clayey the component went as deep as possible, with the destruction of the initial crystallites and the adhesion of the silicate layers that became completely free after the turns into new, larger micro aggregates, with a lower specific surface area of clay particles. surface (Table 2). This is evidenced by the change in such parameters as exchange capacity (EC) and clay number (CN). Let’s consider some thermodynamic features of the description of such a process.

3. Thermodynamical aspects of clay swelling process

On the basis of the equations of balance for water and components of a solution (cations and anions of a solute), and also the first Lippmann equation, [3]

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

It is possible to receive a necessary ratio for interlayer distances between clay particles as a function of the concentration of a solution and the basic physical and chemical parameters of clay. As a condition of balance equality serves zero of a variation of free energy of Gibbs of all systems at constants pressure and temperature

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

where μ_i – is the chemical potential of the correspondent component, index “0” – stands for water, index “1” – stands for cations, index “2” – stands for anions, index “s” means component, that is adsorbed on the surface, n_i – the number of moles of i - component in the system, symbol δ means variation (algebraic increment) of corresponding value, γ - modification of specific surface energy (surface tension) at the movement of clayey particles, φ - electrical potential, q – is the electrical charge of the unit of the surface of clay particles, A – square of moisture surface of clay particles. The consequence of Eq. (1) is the equality of chemical potentials of ions in an inter-aggregate and intra-aggregate solute

$$\mu_1 = \mu_1^0, \quad \mu_2 = \mu_2^0, \tag{3}$$

$$\mu_1 = \mu_1^0 + RT \ln C_1 + e z_1 \varphi, \mu_2 = \mu_2^0 + RT \ln C_2 + e z_2 \varphi, \tag{4}$$

$$\mu_1 = \mu_1^0 + RT \ln C_1 + e z_1 \varphi, \mu_2 = \mu_2^0 + RT \ln C_2 + e z_2 \varphi. \tag{4}$$

Here the index «0» remarks pure values of chemical potentials of cations and anions, z_1 and z_2 is a valency of cations and anions respectively, e is a charge of the electron, φ is an electrical potential of the solution, R – is a gas constant. We suppose that in the solution which is situated in transport pores $\varphi=0$ and in the solution between clay particles because it's determined by exchange cations of clay. Also suppose that $z_1=1$, $z_2=-1$ (binary 1-1 electrolyte). So, adding the first of Eq. (4) with the second we receive:

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

Here C – is concentration, feature from above marks an accessory of the parameter to a pore solution, C_0 - concentration of inter-aggregate solution. From condition for electrical neutrality of «particles – solute» system in general

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

we receive

$$\begin{aligned} \bar{C}_1 &= (q / H) + \sqrt{(q^2 / H^2) + C_0^2}, \\ \bar{C}_2 &= -(q / H) + \sqrt{(q^2 / H^2) + C_0^2} \end{aligned} \tag{7}$$

Here H – is the interlayer distance (distance between two clayey particles). From a condition for the chemical potential of water we have, according to [1], the equation

$$2\gamma / H = RT(C_1 + C_2 - 2C_0). \tag{8}$$

The last with account (7), becomes

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

Equation (9) can be solved to find H :

$$H = A / C_0, \quad A = [q^2 - \gamma^2 / (R^2 T^2)] / [2\gamma / (RT)]. \tag{10}$$

It is possible to consider two limiting situations. When the concentration of an inter-aggregate solute is small, that, as is known from colloid chemistry, the charge of Stern layer

behaves proportionally the square root from the concentration of a solution, and we receive from Eq. (1) and Eq. (10)

$$q \cong \sqrt{C_0} \Rightarrow H \cong 1 / \sqrt{C_0}. \tag{11}$$

When the concentration of an inter-aggregate solute is great, the charge of the Stern layer behaves proportionally to the first degree of concentration of a solution, and

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

Such behavior is well coordinated with the results of well-known experiments on intra-crystal swelling of montmorillonite, [10].

The movement of clayey particles in course of swelling (change of chemical content of inter-particle solute) looks like the movement of fan in course of its opening, and it leads to a significant role of wetting effects in such process. Let's consider the dynamic scenario of this process. Physically, this scenario means that the swelling system, consisting of aggregates of clay particles, tends to absorb additional water and increase its volume, however, the system reacts differently: additional pores (micropores) are formed that absorb additional water from the interaggregate space, and, in general, volume changes system does not occur.

4. Physicochemical mechanics and features of clay swelling process

In [11], a model was proposed that well describes the process of clay rock swelling, when the volume of transport pores decreases due to the swelling of clay minerals without changing the total rock volume. The process is described by the next equation

$$\partial m / \partial t = -\beta \{ RTq / [V_0(1-m) - V_s] - \Gamma \} \tag{14}$$

Here m – the proportion of free water in the volume of clay soil water transport pores, V_0 - clay volume, R – gas constant, T - temperature, Γ - external load, β - swelling rate constant at the first stage. The minus sign on the right side of the equation emphasizes the fact that at this stage there is a decrease in the content of free water, and due to this, m decreases. The subscript “0” means the initial value of the corresponding value.

Obviously, in the resulting differential equation, the variables are separated, and it can be integrated:

$$\frac{RTq_0 / V_0}{\Gamma} \ln \left[\frac{RTq_0 / V_0 - \Gamma(1-m - V_s / V_0)}{RTq_0 / V_0 - \Gamma(1-m_0 - V_s / V_0)} \right] + (m - m_0) + \Gamma \beta t = 0 \tag{15}$$

The data of [12] were used to verify the obtained calculations.

In our case, it is necessary to modify Eq. (14) in such a way as to take into account the above experimentally observed phenomenon. During the process, the parameter q in Eq. (14) actually changes (increases), due to the fact that when the clay particles move apart, new surfaces of previously densely packed clay particles are released for complete hydration and the formation of a full-fledged diffusion layer. Therefore, we put instead of Eq. (14)

$$\partial m / \partial t = -\beta \left\{ RT \left[q_0 + \chi [V_0(1-m) - V_s]^\delta \right] / [V_0(1-m) - V_s] - \Gamma \right\} \tag{16}$$

Constant δ emphasizes the possibility of a nonlinear course of the swelling process. The physical meaning of the

modification of Eq. (14) made becomes transparent if we set $\delta=1$. In this case, it can be seen that the load Γ , preventing swelling, will decrease by the amount χ , and the swelling process will go faster.

$$\frac{RTq_0/V_0}{\Gamma - RT\chi} \ln \left[\frac{RTq_0/V_0 - (\Gamma - RT\chi)(1 - m - V_s/V_0)}{RTq_0/V_0 - (\Gamma - RT\chi)(1 - m_0 - V_s/V_0)} \right] + (m - m_0) + (\Gamma - RT\chi)\beta t = 0 \quad (17)$$

The type of dependencies is shown in Fig. 4.

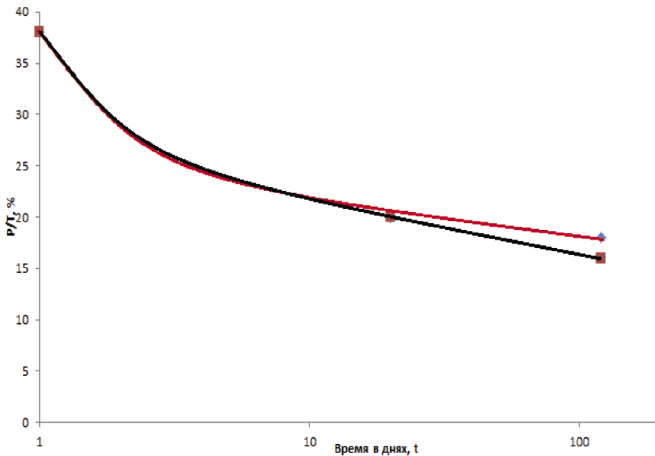


Fig. 4 Dependence of microstructural porosity of clays on time. Points correspond to experimental data from [12], solid lines are theoretical curves

4. ábra Az agyagok mikroszerkezeti porozitásának függése az időtől. A pontok a [12] kísérleti adatoknak felelnek meg, a folytonos vonalak az elméleti görbék

5. Conclusions

It was important for us to offer a model of coupled physical and chemical processes and their role in course of the swelling process and filtration of clays, which doesn't use a priori any suppositions about this rheology but uses only known facts about properties of components of clayey rocks.

The model is based on the concept of “fan” movement of clayey particles in aggregates of clayey rock at swelling. The obvious mechanism of recycling of superfluous surface energy of clay particles is put in a basis of a model with modification of some parameters of the environment, for example, the concentration of a solution, through the change of relative orientation of clay particles, mainly, through turns from each other [2]. Physically such process appears in a change of a superficial tension on moistened sites of particles at movement during mutual turns. One of the major parameters of clay rock – micro-porosity in this case varies. In [2] this phenomenon has been experimentally investigated with the use of methods of static moisture capacity and Messbauer spectroscopy.

The proposed model allows to give explanation of the main features of the relationship between interlayer distance (distance between two clayey particles) and concentration of interlayer solute. Also, it permits to obtain a suitable explanation of the change in microporosity and the type of packing of clay particles during the formation of the structure of clay rock.

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