Modeling of rheological and electro-chemical properties of hydrated clays

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Abstract

A unite mathematical model of rheological and electro-chemical properties of saturated clays is proposed. The foundation of the model is the unification of filtration's consolidation theory, the theory of stability of lyophobic colloids and the experimental data on electro-chemical properties of clays and clayey suspensions. Conception of disjoining pressure as a surplus in comparison with hydraulic plays the important role in clays properties description. This pressure is caused by surface capacities and exists in water films between clay particles. We obtained the exact solution about wringing the water out of clay layer. The solution that we received not demands to introduce a concept of limit shear stress for clays. We investigate the peculiarities of the model, which are important for explaining some character features of electro- and mass-transfer processes in clays with coupling of rheological behavior of clays. It is shown that solutions which we've received are in good harmony with results of experiments.

Keywords: kaolinite, montmorillonite, modelling, viscosity, electro-conductivity

Kulcsszavak: kaolinit, montmorillonit, modellezés, viszkozitás, elektromos vezetőképesség

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1. Introduction

The specific properties of clays and their compositions (low permeability and thermo-conductivity, plasticity in moist condition) are caused by existence of specific particles and their compositions-clay minerals. Clay minerals are hydro-alumosilicates of calcium, sodium, potassium and they often are structurally arranged like thin sheet particles (about 50-100nm in diameter and 1nm in height) [1]. Generally speaking, particles of clay minerals have the appearance of thin isometric or elongated plates, scales, needles and tubes.

Before we proceed to theoretical examination of electro-chemical and rheological properties of clays, we describe the simplest structure of clay sample or clayey rock. We will consider clays like solid porous skeleton (not essential coherent), which pores can change own size and form during swelling of clay minerals. After the filling of all pore volume by swelled clay, the process of total sample or rock swelling is started. In that case any process, connected with deformation of clays, could be described like:

1. Electro-chemical process in pores (part of medium volume, which is filled by clay particles, and their interlayer intervals).
2. Mechanical processes, connected with deformation of hard particles and dynamics of water films between them.

It is very important that their two processes are always conducted instantaneously. After solution of mass and energy balance equations for liquid and solid phase we obtain the equations for description of rheology and mass transport processes in clays [2]. On the first stage of deformation, until the full disappearing of transport pores, water in interlayer between clay particles doesn't perceive the effective tensions of skeleton [3] and it is in thermodynamic equilibrium [4-8] with water in transport pores, so it satisfies the equation that disjoining pressure is zero. This fact means that the volume

which is filled with clay particles and interlayer water, reserves. On the second stage free porosity is zero and we will have to specify the law of filtration in such a system (on the first stage we supposed that filtration velocity $\vec{q}$ satisfies the law of Darcy) In this case we will have a contribution of disjoining pressure to free energy of system. In the moment disjoining pressure is able to give an addition to hydraulic pressure, in dependence of the value of dilation. This fact can explain the nature of anomalous high seam pressures in deep-laying clay-containing reservoirs. Also the electro-chemical effects give impact in rheological behavior of clays.

2. Mechanics of clays and clayey rocks

The specific properties of clay rocks (low permeability, plasticity in moist condition) are caused by existence of clay minerals in their composition. Because of isomorphic replacement in crystal matrix this particles usual carry electrical charge (usually negative), which is compensated by cations. Cations are adsorbed on to the surface of particles and at hydration they are able to dissociate (totally or partly) and make the double diffusion layer [1, 2]. As already it has been told above, any process, connected with deformation of clay rocks, could be divide in two stages: 1) free (transport) porosity (part of pore volume, which is not filled by clay particles and their interlayer intervals) is not equal zero; 2) free (transport) porosity is equal zero, it means that all pores are filled by clay particles and interlayer films of water. We begin examination from the first stage. We will consider that the filtration is going only in free part of pores. Now we can write mass balance equations for liquid and solid phase:

$$\frac{\partial(m_{p,c}\rho_f)}{\partial t} + \text{div}(\rho_f m_{p,c} \vec{V}_{f,c}) \pm j = 0, \quad (1)$$

$$\frac{\partial[(1-m_p-m_c)\rho_s]}{\partial t} + \text{div}[\rho_s(1-m_p-m_c)\bar{V}_s] = 0 \quad (2)$$

In this equations ρ_f is a density of fluid (water), ρ_s – density of solid phase, $\bar{V}_f$ – fluid velocity in transport pores, $\bar{V}_c$ – fluid velocity between clay particles, $\bar{V}_s$ – solid phase velocity, m_p – free (transport) porosity, m_c – part of interlayer water in volume (internal porosity of clay minerals), j – water exchanging flow in the system «transport pores – water between clay particles». We assume that ρ_f and ρ_s are constants. Then after adding (1) and (2), and after accounting $\text{div}\bar{V}_s = \partial\theta / \partial t = \dot{\theta}$, $\text{div}[m_p(\bar{V}_f - \bar{V}_s)] = \dot{q}$, we receive the equation

$$\dot{\theta} + \text{div}\bar{q} = 0, \quad (3)$$

where we adopt that $\bar{V}_c = \bar{V}_s$ for clay particles (it means that filtration of water in water films between of clay particles is absent). Here θ is dilation (shrinkage in the case of consolidation), $\bar{q}$ – filtration velocity. Now we write conditions of mechanical balance. We suppose that an external load G is exerted to clay. Then the distribution of load between the rock components gives an equation

$$G_{ij} = (1-m_p-m_c)\sigma_{ij} - m_c(p+\Pi)\delta_{ij} - m_p p \delta_{ij}, \quad (4)$$

which after the designation

$$(1-m_p-m_c)(\sigma_{ij} + p\delta_{ij}) = \sigma'_{ij} \quad (5)$$

can be written in such a form

$$G_{ij} = \sigma'_{ij} - m_c \Pi \delta_{ij} - p \delta_{ij}. \quad (6)$$

In this equations p – pressure in liquid, Π – disjoining (additional to hydraulic) pressure in water interlayer films between clay particles, the aim of introduction of the σ'_{ij} will be explained below. Now proceed to thermodynamic balance. Denote free energy of solid phase through macro-parameters σ' , m_p , m_c , θ , Π . For this purpose we will write first and second law of thermodynamic for solid phase

$$dU_s = \delta Q^{(e)} + \delta A^{(i)} + \delta A^{(e)}, T dS_s = \delta Q^{(e)} + \delta Q'. \quad (7)$$

Here U_s is an internal energy of skeleton, S_s – entropy of solid phase, $\delta Q^{(e)}$ – external stream of heat, $\delta Q' \geq 0$ – summary internal stream of heat (dissipation energy function), $\delta A^{(i)}$ – elementary mechanical work of internal surface strength. We will assume that in our case $\delta A^{(i)}$ is caused by transformation of part of total deformation energy in deformation of solid particles, and $\delta A^{(e)}$ is caused mainly by transformation of part of total deformation energy in a work on the displacement of particle with electrical charge. In isothermal conditions

$$\delta A^{(i)} + \delta A^{(e)} = dU_s - T dS_s + \delta Q' = dF_s + \delta Q'. \quad (8)$$

Let's examine mechanical properties of solid phase. Then in conditions of absence of mass forces we have the equation

$$\frac{\delta A^{(i)}}{dt} = \int_{V_s} \sigma'_{ij} \frac{\partial u_i}{\partial x_j} dV = \int_{V_s} \frac{\partial \sigma'_{ij} u_i}{\partial x_i} dV, \quad (9)$$

where u_i is a component of the vector of transference velocity of skeleton's particles, σ'_{ij} is a skeleton's stresses. After transformation volume integral into surface integral we obtain:

$$\frac{\delta A^{(i)}}{dt} = \int_{V_0} \frac{\partial(\sigma'_{ij} u_i)}{\partial x_i} dV_0 + (-p) \int_{\Sigma_s} u_i n_i dS + (-\Pi) \int_{\Sigma_{s-c}} u_i n_i dS, \quad (10)$$

where $\sigma'_{ij} = (1-m_p-m_c)(\langle i_{ij}^s \rangle - \langle \sigma - p \rangle \delta_{ij})$ is a tensor of effective tensions, corresponding to eq. (4), $\sigma = -(1/3)\sigma'_{ii}$ is the pressure in the solid phase, i_{ij}^s is a deviator of the σ'_{ij} . It is clear that

$$\sum_s \int u_i n_i dS = \dot{V}_s$$

is the velocity of changing of the solid phase volume.

Taking into account that in our case

$$\delta A^{(e)} / dt = \int_{V_c} \varphi \cdot dE / dt, \quad ,$$

where φ – electrical potential in the volume near clay particle, E – volume density of electrical charge of clay particles, and both value φ , E are functions of the displacement of clay particles and depend from deformation's velocity tensor, we will use Ohm law $\varphi - \varphi_0 = \kappa^{-1} j$, $dE / dt = j$, and also we will assume that $j = \gamma_{ij} e_{ij}$, so for member $\varphi dE / dt$ we have $\varphi dE / dt = (\gamma_{ij} \gamma_{ij})^2 \cdot \kappa^{-1} (\dot{\theta})^2 + \kappa^{-1} (\gamma_{ij} e'_{ij})^2 + \gamma_{ij} \cdot \varphi_0 e_{ij}$. Here e_{ij} is a tensor of deformation's velocities, e'_{ij} is a deviator of the tensor of deformation's velocities, γ_{ij} – tensor of structural characteristics of clay particle arrangement, κ – electroconductivity of water film, φ_0 – electrical potential in the middle part of clayey pores.

During the first stage of deformation, until the full disappearing of transport pores, water in interlayer between clay particles doesn't perceive the effective tensions of skeleton and it is in thermodynamic balance with water in transport pores, so it satisfies the equation $\Pi=0$. So in during of the first stage from the condition $\rho_s V_s = M_s$, $M_s = \text{const}$ we receive

$$\frac{1}{V_0} (\dot{V}_s + \frac{\delta Q'}{dt}) = \sigma'_{ij} e_{ij} + \frac{(1-m_p-m_c)p}{\rho_s} \dot{\rho}_s + [(\gamma_{ij} \gamma_{ij})^2 \cdot \kappa^{-1} (\dot{\theta})^2 + \kappa^{-1} (\gamma_{ij} e'_{ij})^2 + \varphi_0 \cdot (\gamma_{ij} e_{ij})] \quad (11)$$

For the case of elastic solid material $\delta Q' / dt = 0$. Then from the last equation we receive that

$$\dot{F}_s = T \gamma_{ij} e'_{ij} - \sigma' \dot{\theta} + (1-m_p-m_c)p \frac{\dot{\rho}_s}{\rho_s} + [(\gamma_{ij} \gamma_{ij})^2 \cdot \kappa^{-1} (\dot{\theta})^2 + \kappa^{-1} (\gamma_{ij} e'_{ij})^2 + \varphi_0 \cdot (\gamma_{ij} e_{ij})] \quad (12)$$

So far as disjoining pressure Π is a function of thickness of water interlayer h between clay particles, that's why condition $\Pi=0$ is equivalent to condition $h = \text{const}$. This means that the volume which is filled with clay particles and interlayer water V_c preserves. Let's write it as $m_c V_0 = V_c$, $V_c = \text{const}$. Then from the last equation we obtain: $\dot{m}_c / m_c = -\dot{V}_0 / V_0 = -\dot{\theta}$, so

$$m_c = m_c^{(0)} \exp(-\theta). \quad (13)$$

Because $(1-m_p-m_c)\rho_s V_0 = M_s = \text{const}$, then

$$\frac{d[\ln V_0 + \ln \rho_s + \ln(1-m_p-m_c)]}{dt} = 0, \quad (14)$$

and we'll receive one equation for three variables. In the most simple case, when $\rho_s = \text{const}$ it can be written in such a form

$$\frac{1-m_p^{(0)}-m_c^{(0)}}{1-m_p-m_c} = 1 + \theta. \quad (15)$$

Then for the free energy we have a dependence $F_s = F(J_2', \theta, \rho_s)$, where J_2' – is the second invariant of the tensor of deformations, then

$$\dot{F}_s = \frac{\partial F}{\partial J_2'} \dot{\epsilon}_{ij}' + \frac{\partial F}{\partial \theta} \dot{\theta} + \frac{\partial F}{\partial \rho_s} \dot{\rho}_s.$$

Comparing right parts of equations for the $\dot{F}_s$ gives for concrete view of the F for the elastic skeleton [8] $F = \frac{\lambda}{2} \theta^2 + \mu J_2' - \nu \theta \sqrt{J_2'}$, where $\lambda, \mu, \nu = \text{const}$, next correlation

$$-\sigma^f - (\gamma_{ij} \gamma_{ij})^2 \cdot \kappa^{-1} \dot{\theta} = \lambda \theta - \nu \sqrt{J_2'},$$

$$(T_{ij} + \varphi_0 \cdot \gamma_{ij}) - (\gamma_{ij} \gamma_{ij})^2 \cdot \kappa^{-1} \dot{\epsilon}_{ij}' = (2\mu - \nu \theta / \sqrt{J_2'}) \dot{\epsilon}_{ij}' \quad (16)$$

Last equations play roles of rheological correlations. They give us an ability to get closed system of equations for filtration consolidation of clays on the first stage. On the second stage $m = 0$, and we have to specify the law of the filtration in such a system, because we have ignored the filtration of water between clay particles till this moment (on the first stage we consider that for the q the law of Darcy [8] is carry out). Let's use the correlation for case $m_p = 0$:

$$m_c = \beta - (1 - \beta)\theta, \quad \beta = m_c^{(0)} + m_p^{(0)}, \quad (17)$$

so $\dot{m}_c = -(1 - \beta)\dot{\theta}$. In this case we must take into account the last term of (10). This item describes the pressure of water between clay particles,

$$\Pi \int_{S_c} u_i n_i dS / V_0 = -\Pi \dot{V}_c / V_0 = -\Pi(\dot{m}_c + \dot{\theta} m_c) \quad (18)$$

Then for the elastic pore environment we have analogically in this case

$$-\sigma^f - [m_c - (1 - \beta)]\Pi - (\gamma_{ij} \gamma_{ij})^2 \cdot \kappa^{-1} \dot{\theta} = \lambda \theta - \nu \sqrt{J_2'},$$

$$(T_{ij} + \varphi_0 \cdot \gamma_{ij}) - (\gamma_{ij} \gamma_{ij})^2 \cdot \kappa^{-1} \dot{\epsilon}_{ij}' = (2\mu - \nu \theta / \sqrt{J_2'}) \dot{\epsilon}_{ij}' \quad (19)$$

As far as in the first equation there is a term which contains the disjoining pressure which itself depends on the thickness of interlayer film of water h , it's necessary to determine the form of function $h(\theta)$, that is to say to connect micro-parameter h with macro-variables of process. From one side we have the correlation (15) for m_c and from another side $m_c = S_c h / V_0, S_c = \text{const}$. Here S_c is a half-square of the surface of clay particles which are situated in the volume V_0 . Let's differentiate the left and right part of the last correlation with respect to time, so we receive

$$h = \frac{h^{(1)}}{m^{(1)}} [\beta - (1 - \beta)\theta] \exp(\theta). \quad (20)$$

Here $h^{(1)}, m_c^{(1)}$ – constants, which provides connection of the first and second stages. The last correlation will become more physical clear if we recall that shrinkage $\theta < 0$. So process of consolidation of clay rocks on the second stage determines the value h and, consequently the disjoining pressure as a function of macro-variable θ . In the moment disjoining pressure is able to give an addition to hydraulic pressure, in dependence of the value of θ . This fact can explain the nature of anomalous high seam pressures in deep-laying clay-containing reservoirs.

3. Rheological and electro-chemical properties of clays

Let's analyze the solution of second equation of (19). In the case of pure shift this solution has a simple view

$$\dot{\epsilon}_{ij}' = \frac{(T_{ij} + \varphi_0 \cdot \gamma_{ij})}{(2\mu - \nu \theta / \sqrt{J_2'})} \times \left[1 - \exp \left[-\frac{\kappa(2\mu - \nu \theta / \sqrt{J_2'}) t}{(\gamma_{ij} \gamma_{ij})^2} \right] \right] \quad (21)$$

This solution is corresponded to Kelvin-Voigt rheology [9].

Return to eq. (16). For Kelvin-Voigt rheology the member $(\gamma_{ij} \gamma_{ij})^2 \cdot \kappa^{-1}$ is corresponded to viscosity, so that we'll call this member "effective viscosity" and denote η . So, we can finally write for effective viscosity of clay

$$(\gamma_{ij} \gamma_{ij})^2 \cdot \kappa^{-1} = \eta, \quad (22)$$

and experimentally check the last correlation. For this purposes we use the simplest relation of Kelvin-Voigt rheological body

$$\epsilon = (\sigma / E) [1 - \exp(-Et / \eta)]. \quad (23)$$

Where E is the Young modulus. From equation (23) we can obtain the next relation for viscosity

$$\eta = \sigma / (d\epsilon / dt)_{t=0} \quad (24)$$

So, for experimental definition η in accordance with (24) we can use the classical compression experiment, carried out with a sample of clay of a specified mineral composition. At the time we'll measure the electro-conductivity of sample of the same clay, and after use the relation (22). Below we demonstrate results of measurements and its comparison with calculation's results.

On Fig. 1 plots of measured values of electro-conductivity and viscosity of kaolinite are presented. Also calculated values of viscosity are shown.

Fig. 1. The experimental (exp.) and calculated (calc.) values of viscosity and electro-conductivity of kaolinite in dependence on humidity. Definitions:
1. ábra Kísérleti és számított értékek kaolinit viszkozitására és elektromos vezetőképességére a nedvességtartalom függvényében.

One can see a good agreement between experimental and calculated data.

On Fig. 2 plots of measured values of electro-conductivity and viscosity of mica are presented. Also calculated values of viscosity are shown. One also can see a good agreement between experimental and calculated data.

1, 2 – Viscosity, calc.
3 – Viscosity, exp.
4 – Electro-conductivity, exp.

Fig. 2. The experimental (exp.) and calculated (calc.) values of viscosity and electro-conductivity of mica in dependence on humidity. Definitions:

2. ábra Kísérleti és számított értékek csillám viszkozitására és elektromos vezetőképességére a nedvességtartalom függvényében.

In the case of montmorillonite clay we have to take into account additional impact to electro-conductivity of cations on basal surface of clay particles, and after we have to change the formula (22) for montmorillonite and obtain finally

$$\alpha(\gamma_{ij}\gamma_{ij})^2 \cdot \kappa^{-1,3} = \eta, \quad (25)$$

where α is correction factor. On Fig. 3 plots of measured values of electro-conductivity and viscosity of montmorillonite are presented. Also calculated values of viscosity are shown. One also can see a good agreement between experimental and calculated data.

1 - Viscosity, calc.
2 - Viscosity, exp.
3 - Electro-conductivity, exp.

Fig. 3. The experimental (triangles and rhombuses) and calculated (line) values of viscosity and electro-conductivity of montmorillonite in dependence on humidity. Definitions:

3. ábra Kísérleti és számított értékek montmorillonit viszkozitására és elektromos vezetőképességére a nedvességtartalom függvényében.

4. Conclusions

It was important for us to offer a model of physical, electro-chemical and mechanical properties of clay, which doesn't use a priori any suppositions about the its rheology, but use only known facts about properties of components of clayey rocks. Such a model was created by the unification of the theory of filtration consolidation and the theory of DLVO. On the base of this model we solved a simple problem of clay's rheological and electro-chemical properties and we showed that the model gives an ability to describe the rheology of clays with correlation of electro-chemical properties of clays, which was received experimentally. On the foundation of developing ideas we created the mathematical model of electro-chemical phenomena in clay. The correlations we've received are well co-ordinated with experiments. It's also showed that the developing is a physical substantiation of well-known hydrogeological schemes for calculation of yield clay water into the aquifer [10–11].

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