Acta Geodyn. Geomater., Vol.2, No.2 (138), 47-52, 2005

PHYSICO-CHEMICAL MECHANICS OF CLAY SWELLING

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(*Received* September 2004*, accepted* May 2005)

ABSTRACT

The mathematical model of the swelling systems rheology is considered. As a basis of a model the generalization of the consolidation theory was used on a case when the mass of a solid phase of a porous skeleton changes due to an overflow of a fluid during processes of swelling / shrinkage under action of osmotic pressure. The problem of swelling / shrinkage of a clay layer is put and solved. On the basis of the analysis the decision features of a model, important for the explanation of some characteristic properties of processes in swelling systems, are investigated. It is shown, that the received decisions are in the good consent with results of experiments.

KEYWORDS: clays, swelling, rheology, mathematical model

1. INTRODUCTION

Swelling systems are traditionally the object of steadfast attention and research on physical and chemical mechanics, biomechanics and biophysics, physics of polymers, hydrogeology and of some other disciplines. Soils, clayey rocks, some polymers and also some polymer systems in live organisms are examples of swelling systems in the nature. Usually the mechanics of such systems is constructed on the basis of empirical rheological models, which can tell us a little about the physical nature of swelling in such systems. There is an imperative need of association of only mechanical representations about processes in swelling systems with physical and chemical properties of such systems, which are common both for inorganic, and for organic objects. In our opinion, such property can be osmotic pressure in swelling the systems, which is «driving force» of the process of swelling. Osmotic pressure is the reason of an overflow of a fluid in a solid matrix to an occurrence of the additional pressures stopping finally process of swelling. Therefore the swelling matrix can be considered as the porous environment with a swelling skeleton. As the model describing mechanics of such systems, it is possible to choose well known model of consolidation (Nikolaevskiy, 1996), however last is necessary for generalizing on a case of a porous skeleton of variable mass. The thermodynamics of swelling is stated in a lot of fine works which we shall use (Guggenheim, 1933).

2. PHYSICAL AND CHEMICAL MECHANICS OF CLAYS SWELLING

We shall write down the basic equations of mechanics for such systems. We start with the equation of balance of mass. For mass of a liquid phase we have:

$$\frac{\partial m\rho_f}{\partial t} + \operatorname{div}(m\rho_f \mathbf{V}_f) + j = 0, \quad \rho_f = \text{const} \qquad (1)$$

For mass of substance of a skeleton we have accordingly

$$\frac{\partial (1-m)\rho_s}{\partial t} + \operatorname{div}[(1-m)\rho_s \mathbf{V}_s] - j = 0, \quad \rho_s \neq \text{const} \ (2)$$

The mass of a representative element of volume of the porous environment is

$$M_s = \rho_s^0 \cdot V_s^0 + \rho_f \left[(1-m)V_0 - V_s^0 \right] \ ; \qquad (3)$$

$$V_s^0, \rho_s^0 - \text{const}$$

From (3) for the density of substance of a skeleton we have:

$$\rho_s = \frac{M_s}{(1-m)V_0} = \frac{\varepsilon V_s^0}{(1-m)V_0} + \rho_f, \quad \varepsilon = \rho_{\text{s}}^0 - \rho_f \quad (4)$$

We divide the equations (1) and (2) on ρ_f and after we fold results. Then with the account (4) we receive

$$\operatorname{div}\frac{\kappa\mathbf{V}_s}{V_0}+\operatorname{div}\mathbf{q}+\operatorname{div}\mathbf{V}_s+\frac{\partial}{\partial t}\left(\frac{\kappa}{V_0}\right)=0. \qquad (5)$$

Let's explain a view of the equation (5). It immediately follows from definition of shrinkage $dV_0/V_0=d\vartheta$, introductions of designations $\frac{\varepsilon V_s^0}{\rho_f}=\kappa$ and $\mathbf{q}=m(\mathbf{V}_f-\mathbf{V}_s)$. The equation (5) can be easily transformed to a view

$$\operatorname{div}\mathbf{q}+\kappa a e^{-\vartheta}(-\mathbf{V}_s\nabla\vartheta+\operatorname{div}\mathbf{V}_s)+\operatorname{div}\mathbf{V}_s-a\kappa e^{-\vartheta}\frac{\partial\vartheta}{\partial t}=0$$

$$V_0=Ae^{\vartheta}, V_0^{-1}=ae^{-\vartheta},\ a=1/A. \qquad (6)$$

It is obvious $\vec{V}_s\nabla\vartheta\to 0$ as a value of the second order of trifle. Then from (6) we have

$$\operatorname{div}\mathbf{q}+\operatorname{div}\mathbf{V}_s+\kappa a e^{-\vartheta}\left(\operatorname{div}\mathbf{V}_s-\frac{\partial\vartheta}{\partial t}\right)=0. \qquad (7)$$

Let's define $\operatorname{div}\mathbf{V}_s=\partial\vartheta/\partial t$. Then from (7) it is finally received:

$$\operatorname{div}\mathbf{q}+\frac{\partial\vartheta}{\partial t}=0. \qquad (8)$$

We shall pass now to the equation of balance of forces. We shall write down it in the form of the equation of balance:

$$G_{ij}=(1-m)\sigma^s{}_{ij}-mp\delta_{ij}=(1-m)(\sigma^s{}_{ij}+p\delta_{ij})-p\delta_{ij},$$

which after introduction of a designation $(1-m)(\sigma^s{}_{ij}+p\delta_{ij})=\sigma_{ij}^f$ comes to the view, which is traditional for the theory of consolidation:

$$G_{ij}=\sigma_{ij}^f-p\delta_{ij}. \qquad (9)$$

We will address now to the equation of balance of energy. We shall write down the first and the second laws of thermodynamics as

$$\left.\begin{array}{l} dU_s=\delta Q^{(e)}+\delta A^{(i)} \\ TdS_s=\delta Q^{(e)}+\delta Q',\quad \delta Q'\geq 0 \end{array}\right\}\Rightarrow \qquad (10)$$
$$\Rightarrow\delta A^{(i)}=dU_s-\delta Q^{(e)}=dF_s+\delta Q'$$

According to the theorem of alive forces we shall write down for a case of absence of action of mass forces

$$\begin{aligned}\frac{\delta A^{(i)}}{dt}&=\int_{V_s}\sigma_{ij}^s\frac{\partial U_i}{\partial x_j}dV=\int_{V_s}\frac{\partial}{\partial x_j}(U_i\sigma_{ij}^s)dV=\\ &=\int_{\Sigma_s}\sigma_{ij}^s n_jU_idS=\int_{S_s^e}\sigma_{ij}^s n_jU_idS+\int_{\Sigma_{s-f}}-pn_iU_idS=\\ &=\int_{S_s^e}\tau_{ij}^s n_jU_idS+\int_{S_s^e}(-\sigma^f+p)n_iU_idS+\\ &+\int_{\Sigma_s}-pn_iU_idS,\quad \sigma^f=-\frac{1}{3}\sigma_{ii}^f\end{aligned} \qquad (11)$$

Passing in (11) to average on representative volume values, we shall receive:

$$\begin{aligned}\frac{\delta A^{(i)}}{dt}&=\int_{\partial V_0}(1-m)\langle\tau_{ij}\rangle\langle U_i\rangle n_jdS_0+\\ &+\int_{\partial V_0}(1-m)\langle-\sigma+p\rangle\langle U_i\rangle n_idS_0+\int_{\Sigma_s}-pU_in_idS\end{aligned} \qquad (12)$$

Entering definition of tensor of effective stresses

$$\sigma_{ij}^f=T_{ij}-\sigma^f\delta_{ij}=(1-m)\left(\left\langle\tau_{ij}^s\right\rangle-\langle\sigma-p\rangle\delta_{ij}\right).$$

Let's write down for (12)

$$\begin{aligned}&\frac{\delta A^{(i)}}{dt}=\int_{V_0}\frac{\partial}{\partial x_j}\left(\sigma_{ij}^f\langle U_i\rangle\right)dV+\int_{\Sigma_s}-pU_ndS=\\ &V_0\sigma_{ij}^f e_{ij}+\int_{\Sigma_s}-pU_ndS.\end{aligned} \qquad (13)$$

Let's consider the last member (13):

$$\begin{aligned}&\int_{\Sigma_s}-pU_ndS=-p\int_{\Sigma_s}U_ndS=-p\dot{V}_s=\\ &=-p\frac{\partial}{\partial t}\left[(1-m)V_0\right]=pV_0\dot{m}-p(1-m)\dot{V}_0,\end{aligned}$$

Noticing, that $\dot{V}_0=V_0\dot{\vartheta}$, we shall receive:

$$\int_{\Sigma_s}-pU_ndS=V_0p\dot{m}-p(1-m)V_0\dot{\vartheta} \qquad (14)$$

Let's consider now a situation when actually the skeleton shows elastic properties. As the experiment shows, it is fair for small deformations, but is not carried out for big ones. In this case from (13) and (14) we have:

$$\frac{\delta Q'}{dt}=0\ \Rightarrow\frac{1}{V_0}\dot{F}_s=\sigma_{ij}^f e_{ij}+p\dot{m}-p(1-m)\dot{\vartheta} \qquad (15)$$

As free energy of a skeleton, generally speaking, is function $F_s=F_s(J_2',\vartheta,m)$, then

$$\dot{F}_s=2\frac{\partial F}{\partial J_2'}\varepsilon_{ij}'e_{ij}'+\frac{\partial F}{\partial\vartheta}\dot{\vartheta}+\frac{\partial F}{\partial m}\dot{m} \qquad (16)$$

From (15) and (16) follows that

$$-p(1-m)+\sigma^f=\frac{\partial F}{\partial\vartheta},\quad T_{ij}=2\frac{\partial F}{\partial J_2'}\varepsilon_{ij}',\quad \frac{\partial F}{\partial m}=p.$$

Believing according to Ljakhovskiy et al., 1984 $F = \frac{\lambda}{2}\vartheta^2 + \mu J_2' - \nu\vartheta\sqrt{J_2'}$ and considering $m << 1$ $\Rightarrow$ $m \approx$ const, we receive finally

$$-\left[p(1-m) - \sigma^f\right] = \lambda\vartheta - \nu\sqrt{J_2'},$$
$$T_{ij} = \left(2\mu - \nu\vartheta / \sqrt{J_2'}\right)\varepsilon_{ij}' \qquad (17)$$

The equations (17) play a role of rheological relations. It is interesting to notice, the first equation (17) together with (9) allow explaining the occurrence of abnormal high pressures of a fluid in a layer with a swelling skeleton (Duynin, 2000).

3. DYNAMICS OF CLAY SWELLING

Now the process of swelling will be examined in more detail. We shall come out of the concept of an osmotic cell suggested by one of the authors in Khramchenkov, 2004, according to which, in equilibrium conditions, the osmotic pressure can be found from the equality of chemical ionic potentials of a solution inside a firm skeleton and of a solution in transport pores:

$$\mu_i = \bar{\mu}_i,\ i = 1,2 \qquad (18)$$

Choosing as an example for calculation 1-1 electrolyte and using standard representation for a view of chemical potential, we shall receive

$$\mu_i = \mu_i^0(p,T) + RT\ln C_i + ez_i\Phi, \quad z_i = \pm 1:$$
$$C_1C_2 = C^2 = \bar{C}_1\bar{C}_2 \qquad (19)$$

Last equation in (19) represents a condition of Donnan's balance (Guggenheim, 1933). However, the system of the equations (19) is not closed. For its closing we use a condition of an electroneutrality of a system « a firm phase of a skeleton - a solution in pores»:

$$(\bar{C}_1 - \bar{C}_2)\left[(1-m)V_0 - V_s\right] = e,\ e' = \mathrm{e}/\left[(1\text{-m})\mathrm{V}_0 - V_s\right] \qquad (20)$$

In physical sense the equation (20) means that firm particles of a skeleton carry superfluous (for the definiteness let's consider it to be negative) electric charge. This charge is compensated by cations of pore solution, so there is a surplus of cations in comparison with anions of pore solution, which brings to the occurrence of osmotic forces. The described script entirely concerns such swelling systems, like clays, and also a number of others. The decision of the equations (19) with the account (20) is

$$\bar{C}_1 = \frac{e'}{2} + \sqrt{\frac{e'^2}{4} + C^2},\quad \bar{C}_2 = -\frac{e'}{2} + \sqrt{\frac{e'^2}{4} + C^2}. \qquad (21)$$

Then from (21) we have for osmotic pressure π:

$$\pi = \frac{RT}{2}\left(\sqrt{e'^2 + 4C^2} - 2C\right). \qquad (22)$$

At case when *C=0* we have from (22)

$$\pi = \frac{1}{2}RTe' = \frac{1/2 \cdot RTe}{(1-m)V_0 - V_s}. \qquad (23)$$

On particles of a skeleton there are two acting forces - osmotic pressure in pore solution and the effective stresses, which prevent swelling. It is obvious, that the difference of these two forces determines the resulting force, which leads either to swelling or to shrinkage. Thus, it is rational to write down the equation of swelling as

$$\frac{\partial}{\partial t}\left[V_s(\rho_s - \rho_w) + (1-m)\rho_w V_0\right] = \alpha\left[(1-m)\pi - \sigma^f\right]. \qquad (24)$$

The equation (24) describes the dynamics of change of a skeleton mass due to inflow (expression) of water during swelling (shrinkage). The equations (23) and (24) close the general system of the equations of mechanics of swelling (shrinkage) process.

4. RHEOLOGICAL PROPERTIES OF SWELLING CLAYS

The rheology of swelling systems will be examined on the example of one-dimensional problem of swelling/shrinkage of swelling layer under the action of the constant load being enclosed to a layer. Statement of a problem follows from the equations (8), (9), (17), (20), (23), (24) being added to the law of Darcy for a speed of a filtration and definition of swelling/shrinkage.

$$\Gamma = \sigma^{\mathrm{f}} + p, \quad \Gamma = const \qquad (25)$$
$$(1-m)p + \sigma^f = -\varphi(\vartheta) \qquad (26)$$
$$\dot{\vartheta} + \partial q / \partial z = 0 \qquad (27)$$
$$q = -(k/\eta)\partial p / \partial z \qquad (28)$$
$$k = k_0 + B \cdot m; \quad k_0, \quad B - \text{const}$$
$$V_0 = V_0^{(0)} \exp\vartheta \qquad (29)$$
$$\frac{\partial}{\partial t}\left[V_s(\rho_s - \rho_w) + \rho_w(1-m)V_0\right] =$$
$$= \alpha\left[(1-m)\pi - \sigma^f\right] \qquad (30)$$
$$\pi = \frac{0.5eRT}{(1-m)V_0 - V_s} \qquad (31)$$

Thus, required functions of the system (25) - (31) are σ^f, p, ϑ, m, k, q, V_0, π. Constants of the model are Γ, η, k_0, A, $V_0^{(0)}$, ρ_w, ρ_s, e, α, R, T. Boundary conditions of the first type look like:

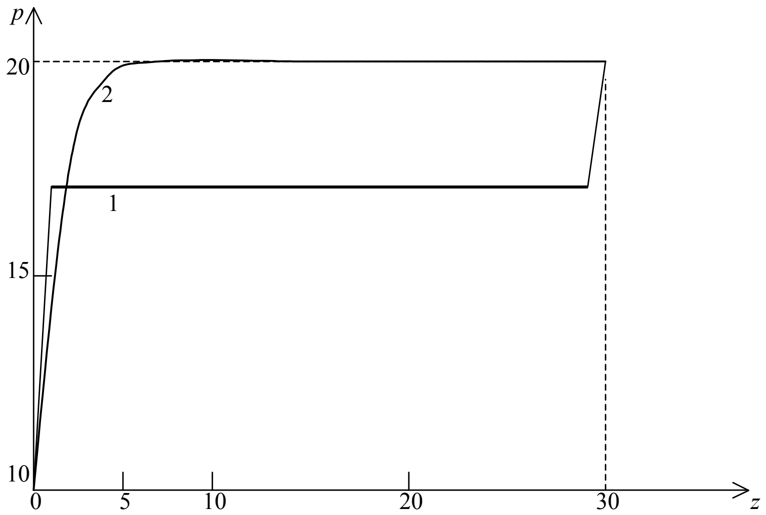

Fig. 1 Steady state pressure profile in layer:
1 – first type boundary condition on right bound;
2 – second type boundary condition on right bound

$$p_{|z=z_0} = \Gamma\,,\ p_{|z=0} = p_0 \tag{32}$$

or the second type

$$\partial p / \partial z_{|z=z_0} = 0\,,\ p_{|z=0} = p_0 \tag{33}$$

Initial condition is:

$$\vartheta(z,0) = 0 \tag{34}$$

The view of the equation (26) can be accounted for an unknown rheological ratio as the assumption of elastic character of reaction to the enclosed load being fair only for small deformations of the environment. We shall act as follows. We assume that transport porosity of the environment is small, so it is possible to count this assumption fairly in many cases (for example, for such natural swelling systems like clays). As one variable in system (25) - (31) is determined, one equation becomes superfluous. Let it be the equation (26). Besides it we shall notice in passing the dependence of filtration speed on a gradient of pressure (28) becomes simpler. Further, the problem was solved numerically. In both problems (for boundary conditions of the first and second sort (32) and (33) accordingly) the circuit used obvious difference scheme. In the second problem (i.e. for a boundary condition of the second sort (33) on an entrance in a layer) the method of prorace was used for finding a structure of pressure. Results of calculations are shown in Fig. 1, 2, 3.

5. ANALYSIS OF THE RESULTS

As experimental data of the distribution of pressure and shrinkage in a deformable layer, which should be defined in parallel rheological experiences, are absent, values of parameters of model got out of reasons of convenience of the calculations; therefore conclusions of the unit have a qualitative character. The variation of values of parameters did not change a view of received dependences. Calculations have confirmed the expectations of physical character showed in the model. So, in our opinion, it is interesting to see the structure of pressure for a case of using a boundary condition (32). It is visible, that the stationary zone appears in the central part of a layer, where is no current. In this zone, the stream arrives from the right part being removed from the left side. Corresponding distribution of shrinkage is resulted at Fig. 2. It is visible, that the zone of an entrance of the stream corresponds to both the zone of swelling (positive values) and to the zone of removal of the stream - the zone of shrinkage (negative) so that a deformation appears as non-uniform on a structure. It is interesting, that schedules of shrinkage for both problems coincide. Basically in the second case (condition 33), water starts to be squeezed out of a layer. If on the left border is the place where the water passes and the zone of shrinkage appears, on right border there is no place for water to pass, and the zone of swelling appears. The graphs of dependence of shrinkage speed being averaged by the layer from the enclosed load, well coincides too (Fig. 3). It is visible, that the character of the received curve corresponds to

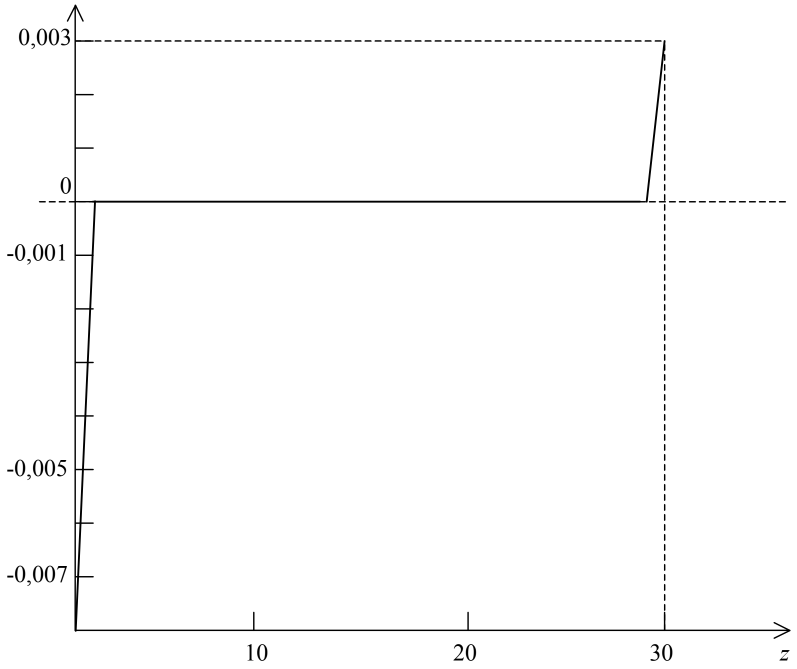

Fig. 2 Shrinkage profile in layer

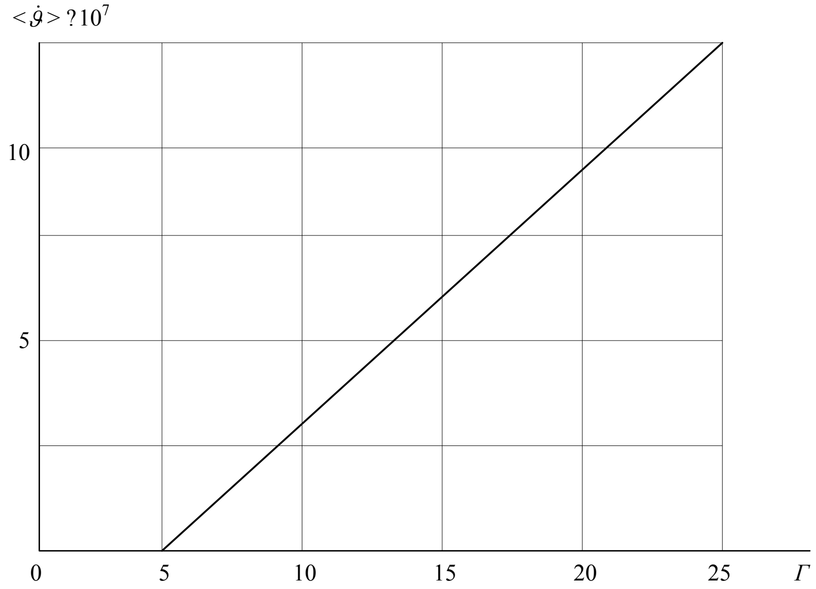

Fig. 3 Average shrinkage velocity versus stress load

the Bingham's rheology, and it is seemed to be quite plausible for swelling systems such as clay (Mitchell, 1993). It is interesting that the value of a maximum load on a layer physically providing absence of swelling of mass linearly depends on the size of exchange capacity e and parameter α and practically does not depend on the permeability of environment.

6. CONCLUSIONS

The problems comprising in this or that way rheological models of swelling environments, such as clay or clay rocks, frequently appear in technology or engineering geology. As usual, some of hypotheses about the rock rheology, for example, Bingham's rheology, are necessarily included in such models throughout. Necessarily we had to offer such model of environment, which could not use a priori any assumptions about the rheology of environment being at the same time based on the known experimental facts concerning the properties of environment (for example, presence of osmotic pressure in the system, which leads to swelling). Such model has been developed by association of the theory of consolidation with model of an osmotic cell. Based on the developed model the elementary problem about the shrinkage of swelling layer under load has been solved proving, that the model allows correct description of an experimentally observable rheology of clays and clayey rocks.

ACKNOWLEDGEMENTS

Work was executed at the support of ISTC (grant no. 2364).

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DESIGNATIONS

Latin: $A^{(i)}$ - work of internal superficial forces;
C - concentration of solution in transport pores;
C_1 - concentration of cations in a solution;
C_2 - concentration of anions in a solution;
dS - an element of the area on which integration is spent;
G_{ij} - the tensor of external load;
e - exchange capacity of clay;
e_{ij} - the tensor of speeds of deformations;
F - free energy of a body with micro-fractures;
F_s - free energy of a firm phase of a skeleton;
i_{ij}^{s} - deviator σ_{ij}^{s};
j - an exchange stream between a skeleton and transport pores;
J_2' - the second invariant of deviator of the tensor of deformations;
k - permeability of environment;
z_0 - thickness of a layer of clay;
M_s - weight of a firm phase;
m - free (transport) porosity;
$\mathbf{q}$ - speed of a filtration;
q - the module of $\mathbf{q}$;
p - pressure in a liquid phase;
$Q^{(e)}$ - external heat;
Q' - non-compensated heat;
R - a universal gas constant;
T - temperature;
t - time;
S_s - entropy of a firm phase;
S_s^e - a free surface of particles of a firm phase;
T_{ij} - deviator of the tensor of effective pressures;
U_s - internal energy of a firm phase;
U_i - components of a vector of the speed of skeleton particles displacement;
dV - the element of volume;
V_0 - representative volume;
V_s - volume of a firm phase;
$\mathbf{V}_f$ - speed of a fluid in transport pores;
$\mathbf{V}_s$ - speed of a firm phase;
x_i, x_j - coordinate axes;
z - a vertical axis.
Greek: α - mass transfer constant;
Γ- external load;
ε_{ij} - tensor of deformations;
δ_{ij} - delta-symbol of Kronoker;
η - viscosity of water;
λ, μ, ν - elastic constants;
μ_i - chemical potential of an ion in a solution (the index 1 concerns to cation, an index 2 - to anion);
π- osmotic pressure;
θ - shrinkage;
$\dot{\theta}$ - speed of shrinkage;
ρ_f - density of a fluid;
ρ_s - density of a firm phase;
σ_{ij}^{f} - tensor of effective pressure;
σ^{f} - a trace of the tensor of the effective pressure;
σ_{ij}^{s} - the tensor of the true pressure of a skeleton;
σ - a trace of the tensor of the true skeleton pressure
Σ_s - a general surface of a firm phase;
Σ_{s-f} - a surface of contact of fluid-skeleton.

Indexes: e - means an external part; f - a designation of an accessory to a liquid phase; 0 - designates an initial condition; s - a designation of an accessory to a firm (solid) phase, or a porous skeleton; f, s, e, 0 - have the same sense both in top and in the bottom position; i, j - without brackets mean projections to axes of coordinates; (i) - concerns to work of internal superficial forces; (e) - concerns to external heat; the point above the letter designates a partial derivative on time; the stroke means the deviator of corresponding tensor, behind the exception of Q' (non-compensated heat); feature from above marks an accessory of parameters to the pore solution, i.e. a solution in structure of a skeleton of environment.