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EQUILIBRIUM SELF-POLARIZATION OF CLAY

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A condition of equilibrium between charged clay particle surfaces and the solution contained in the pore space of the rock is derived using electrical double layer theory. This condition is the relation linking the cation concentration in the middle surface of the pores with the exchange capacity of the clay, the total ion charges, and the specific surface area of the particles.

Key words: *self-polarization potential, equilibrium, clay, electrical double layer, anion displacement, cationite.*

Introduction. The occurrence of a self-polarization potential in clay-containing rocks is often associated with diffusion and adsorption (membrane) effects [1, 2], which are described by Nernst theory for semipermeable membranes. By the membrane is meant a certain boundary between solutions with different salt concentrations.

There is also another approach based on the theory of the electrical double layer [3–5] formed on the surface of charged clay particles. Some aspects of using this theory were studied, for example, in [6–9] and other papers.

Clays of various types, constituting half of all sedimentary rocks of the Earth's crust, have special properties that distinguish them from the other minerals. The clay-mineral skeleton is formed of thin (about a few tens of angstroms) flakes. Clays, while exhibiting fairly high porosity, are poorly permeable to native fluids [10]. Their crystal lattice contains molecules of $\mathrm{Al_2[Si_4O_{10}(OH)_2]}n\mathrm{H_2O}$. Instead of aluminum the molecules can contain iron atoms or, much more rarely, other metal atoms.

Because clay molecules contain a large amount of oxygen atoms, the flake surface has a stationary negative charge related to the crystal lattice. In the presence of fresh water, the flakes are hydrated similarly to salt ions in electrolytes, leading to a volume increase (swelling) of the clay. Conversely, if the pore space of a clay mineral is filled with a solution of salts, some of the water molecules adsorbed on the flake surface can pass into the solution, thus diluting it, and the active centers (vacancies) that have become free are occupied by cations from the pore solution. An excessive number of negative charges (anions) appear in the solution. This phenomenon was called anion displacement or negative adsorption [6].

Thus, the displacement of fresh water from a clay bed by a salt solution gives rise to a negative potential difference in the penetration region. With time, the excessive negative charge "drains" into the ambient rocks under the action of the generated electric field and diffusion until general equilibrium is established, i.e., until the electric potentials of the bed are equalized.

Obviously, the equilibrium is also disturbed if re fresh water is injected in a clay bed saturated with an electrolyte solution. As a result, the initially neutral infiltrate is saturated with the cations desorbed from the clay particle surface, and the vacancies are filled by dipole water molecules. A potential with a positive sign occurs in the penetration region.

In the construction of a mathematical model for the formation and decay of the self-polarization potential field, the first step is to study the conditions for the existence of equilibrium self-polarization. We examine these conditions in terms of electrical double layer theory.

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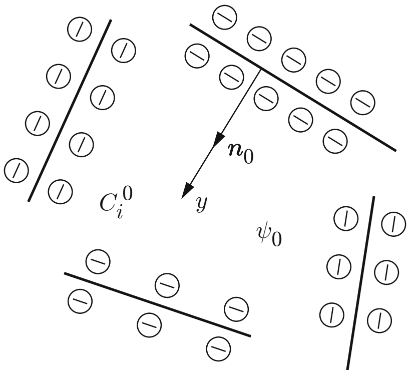

Fig. 1. Structure of clay rock.

1. Elements of Electrical Double Layer Theory. Static Potential in Pores. In a moving free solution or in a solution filling the pore space of a porous medium, the total flux $\boldsymbol{j}_i$ of the i-th ion includes three components [7]:

$$\boldsymbol{j}_i = -u_i kT \nabla C_i - u_i e z_i C_i \nabla\psi + \boldsymbol{v} C_i. \tag{1}$$

Here u_i is the ion mobility, T is the temperature, k is the Boltzmann constant, C_i is the concentration, e is the electron charge, z_i is the valence, ψ is the electric potential, and $\boldsymbol{v}$ is the velocity. Under the equilibrium conditions ($\boldsymbol{j}_i = \boldsymbol{v} = 0$), expression (1) becomes

$$\frac{\nabla C_i}{C_i} = -\frac{z_i e}{kT}\,\nabla\psi. \tag{2}$$

The structure of clay rock is given schematically in Fig. 1. The lines show negatively charged clay particles. In the chosen local natural coordinates, the y axis is normal to the particle surface inside a pore. Scalar multiplication of relation (2) into the normal unit vector yields the ordinary differential equation

$$\frac{1}{C_i}\,\frac{dC_i}{dy} = -\frac{z_i e}{kT}\,\frac{d\psi}{dy}.$$

Integrating this equation with respect to C_i and ψ within the equilibrium values of C_i^0 and ψ_0 reached at a sufficient distance from the pore surface, we obtain the well-known Boltzmann formula

$$C_i = C_i^0 \exp\Big(-\frac{z_i e(\psi - \psi_0)}{kT}\Big), \tag{3}$$

which allows the spatial distribution of cations ($z_i > 0$) and anions ($z_i < 0$) to be determined from the specified distribution of the electric potential in the pore. Depending on the sign of the surface charge, the cation concentration can decrease monotonically with distance from the particle surface (cationites with a negative particle charge) or increase (anionites with a positive particle charge).

Clay particles, as a rule, are cationites. Their negatively charged surfaces attract electrolyte cations and repel anions. In a free solution, clay particles are hydrated similarly to anions. The differences are that, first, clay particles are much larger and, second, they are almost immovable (connected to the porous bed of the rock, which can also contain particles of other minerals).

In close proximity to the surface, the anion concentration $C_a \to 0$, the cation concentration $C_c \to \infty$, the potential $\psi \to -\infty$, and the negatively charged surface of a clay flake, together with the adsorbed cation charges, form an electrical double layer [3–8].

In any elementary volume of the free electrolyte solution, the sum of the charges of all ions is equal to zero:

$$\sum_{i=1}^{n} z_i C_i = 0. \tag{4}$$

During interaction (saturation) of the clay rock with the electrolyte, the volume electroneutrality of the form (4) is violated, according to formula (3), resulting in the occurrence of negative adsorption (anion displacement).

In this case, an isolated rock sample acquires negative charges capable of moving, in particular, under electric field action.

The magnitude of the anion displacement or negative adsorption Γ^- is determined from the formula [6]

$$\Gamma^- = C_a^0\Big[\int\limits_0^\infty \Big(1 - \exp\Big(\frac{z_a e(\psi(Y) - \psi_b)}{kT}\Big)dY - \delta\Big],$$

where $\delta = 4/(z_a\beta q_s) \approx 4 \cdot 10^{-10}$ m is the thickness of the dense layer, $Y = y - \delta$, and ψ_b is the potential inside a pore at a distance b. The anion displacement distance is defined as

$$d_s = \Gamma^-/C_a^0 \approx q_s/\sqrt{\beta C_0} - \delta,$$

where $q_s = E_c/\Sigma$ (E_c is the exchange capacity and Σ is the specific surface area). For bentonite, $q_s \approx 10^{-9}$ kg-equiv./m^2 and $\beta = 1.06 \cdot 10^{19}$ m/kg-equiv.

We restrict ourselves to the case where the valences $z_a = -1$ and $z_c = 1$, which is valid, for example, for a table salt solution. In the region between the pore wall and the plane located at a distance b from it, the cation and anion distributions, according to formula (3), are given by

$$C_a = C_a^b \exp\Big(\frac{e(\psi - \psi_b)}{kT}\Big), \qquad C_c = C_c^b \exp\Big(-\frac{e(\psi - \psi_b)}{kT}\Big).$$

Here $C_a^b < C_c^b$ are the concentrations of the corresponding ions of the solution at a distance from the particle surface $y = b$.

The electric field potential should satisfy the Poisson–Boltzmann equation [8]

$$\operatorname{div}(\varepsilon \operatorname{grad}\psi) = -4\pi q, \tag{5}$$

where ε is the dielectric permittivity, $q = N_{\rm A} e(C_c - C_a)$ is the volume charge density, $N_{\rm A}$ is the Avogadro number, and e is the unit charge. Thus, after transformation (5), the one-dimensional distribution of the potential in the pore is described by the ordinary differential equation

$$\frac{d^2\psi}{dy^2} = -\frac{4\pi e_1}{\varepsilon}\Big[C_c^b \exp\Big(-\frac{e(\psi - \psi_b)}{kT}\Big) - C_a^b \exp\Big(\frac{e(\psi - \psi_b)}{kT}\Big)\Big],$$

where $e_1 = eN_{\rm A}$. After the introduction of the weighed potential $u = -(e/(kT))(\psi - \psi_b)$, this equation becomes

$$\frac{d^2u}{dy^2} = A(C_c^b\,\mathrm{e}^u - C_a^b\,\mathrm{e}^{-u}), \qquad 0 \leqslant u < \infty, \tag{6}$$

where $A = 4\pi e e_1/(\varepsilon kT)$.

2. Interaction of the Charges with the Pore Walls. We assume that the pore volume is bounded by two parallel surfaces of clay particles, and the coordinate $y = b$ corresponds to the middle plane of the pore, where $\psi = \psi_b$. The arrangement of the particles is shown schematically in Fig. 2.

In view of the symmetry of the examined model, we write the following Cauchy conditions for Eq. (6):

$$y = b: \qquad u = u'_y = 0. \tag{7}$$

In integrating Eq. (6), one should taken into account that in the interval $0 \leqslant y \leqslant b$ the weighed potential is a positive function of the coordinate y which decreases to zero. Therefore, in the given interval, $u'_y \leqslant 0$ and the required solution satisfying conditions (7) has the form

$$y = b - \int\limits_0^u \frac{du}{\sqrt{2A[C_c^b(\mathrm{e}^u - 1) + C_a^b(\mathrm{e}^{-u} - 1)]}}. \tag{8}$$

Decomposing expression (8) in the vicinity of the middle surface, where $u \approx 0$, we obtain

$$y \approx b - \sqrt{2u/[A(C_c^b - C_a^b)]}.$$

Thus, in the vicinity of this surface, the electric potential distribution has the shape of a parabola:

$$\psi \approx \psi_b - 2\pi e_1(C_c^b - C_a^b)(b - y)^2/\varepsilon.$$

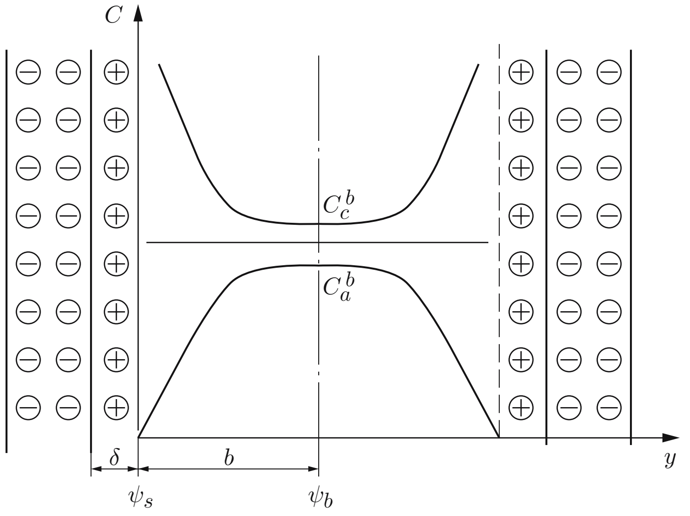

Fig. 2. Distributions of charges and electric potential in a pore.

Let us study the behavior of the potential near the surface of the clay flakes. Integration of the expression

$$\frac{du}{\sqrt{2A}\sqrt{C_c^b(\mathrm{e}^u - 1) + C_a^b(\mathrm{e}^{-u} - 1)}} = -dy$$

with respect to y from 0 to y and with respect to u from u_s to u yields

$$\sqrt{2AC_c^b}\, y = -\int\limits_{u_s}^{u} \frac{du}{\sqrt{\mathrm{e}^u - 1 + \alpha(\mathrm{e}^{-u} - 1)}} \approx \mathrm{e}^{-u_s/2} \int\limits_{0}^{u_s - u_1} \frac{du_1}{1 - u_1/2},$$

where $\alpha = C_a^b/C_c^b < 1$ and $u_1 = u_s - u$. Integrating the expression obtained and performing the corresponding substitutions for the electric potential in the vicinity of the charged surface, we have the following linear asymptotic relation:

$$\psi = \psi_s + \sqrt{8\pi kTC_c^b} \exp\Big(-\frac{e}{2kT}\,(\psi_s - \psi_b)y\Big).$$

Generally, Eq. (8) is solved numerically.

Introducing the independent variable $x = \sqrt{2AC_c^b}\, y$, we write expression (8) in the form

$$x = x_b - I(u), \qquad I(u) = \int\limits_{0}^{u} \frac{du}{\sqrt{\mathrm{e}^u + \alpha\,\mathrm{e}^{-u} - (\alpha + 1)}}, \qquad x_b = \sqrt{2AC_c^b}\, b = I(u_s).$$

Figure 3 gives the distribution of the weighed potential in the pore space between parallel planes at $\alpha = 0.8$ (on the ordinate is the variable $\xi = x_b - x$). In this case, the dimensionless distances from the particle surface to the middle plane of the pore $x_b = 3.80$, 3.85, and 4.40 correspond to the values $u_s = 2$, 4, and 6.

The results obtained correspond to the pore sizes and weighed potentials near the pore walls for bentonite clay at an absolute temperature $T \approx 300$ K (27°C) and $\varepsilon = 80$. In this case, $kT/(ze) \approx 27$ mV.

3. Charge Balance for Self-Polarization. Let an initially free electroneutral solution with anion concentration C_a^0 and cation concentration $C_c^0 = C_a^0$ interact with the surface of clay flakes. Under equilibrium conditions, the total anion charge in the pore space is conserved:

$$C_a^0 b = C_a^b \int\limits_{0}^{b} \mathrm{e}^{-u}\; dy = C_a^b \int\limits_{u_s}^{0} \mathrm{e}^{-y}\, \frac{dy}{du}\, du.$$

From this, using formulas (3) and (8), we obtain

$$C_a^0 I(u_s) = C_a^b I^-(u_s), \tag{9}$$

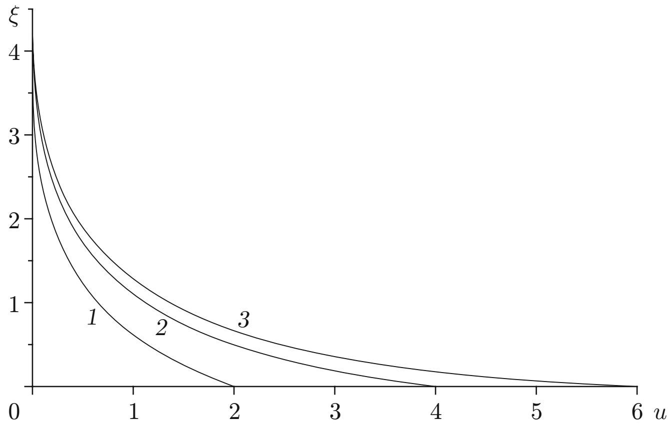

Fig. 3. Distribution of the weighed potential in the pore space between parallel planes for $\alpha = 0.8$ and $u_s = 2$ (1), 4 (2), and 6 (3).

where

$$I^-(u) = \int\limits_0^u \frac{\mathrm{e}^{-u}\ du}{\sqrt{\mathrm{e}^u + \alpha\,\mathrm{e}^{-u} - (\alpha+1)}}\,.$$

The balance equation for the total cation charge should take into account cation adsorption on the flake surface. Thus, in the equilibrium state, the mobile positive charges are linked by the relation

$$-q_s + C_c^b \int\limits_0^b \mathrm{e}^u\ dy = C_c^0 b. \tag{10}$$

We recall that $q_s = E_c/\Sigma$ is the specific exchange capacity. Relation (10) becomes

$$-\sqrt{2AC_c^b}\, q_s + C_c^b I^+(u_s) = C_c^0 I(u_s), \tag{11}$$

where

$$I^+(u_s) = \int\limits_0^{u_s} \frac{\mathrm{e}^u\ du}{\sqrt{\mathrm{e}^u + \alpha\,\mathrm{e}^{-u} - (\alpha+1)}}.$$

Taking into account the electroneutrality equation (4) for the mobile solution, from Eqs. (9) and (11) we obtain the electric equilibrium condition for the pore solution of a clay-containing rock in the state of self-polarization. This condition is written as

$$\sqrt{2A/C_c^b}\, q_s = I^+ - \alpha I^-. \tag{12}$$

Let a clay mineral be saturated with a solution of table salt NaCl. We consider the following examples.

1. $\alpha = 0.8$, $u_s = 4$, $\varepsilon = 80$, and $2A = 10^{16}$ m/mole. Then, we obtain $I^+ = 16.69$ and $I^- = 2.7$. In the middle plane, the cation concentration $C_c^b = q_s^2/(I^+ - I^-)^2 = 0.0474$ mole/liter $= 2.77$ g/liter and the anion concentration $C_a^b = 0.0379$ mole/liter; $x_b = 3.85$; $b = x_b/\sqrt{2AC_c^b} = 56 \cdot 10^{-10}$ m. The pore diameter is $2b = 112 \cdot 10^{-10}$ m. The concentration of the equilibrium solution is obtained from formula (9): $C_a^b = I^-/x_b \approx 0.0265$ mole/liter $=$ 1.55 g/liter.

2. $\alpha = 0.95$ and $u_s = 6$. Then, other things being equal, $x_b = 5.0$, $I^+ = 43.76$, $I^- = 3.89$, $C_c^b = 0.368$ g/liter, and $b \approx 2 \cdot 10^{-8}$ m.

We determine the average integral weighed potential over the rock pore space from the formula

$$\langle u \rangle = \frac{1}{x_b} \int\limits_0^{x_b} u(x)\, dx. \tag{13}$$

TABLE 1

Dependence of the Quantity $\langle u\rangle$ on α and u_s

α	$\langle u\rangle$		
	$u_s = 2$	$u_s = 4$	$u_s = 6$
0.80	0.440	0.799	0.888
0.90	0.439	0.734	0.887
0.95	0.411	0.656	0.809

We denote $I_1 = x_b - I(u)$. After simple transformations related to the change of integration variables, from formula (13) we find the double integral

$$\langle u\rangle = \frac{1}{x_b}\int\limits_0^{u_s} I_1(u)\,du.$$

By numerical integration for various values of α and u_s, we obtain the values of the average integral quantity $\langle u\rangle$ given in Table 1.

For bentonite clay at $T \approx 300$ K (27°C), $\varepsilon = 80$, $kT/(ze) \approx 27$ mV, the definition of the weighed potential implies the relation

$$\langle u\rangle = (\psi_b - \langle\psi\rangle)/27.$$

Actually, existing devices can measure potentials $\langle\psi\rangle$ averaged over a certain volume. For beds with undisturbed charge balance, $\langle\psi\rangle = 0$, i.e., the average potential difference is equal to zero relative to the reference point $\psi_b = 27\langle u\rangle$ mV. Generally, the potential of the reference point is expressed as

$$\psi_b = \langle u\rangle kT/(ze).$$

We note that the equilibrium condition for the total anion charge implies

$$C_a^0 = C_a^b I^-(u_s)/I(u_s) = \alpha C_c^b I^-(u_s)/I(u_s).$$

Substituting the expression $C_c^b = 2Aq_s(I^+ - I^-)^{-2}$ into this formula from Eq. (12), we obtain an analog of the Henry law for equilibrium sorption:

$$C_a^0 = \gamma E_c^2. \tag{14}$$

Here

$$\gamma = \frac{2A\alpha I^-(u_s)}{I(u_s)(I^+(u_s) - \alpha I^-(u_s))^2\Sigma^2}$$

(I^+ and I^- are the total cation and anion charges in a pore).

Conclusions. The main propositions of electrical double layer theory allow one to obtain conditions for the equilibrium state of clay rocks. This state is described by relations (4), (10), (12), and (14), which link the characteristic physical and chemical parameters of a clay rock and the solution saturating its pore space. The results obtained provide a theoretical justification for the occurrence of spontaneous polarization potentials of rocks during disturbance of the natural electrical equilibrium of rock strata, for example, in making holes with drilling mud infiltration. The sign of the self-polarization potential depends on the ratio of the ionic forces of the filtrate and native water in layers. The presence of a fresh filtrate is responsible for the occurrence of positive self-polarization potentials; if the filtrate is more salty than natural water, the self-polarization potential has a negative sign. The value of the measured potential depends on the sorption capacity and the content of clay in the rock.

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