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Electrical cross effects in porous media with ice inclusions. Part II: Double electrical layer mechanism

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ABSTRACT

The paper continues theoretical studying the heat and mass transfer in the biporous material with the coupled phase transformations. The fine-pored part of the medium is saturated by electrolytic solution and has osmotic and electroosmotic properties. Ice is contained in coarse pores.

At the low solution concentration the electric polarization of the medium induced by the temperature gradient may be up to 1 V/K.

1. Introduction

Freezing the fine-grained soils leads to the redistribution of the medium components, formation of the cryogenic structures, and appearance of the electrical potential difference between the frozen and unfrozen soils [1,2]. The source of all changes locates in the transition region ("frozen fringe") of the medium, which contains ice and adequate quantity of liquid phase. The system studied (Fig. 1) may be considered as the simplest model of the frozen fringe [3].

Heat and mass exchange in the similar media is accompanied by the ice movement relative to the mineral component and has some distinctive features.

It is well known, that the phase transition temperature of solid–liquid in confined space falls with decreasing the cavity size [4]. Therefore the temperature region of the system existence is limited by the melting temperature of the bulk ice and the freezing-point of water into the fine-pored medium.

In the previous paper it was supposed that the liquid movement through the fine-pored element of the biporous medium (Fig. 1) is subjected to Darcy's law. This assumption is valid for relatively macroporous bodies. In that case, the temperature region of existence is less than tenth parts of a degree. In practice that interval may be considerably greater. For example, the freezing-point of water in clays may be on a degree of Celsius below that of bulk water. In this case, the liquid flow through the fine-pored medium is subjected to more complicated law [5].

A purpose of the presented paper is studying the features of the heat and mass transfer through the biporous medium with ice inclusion, the fine-pored part of that has osmotic and electroosmotic properties.

2. Problem statement

Consider the unidimensional stationary process of the heat and mass transfer through the specific biporous medium (Fig. 1). Detailed specification of its properties is given earlier [6]. Here, it will be presented major ones. The fine-pored medium (E_2) is saturated by binary solution of strong electrolyte. Elements of E_1 and E_2 are homogeneous and isotropic. Framework of the porous medium is rigid, does not react with solute matter. Ice rejects all foreign matter. The fine-pored medium has osmotic and electroosmotic properties. Thermodynamic conditions forbid ice from penetrating in element E_2.

The ice inclusion may move relative to framework of the porous medium. That movement is realized due to regelation and is accompanied by the coupled phase transitions of melting–freezing.

Heat and mass problem for the medium as whole is reduced to the similar problem for a separate cell (Fig. 2).

2.1. Heat and mass transfer equations

Fix the system co-ordinate to the mineral framework of the medium. Neglecting the convective transport of energy the

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Nomenclature

b	height of the cell [m], Fig. 2
C	transport coefficient
c_k	amount concentration of k-ion [mol m^{-3}]
c_s	amount concentration of solution [mol m^{-3}]
c_{s0}	average amount concentration [mol m^{-3}]
D_k	diffusion coefficient of k-ion [m^2 s^{-1}]
e	elementary charge, $e = 1.602 \times 10^{-19}$ C
F	Faraday constant, $F = 96{,}484$ [C mol^{-1}]
J_e	current density across the base of the cell [A m^{-2}]
J_q	heat flow across the base of the cell [W m^{-2}]
J_s	molar solute flow across the base of the cell [mol m^{-2} s^{-1}]
J_V	volume flow across the base of the cell [m s^{-1}]
J_w	molar flow of water across the base of the cell [mol m^{-2} s^{-1}]
$\mathbf{j}_e$	current density [A m^{-2}]
$\mathbf{j}_k$	molar flux of k-ion [mol m^{-2} s^{-1}]
$\mathbf{j}_q$	heat flux [W m^{-2}]
$\mathbf{j}_s$	molar solute flux [mol m^{-2} s^{-1}]
$\mathbf{j}_V$	volume flux [m s^{-1}]
$\mathbf{j}_w$	molar water flux [mol m^{-2} s^{-1}]
k_B	Boltzmann constant, $k_B = 1.38 \times 10^{-23}$ J K^{-1}
K_h	hydroconductivity coefficient of fine-pored medium E$_2$[m^3 s kg^{-1}]
$\mathbf{n}$	unit vector
p	liquid pressure [Pa]
R	radius of ice inclusion [m]
R_g	gas constant, $R_g = 8.31$ J K^{-1}mol^{-1}
S_a	area of the cell base [m^2], Fig. 2
T	temperature [K]
T_0	temperature of ice–water equilibrium at 10^5 Pa,$T_0 = 273.15$ K
u_k	electric mobility of k-ion [m^2 V^{-1} s^{-1}]
V_i	molar volume of ice [m^3 mol^{-1}]
V_k	partial molar volume of k-ion in solution [m^3 mol^{-1}]
V_w	partial molar volume of water in solution [m^3 mol^{-1}]
$\mathbf{v}_i$	velocity of ice [m s^{-1}]
X	thermodynamical force
z_k	charge number of k-ion

Greek symbols

κ	latent heat of fusion [J mol^{-1}]
λ_1	thermal conductivity of ice [W m^{-1} K^{-1}]
λ_2	thermal conductivity of fine-pored medium [W m^{-1} K^{-1}]

$\Delta\lambda_{21} = \lambda_2 - \lambda_1$

μ	chemical potential [J mol^{-1}]
ν_k	number of k-ion in a solute molecule

Subscripts

i	ice
q	heat
R	surface of inclusion
s	solute
w	water

Dimensionless parameters

$\alpha = \frac{\pi R^2}{S_a}$

$\beta = \frac{2R}{b}$

$\varepsilon_t^2 = \frac{|\Delta\lambda_{21}|\alpha}{\lambda_2 - \Delta\lambda_{21}\alpha}$

$\varepsilon_p^2 = \frac{\alpha}{1-\alpha}$

$\varepsilon_{t0} = \beta\left(\frac{\lambda_2}{\lambda_1} - 1\right)$

$$f_1 = \begin{cases} \frac{2\varepsilon_t}{(1-\varepsilon_t^2)\ln\left|\frac{1+\varepsilon_t}{1-\varepsilon_t}\right|} & \text{where } \Delta\lambda_{21} < 0 \\ \frac{\varepsilon_t}{(1+\varepsilon_t^2)\mathrm{arctg}\varepsilon_t} & \text{where } \Delta\lambda_{21} > 0 \end{cases}$$

$$f_t = \begin{cases} \frac{(1-f_1)}{[\beta+(1-\beta)f_1]} \cdot \frac{(\varepsilon_t^2-1)}{\varepsilon_t^2} & \text{where } \Delta\lambda_{21} < 0 \\ \frac{(1-f_1)}{[\beta+(1-\beta)f_1]} \cdot \frac{(\varepsilon_t^2+1)}{\varepsilon_t^2} & \text{where } \Delta\lambda_{21} > 0 \end{cases}$$

$f_q = \frac{f_1}{\beta+(1-\beta)f_1}$

$I_{3t} = \frac{1}{\varepsilon_{t0}} - \frac{2}{\varepsilon_{t0}^2} + \frac{2}{\varepsilon_{t0}^3}\ln(1+\varepsilon_{t0})$

$I_{4t} = \frac{2}{3\varepsilon_{t0}} - \frac{1}{\varepsilon_{t0}^2} + \frac{2}{\varepsilon_{t0}^3} - \frac{2}{\varepsilon_{t0}^4}\ln(1+\varepsilon_{t0})$

$I_\lambda = (1-\alpha) + \frac{2\alpha}{\varepsilon_{t0}^2}[\varepsilon_{t0} - \ln(1+\varepsilon_{t0})]$

$f_2 = \frac{\varepsilon_p}{(1+\varepsilon_p^2)\mathrm{arctg}\varepsilon_p}$

$f_p = \frac{(1-f_2)(1+\varepsilon_p^2)}{[\beta+(1-\beta)f_2]\varepsilon_p^2}$

$f_w = \frac{f_2}{\beta+(1-\beta)f_2}$

$I_{3e} = 1 + \frac{2}{\beta} + \frac{2}{\beta^2}\ln(1-\beta)$

$I_\varepsilon = 1 - \alpha - \frac{2\alpha}{\beta^2}[\beta + \ln(1-\beta)]$

Other symbols

∇	vector gradient operator
∇_b	difference gradient operator, for example, $\nabla_b T = \frac{T_2-T_1}{b}$

temperature distribution in the elements of E$_1$ and E$_2$ is subjected to Laplace's equation:

$$\Delta T = 0 \tag{1}$$

The mass transfer equations will be given below in more detail. Three constituents of solution are transferred through the element E$_2$.

Neglecting the thermoosmotic properties of the fine-pored medium the matter fluxes depend linearly on the gradients of pressure, concentration, and electrical potential:

$$\mathbf{j}_V = k_{pp}\nabla p + k_{pe}\nabla\varphi + k_{ps}\nabla c_s \tag{2}$$

$$\mathbf{j}_e = k_{ep}\nabla p + k_{ee}\nabla\varphi + k_{es}\nabla c_s \tag{3}$$

$$\mathbf{j}_s = k_{sp}\nabla p + k_{se}\nabla\varphi + k_{ss}\nabla c_s \tag{4}$$

where $k_{pp}, k_{pe}, \ldots, k_{ss}$ – transfer coefficients, those are not independent. Relations between them follow from Onsager's reciprocity principle [7,6]:

$$k_{pe} = k_{ep} \tag{5}$$

$$k_{sp} = c_s\left(k_{pp} - k_\pi k_{pe} - \frac{V_w}{\gamma_w}k_{ps}\right) \tag{6}$$

$$k_{se} = c_s\left(k_{ep} - k_\pi k_{ee} - \frac{V_w}{\gamma_w}k_{es}\right) \tag{7}$$

where k_π is a parameter, $\gamma_w = \frac{\partial\mu_w}{\partial c_s}$, μ_w – chemical potential of water in solution.

Express k-coefficients in terms of measurable values.

The solute molecules in the electrolyte solution dissociate into ions, those interact with the mineral framework of porous medium

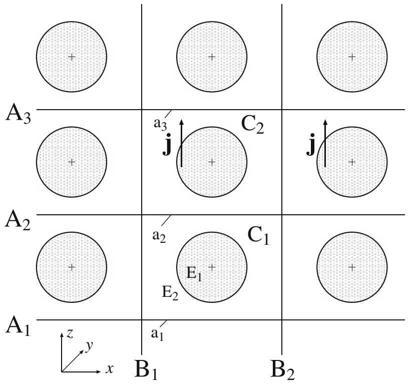

Fig. 1. A fragment of the model porous medium. E$_1$ – ice inclusion, E$_2$ – fine-pored medium.

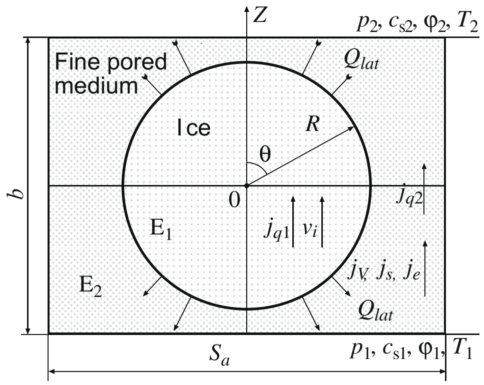

Fig. 2. Scheme of fluxes in an elementary cell. Q_{lat} is heat production at the phase transition surface.

and form the double electrical layer near the interface. When liquid flows through porous medium the ion velocity in the double electrical layer is different from the velocity of ions in the remainder of the solution. If the double layer thickness is comparable with the pore size then the average ion velocity is not equal to the average velocity of the solution constituents even though the gradients of electrical potential and solution concentration equal zero. Introduce into consideration the entrainment factors δ_k $(k = 1, 2)$ and write the transfer equation for ions in porous medium as follows:

$$\mathbf{j}_k = -c_k u_k \nabla\varphi - D_k \nabla c_k + \delta_k c_k \mathbf{j}_V, \quad k = 1, 2 \tag{8}$$

In general case the values of D_k, u_k differ from the corresponding ones of the volumetric solution and must be received by special measurements [8].

When $\delta_1 = \delta_2 = 1$ the relation (8) gives the known equation for the ion movement in the volumetric electrolyte solution [9].

Assume, that the Einstein relation between the diffusion coefficient and the ionic mobility is valid for solution in porous media as for the bulk one:

$$\frac{D_k}{u_k} = \frac{R_g T}{F z_k}, \quad k = 1, 2$$

By definition the current density $\mathbf{j}_e$ and the molar solute flux $\mathbf{j}_s$ are presented in terms of the molar fluxes of ions $\mathbf{j}_1$ and $\mathbf{j}_2$:

$$\mathbf{j}_e = \tilde{z}_1 \mathbf{j}_1 + \tilde{z}_2 \mathbf{j}_2 \tag{9}$$

$$\mathbf{j}_s = \chi_1 \mathbf{j}_1 + \chi_2 \mathbf{j}_2 \tag{10}$$

where $\tilde{z}_k = F z_k (k = 1, 2)$; $\chi_1 = \frac{u_2}{v_1(u_2 - u_1)}$; $\chi_2 = \frac{u_1}{v_2(u_1 - u_2)}$.

Let us write the volume flux $\mathbf{j}_V$ in the general way having regard to the osmotic and electroosmotic properties of porous medium:

$$\mathbf{j}_V = -K_h \nabla p - K_e \nabla\varphi + K_{os} \nabla c_s \tag{11}$$

In most cases the K-coefficients are positive [10]. That circumstance determines choice of signs in Eq. (11).

The explicit form of the k-coefficients and the values of $\delta_1, \delta_2, k_\pi$ are found from Eqs. (2)–(11) [11]:

$$k_{pp} = -K_h; \quad k_{pe} = -K_e; \quad k_{ps} = K_{os} \tag{12}$$

$$k_{ep} = -K_e; \quad k_{ee} = -c_s k_u - \frac{K_e^2}{K_h}; \quad k_{es} = -k_D \tag{13}$$

$$k_{sp} = -c_s K_h \left(1 + \frac{V_w}{\gamma_w} \frac{K_{os}}{K_h} - \frac{k_\pi K_e}{K_h}\right);$$

$$k_{se} = -c_s K_e \left(1 + \frac{V_w}{\gamma_w} \frac{K_{os}}{K_h} - \frac{k_\pi K_e}{K_h}\right); \quad k_{ss} = -D_n \tag{14}$$

where $k_\pi = -\frac{V_w k_D}{c_s \gamma_w k_u}\left(1 + \frac{K_e K_{os}}{k_D K_h}\right)$; $D_n = \frac{(v_1 + v_2) D_1 D_2}{v_2 D_1 + v_1 D_2}$; $k_D = \tilde{z}_1 v_1 D_1 + \tilde{z}_2 v_2 D_2$; $k_u = \tilde{z}_1 v_1 u_1 + \tilde{z}_2 v_2 u_2$.

At the steady-state the conservation law for the solution constituents has the simple form:

$$\nabla \cdot \mathbf{j}_w = 0; \quad \nabla \cdot \mathbf{j}_k = 0, \quad k = 1, 2 \tag{15}$$

where the flux $\mathbf{j}_w$ is connected with the volume flux $\mathbf{j}_V$ by the following definition:

$$\mathbf{j}_V = V_1 \mathbf{j}_1 + V_2 \mathbf{j}_2 + V_w \mathbf{j}_w \tag{16}$$

The laws of transfer (2)–(4) and conservation of (15) together with the definitions of (9), (10) and (16) allow to find the differential equations for the thermodynamic potential p, c_s, and φ in the region of E$_2$ [11]. The equations and the boundary conditions turn out to be complicated due to some of k-coefficients depend on the concentration c_s. In the present paper the system will be considered near equilibrium state. In this case the k-coefficients containing the value c_s will be accepted as constants at the average concentration of solution in the elementary cell (Fig. 2).

Linear transformations of the equation set (2)–(4), (9), (10), (15), (16) lead to Laplace's equations for the thermodynamic potentials of p, c_s, and φ:

$$\Delta p = 0, \quad \Delta\varphi = 0, \quad \Delta c_s = 0; \quad \mathbf{r} \in \mathrm{E}_2 \tag{17}$$

An equation for finding the electrical potential in the region of E$_1$ (uniform dielectric) is also Laplace's equation.

$$\Delta\varphi = 0; \quad \mathbf{r} \in \mathrm{E}_1 \tag{18}$$

2.2. Boundary conditions

At the cell bases the thermodynamic potentials are constants (Fig. 2):

– *lower surface* $(z = -b/2)$*:*

$$T = T_1, \quad p = p_1, \quad c_s = c_{s1}, \quad \varphi = \varphi_1 \tag{19}$$

– *upper surface* $(z = b/2)$*:*

$$T = T_2, \quad p = p_2, \quad c_s = c_{s2}, \quad \varphi = \varphi_2 \tag{20}$$

Because of symmetry the fluxes through the lateral sides of the cell are equal to zero:

$$\frac{\mathrm{d}T}{\mathrm{d}l} = 0, \quad \frac{\mathrm{d}p}{\mathrm{d}l} = 0, \quad \frac{\mathrm{d}c_s}{\mathrm{d}l} = 0, \quad \frac{\mathrm{d}\varphi}{\mathrm{d}l} = 0 \tag{21}$$

where $\frac{\mathrm{d}}{\mathrm{d}l}$ is the derivative normal to the lateral surface of the cell.

At the inclusion surface the boundary conditions are received from the physical requirements as follow: continuity of temperature and electrical potential, conservation of heat and water, maintenance of the ice purity.

Those requirements give the following two relations for the temperature T:

$$T|_{r=R-0} = T|_{r=R+0} \tag{22}$$

$$-\lambda_1 \frac{\partial T}{\partial r}\bigg|_{r=R-0} - \left(-\lambda_2 \frac{\partial T}{\partial r}\bigg|_{r=R+0}\right) = \kappa v_i \cos\theta / V_i \tag{23}$$

where r, θ are spherical co-ordinates.

The water and solute matter fluxes satisfy the equations as follows:

$$j_{wr}|_{r=R+0} = v_i \cos\theta / V_i \ \text{(mass balance)} \tag{24}$$

$$j_{kr}|_{r=R+0} = 0, \quad k = 1, 2 \ \text{(foreign matter rejection)} \tag{25}$$

By symmetry, the ice velocity is parallel to Z-axis. That is reflected in Eqs. (23), (24).

Taking into account of the definitions (9), (10), (16) and the relations (24), (25), the transfer Eqs. (2)–(4) may be presented in the following matrix form:

$$(\mathbf{k}) \cdot \begin{pmatrix} \frac{\partial p}{\partial r} \\ \frac{\partial \varphi}{\partial r} \\ \frac{\partial c_s}{\partial r} \end{pmatrix}\Bigg|_{r=R+0} = \frac{V_w v_i \cos\theta}{V_i} \cdot \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \tag{26}$$

where $(\mathbf{k})$ is matrix of the transfer coefficients: $(\mathbf{k}) = \begin{pmatrix} k_{pp} & k_{pe} & k_{ps} \\ k_{ep} & k_{ee} & k_{es} \\ k_{sp} & k_{se} & k_{ss} \end{pmatrix}$.

Multiplying the expression (26) by the inverse matrix $(\bar{\mathbf{k}})$ gives the differential equations for the thermodynamic potentials at the inclusion surface:

$$\frac{\partial p}{\partial r}\bigg|_{r=R+0} = \bar{k}_{sp} \frac{V_w v_i \cos\theta}{V_i} \tag{27}$$

$$\frac{\partial \varphi}{\partial r}\bigg|_{r=R+0} = \bar{k}_{ep} \frac{V_w v_i \cos\theta}{V_i} \tag{28}$$

$$\frac{\partial c_s}{\partial r}\bigg|_{r=R+0} = \bar{k}_{sp} \frac{V_w v_i \cos\theta}{V_i} \tag{29}$$

where $\bar{k}_{pp}, \bar{k}_{ep}, \bar{k}_{sp}$ are elements of the inverse matrix $(\bar{\mathbf{k}})$.

In addition, a value of the electrical potential at the ice – porous medium boundary must satisfy the continuity condition:

$$\varphi|_{r=R-0} = \varphi|_{r=R+0} \tag{30}$$

Assume, that the external force fields are absent. So the ice velocity v_i, that is in Eqs. (23), (27)–(29), is found from the conditions of the mechanical equilibrium of the inclusions and the local phase equilibrium of ice and water [6]

$$\frac{V_w}{V_i}\Theta_0(p_R) - \frac{\kappa}{T_0 V_i}\Theta_0(T_R) + \frac{\gamma_w}{V_i}\Theta_0(c_{sR}) = 0 \tag{31}$$

where Θ_0 is a linear functional: $\Theta_0(f) = \int_0^\pi f(\theta)\cos\theta \sin\theta \, d\theta$; p_R, T_R, and c_{sR} is liquid pressure, temperature, and molar concentration of solution at the inclusion surface.

The equation set (19)–(23), (27)–(31) is the boundary condition for the heat and mass transfer problem (1), (17), (18).

The problem will be solved analytically by the "anisotropic conductivity" method and numerically by the modified "control volume" method.

3. Heat transfer problem

The heat problem was solved early by the "anisotropic conductivity" method [12]. The final results are presented below.

The temperature distribution T_R at the inclusion surface and the thermal flux J_q through the bases of the cell are following:

– *infinite horizontal conductivity:*

$$T_R(\theta) = \begin{cases} \frac{\kappa v_i}{V_i \Delta\lambda_{21}} R\cos\theta + \left(\nabla_b T - \frac{\kappa v_i}{V_i \Delta\lambda_{21}}\right) \frac{R}{\beta + f_1(1-\beta)} \frac{\ln\left|\frac{1+\varepsilon_t \cos\theta}{1-\varepsilon_t \cos\theta}\right|}{\ln\left|\frac{1+\varepsilon_t}{1-\varepsilon_t}\right|} + T_m & \text{where } \Delta\lambda_{21} < 0 \\ \frac{\kappa v_i}{V_i \Delta\lambda_{21}} R\cos\theta + \left(\nabla_b T - \frac{\kappa v_i}{V_i \Delta\lambda_{21}}\right) \frac{R}{\beta + f_1(1-\beta)} \cdot \frac{\operatorname{arctg}(\varepsilon_t \cos\theta)}{\operatorname{arctg}\varepsilon_t} + T_m & \text{where } \Delta\lambda_{21} > 0 \end{cases} \tag{32}$$

$$J_q = \lambda_2 \left\{ -\frac{\kappa v_i}{V_i \Delta\lambda_{21}} - \left[\nabla_b T - \frac{\kappa v_i}{V_i \Delta\lambda_{21}}\right] \cdot \frac{f_1}{\beta + f_1(1-\beta)} \right\} \tag{33}$$

– *zero horizontal conductivity:*

$$T_R(\theta) = \frac{\lambda_2}{\lambda_1} \frac{R\cos\theta}{1 + \varepsilon_{t0}|\cos\theta|} \left(\nabla_b T - \frac{\kappa}{V_i} \frac{(1 - \beta|\cos\theta|)}{\lambda_2} v_i\right) + T_m \tag{34}$$

$$J_q = -\lambda_2 I_\lambda \nabla_b T - \frac{\lambda_2 \kappa \alpha \beta}{\lambda_1 V_i} v_i I_{3t} \tag{35}$$

where $T_m = (T_1 + T_2)/2$.

4. Mass transfer problem and transport coefficients

The problem consists in finding the matter flows of J_V, J_s, and J_e through the bases of the cell at the boundary conditions (19)–(21). The mass transfer in liquid phase is realized only in the element E_2 (Fig. 2). At steady-state the matter balance for any volume confined by the surface S produces the following relations:

$$\int_S \left(\mathbf{j}_w + \frac{\mathbf{v}_i}{V_i}\right) \cdot \mathbf{n} \, dS = 0 \tag{36}$$

$$\int_S \mathbf{j}_k \cdot \mathbf{n} \, dS = 0, \quad k = 1, 2 \tag{37}$$

where $\mathbf{n}$ is unit vector normal to dS.

Solution of the problem by the "anisotropic conductivity" method is presented below.

4.1. Infinite horizontal conductivity

The thermodynamic potentials do not depend on the horizontal co-ordinates due to the anisotropic conductivity.

In the range of $z \in [-b/2, -R]$ and $[R, b/2]$ the medium is homogeneous. In direction of Z-axis the mass flows of j_V, j_s, and j_e are constant and equal to the flows of J_V, J_s, and J_e through bases of the cell. The equations may be written in the difference form:

$$\begin{pmatrix} J_V \\ J_e \\ J_s \end{pmatrix} = \frac{2}{b - 2R} \cdot (\mathbf{k}) \cdot \begin{pmatrix} p_1' - p_1 \\ \varphi_1' - \varphi_1 \\ c_{s1}' - c_{s1} \end{pmatrix} \tag{38}$$

$$\begin{pmatrix} J_V \\ J_e \\ J_s \end{pmatrix} = \frac{2}{b - 2R} \cdot (\mathbf{k}) \cdot \begin{pmatrix} p_2 - p_2' \\ \varphi_2 - \varphi_2' \\ c_{s2} - c_{s2}' \end{pmatrix} \tag{39}$$

where $(p_1', c_{s1}', \varphi_1')$ and $(p_2', c_{s2}', \varphi_2')$ are pressure, concentration, and electrical potential in sections $z = -R$ and $z = R$ accordingly.

Summing and subtracting of (38) and (39) gives the following relations:

$$\frac{1}{2}\begin{pmatrix} p_1' + p_2' \\ \varphi_1' + \varphi_2' \\ c_{s1}' + c_{s2}' \end{pmatrix} = \frac{1}{2}\begin{pmatrix} p_1 + p_2 \\ \varphi_1 + \varphi_2 \\ c_{s1} + c_{s2} \end{pmatrix} \equiv \begin{pmatrix} p_m \\ \varphi_m \\ c_{sm} \end{pmatrix} \tag{40}$$

$$\begin{pmatrix} J_V \\ J_e \\ J_s \end{pmatrix} = \frac{1}{(1-\beta)} \cdot (\mathbf{k}) \cdot \begin{pmatrix} \nabla_b p \\ \nabla_b \varphi \\ \nabla_b c_s \end{pmatrix} - \frac{1}{(1-\beta)} \cdot (\mathbf{k}) \cdot \begin{pmatrix} \nabla_b p' \\ \nabla_b \varphi' \\ \nabla_b c_s' \end{pmatrix} \tag{41}$$

In order to determine the explicit form of the column $\begin{pmatrix} \nabla_b p' \\ \nabla_b \varphi' \\ \nabla_b c_s' \end{pmatrix}$, the filtration, diffusion, and electrical conductivity problems must be solved in the region of $z \in [-R, R]$.

Let us consider a cell volume confined by the lateral sides and of the cell, its bottom, and the horizontal section intersecting Z-axis in the point of z ($|z| < R$) (Fig. 3). Applying Eqs. (36), (37) to the selected volume and having in view the definitions (9)–(11) gives

$$\frac{v_i}{V_i}(S_a - S_2(z)) + \frac{j_V(z)}{V_w} S_2(z) - \frac{J_V}{V_w} S_a = 0 \tag{42}$$

$$j_e(z) S_2(z) = J_e S_a \tag{43}$$

$$j_s(z) S_2(z) = J_s S_a \tag{44}$$

where $S_2(z)$ is area of the fine-pored medium E_2 in the horizontal section $z : S_2(z) = S_a - \pi(R^2 - z^2)$.

Transforming the equations of (42)–(44) and representing the result in the matrix form gives:

$$\begin{pmatrix} j_V(z) \\ j_e(z) \\ j_s(z) \end{pmatrix} = \frac{S_a}{S_2(z)} \cdot \begin{pmatrix} J_V \\ J_e \\ J_s \end{pmatrix} + \frac{v_i V_w}{V_i} \cdot \left(1 - \frac{S_a}{S_2(z)}\right) \cdot \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \tag{45}$$

Substituting j_V, j_s, and j_e in (45) from (2)–(4) and multiplying the resultant expression by the inverse matrix $(\bar{\mathbf{k}})$ gives the differential equations for the potentials of p, c_s, φ

$$\begin{pmatrix} \frac{\mathrm{d}p}{\mathrm{d}z} \\ \frac{\mathrm{d}\varphi}{\mathrm{d}z} \\ \frac{\mathrm{d}c_s}{\mathrm{d}z} \end{pmatrix} = \frac{S_a}{S_2(z)} \cdot (\bar{\mathbf{k}}) \cdot \begin{pmatrix} J_V \\ J_e \\ J_s \end{pmatrix} + \frac{v_i V_w}{V_i} \cdot \left(1 - \frac{S_a}{S_2(z)}\right) \cdot (\bar{\mathbf{k}}) \cdot \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \tag{46}$$

Integrating (46) with respect to z from -R to R gives the required column:

$$\begin{pmatrix} \nabla_b p' \\ \nabla_b \varphi' \\ \nabla_b c_s' \end{pmatrix} = \frac{\beta}{f_2} \cdot (\bar{\mathbf{k}}) \cdot \begin{pmatrix} J_V \\ J_e \\ J_s \end{pmatrix} + \frac{v_i V_w \beta}{V_i} \cdot \left(1 - \frac{1}{f_2}\right) \cdot (\bar{\mathbf{k}}) \cdot \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \tag{47}$$

The explicit form for the matter fluxes follows from the solution of the equation set of (41) and (47):

$$\begin{pmatrix} J_V \\ J_e \\ J_s \end{pmatrix} = f_w \cdot (\mathbf{k}) \cdot \begin{pmatrix} \nabla_b p \\ \nabla_b \varphi \\ \nabla_b c_s \end{pmatrix} + \frac{v_i V_w}{V_i}(1 - f_w) \cdot \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \tag{48}$$

The expression (48) contains the unknown velocity v_i. In order to determine the value of v_i the thermodynamic potentials of T, p, c_s at the inclusion surface are needed to know. The temperature distribution is written earlier (Eq. (32)). Let us find the rest.

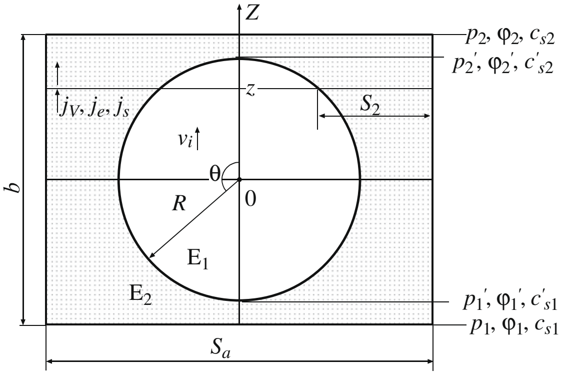

Fig. 3. Scheme of matter fluxes through the cell with infinite horizontal conductivity.

First of all, integrate Eq. (46) with respect to z from 0 to z:

$$\begin{pmatrix} p(z) - p_m \\ \varphi(z) - \varphi_m \\ c_s(z) - c_{sm} \end{pmatrix} = RF(z) \cdot (\bar{\mathbf{k}}) \cdot \begin{pmatrix} J_V \\ J_e \\ J_s \end{pmatrix} + \frac{v_i V_w}{V_i} \cdot (z - RF(z)) \cdot (\bar{\mathbf{k}}) \cdot \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \tag{49}$$

where $F(z) = \frac{S_a}{R} \int_0^z \frac{\mathrm{d}\zeta}{S_2(\zeta)}$.

Substituting the flows J_V, J_e, J_s from Eq. (48) in Eq. (49) and assuming $z = R\cos\theta$ gives the desired values:

$$\begin{pmatrix} p_R(\theta) \\ \varphi_R(\theta) \\ c_{sR}(\theta) \end{pmatrix} = Rf_w F(R\cos\theta) \cdot \begin{pmatrix} \nabla_b p \\ \nabla_b \varphi \\ \nabla_b c_s \end{pmatrix} + \frac{v_i V_i R}{V_i} \cdot (\cos\theta - f_w F(R\cos\theta)) \cdot (\bar{\mathbf{k}}) \cdot \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} + \begin{pmatrix} p_m \\ \varphi_m \\ c_{sm} \end{pmatrix} \tag{50}$$

The properties of the functional Θ_0 as follows: $\Theta_0(\mathrm{const}) = 0$, $\Theta_0(\cos\theta) = \frac{2}{3}$, $\Theta_0(F) = \frac{f_p}{f_w}$ enable to find the value of Θ_0 at the potentials of p_R, φ_R, c_{sR} (50):

$$\Theta_0 \begin{pmatrix} p_R(\theta) \\ \varphi_R(\theta) \\ c_{sR}(\theta) \end{pmatrix} = Rf_p \cdot \begin{pmatrix} \nabla_b p \\ \nabla_b \varphi \\ \nabla_b c_s \end{pmatrix} + \frac{v_i V_w R}{V_i} \cdot \left(\frac{2}{3} - f_p\right) \cdot (\bar{\mathbf{k}}) \cdot \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \tag{51}$$

Calculating the value Θ_0 at the temperature function $T_R(\theta)$ (32) gives:

$$\Theta_0(T_R) = f_t R \nabla_b T + \left(\frac{2}{3} - f_t\right) \frac{\kappa R v_i}{V_i \Delta\lambda_{21}} \tag{52}$$

Substituting the appropriate values Θ_0 from (51), (52) in (31) gives the ice velocity v_i:

$$v_i = -\omega_{p1} \nabla p - \omega_{t1} \nabla T - \omega_{s1} \nabla c_s \tag{53}$$

where $\omega_{p1} = \frac{V_w}{V_i} \frac{f_p}{den_1}$; $\omega_{t1} = -\frac{\kappa}{T_0 V_i} \frac{f_t}{den_1}$; $\omega_{s1} = \frac{\gamma_w}{V_i} \frac{f_p}{den_1}$; $den_1 = \left(\frac{V_w}{V_i}\right)^2 \left(\frac{2}{3} - f_p\right)\bar{k}_{pp} + \left(\frac{\kappa}{V_i}\right)^2 \frac{(f_t - 2/3)}{T_0 \Delta\lambda_{21}} + \frac{\gamma_w V_w}{V_i^2}\left(\frac{2}{3} - f_p\right)\bar{k}_{sp}$. The replacement of the value v_i in Eqs. (33) and (48) by the right side of Eq. (53) leads to the required dependence between the fluxes and the thermodynamic forces:

$$\begin{pmatrix} J_V \\ J_e \\ J_s \\ J_q \end{pmatrix} = \begin{pmatrix} C_{pp} & C_{pe} & C_{ps} & C_{pq} \\ C_{ep} & C_{ee} & C_{es} & C_{eq} \\ C_{sp} & C_{se} & C_{ss} & C_{sq} \\ C_{qp} & C_{qe} & C_{qs} & C_{qq} \end{pmatrix} \begin{pmatrix} \nabla_b p \\ \nabla_b \varphi \\ \nabla_b c_s \\ X_q \end{pmatrix} \tag{54}$$

where $X_q = \frac{\nabla_b T}{T_0}$ and C-coefficients as follows:

$$\begin{aligned} &C_{pp} = k_{pp} f_w - \frac{V_w}{V_i} \alpha\beta f_p \omega_{p1}, \quad C_{pe} = k_{pe} f_w, \quad C_{ps} = k_{ps} f_w - \frac{V_w}{V_i} \alpha\beta f_p \omega_{s1}, \\ &C_{pq} = -\frac{V_w}{V_i} \alpha\beta f_p \omega_{t1} T_0 \\ &C_{ep} = k_{ep} f_w, \quad C_{ee} = k_{ee} f_w, \quad C_{es} = k_{es} f_w, \quad C_{eq} = 0 \\ &C_{sp} = k_{sp} f_w, \quad C_{se} = k_{se} f_w, \quad C_{ss} = k_{ss} f_w, \quad C_{sq} = 0 \\ &C_{qp} = \frac{\kappa}{V_i} \alpha\beta f_t \omega_{p1}, \quad C_{qe} = 0, \quad C_{qs} = \frac{\kappa}{V_i} \cdot \alpha\beta f_t \omega_{s1}, \\ &C_{qq} = \left(\frac{\kappa}{V_i} \cdot \alpha\beta f_t \omega_{t1} - \lambda_2 f_q\right) T_0 \end{aligned} \tag{55}$$

The direct verification shows that the C-coefficients (55) obey the relations similar Eqs. (5), (6) i.e. the Onsager reciprocal relations are valid for the system considered.

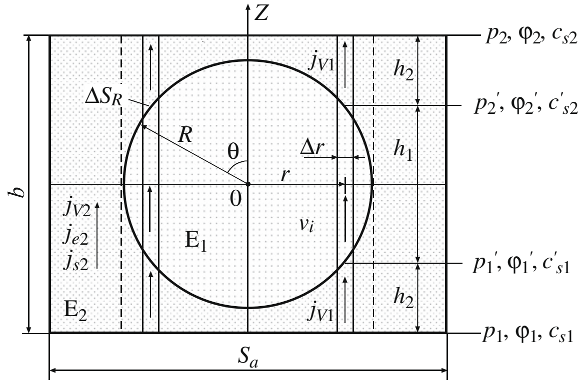

Fig. 4. Scheme of matter fluxes through the cell with zero horizontal conductivity.

4.2. Zero horizontal conductivity

The streamlines of the mass fluxes are parallel to Z-axis because of the anisotropy. Find the values of the mass flows across the bases of the cell and the pressure and concentration distribution at the ice surface.

Introduce into consideration the cylindrical co-ordinate system. In the region of $r > R$ the medium is homogeneous (Fig. 4), therefore the z-components of the fluxes do not depend on z co-ordinate. The values of j_{V2}, j_{e2}, j_{s2} may be expressed in terms of the potential gradients (2)–(4):

$$\begin{pmatrix} j_{V2} \\ j_{e2} \\ j_{s2} \end{pmatrix} = (\mathbf{k}) \cdot \begin{pmatrix} \nabla_b p \\ \nabla_b \varphi \\ \nabla_b c_s \end{pmatrix} \tag{56}$$

In the region of $r < R$ two conditions of the solute rejection and the water continuity lead to the following relation:

$$\begin{pmatrix} j_{V1} \\ j_{e1} \\ j_{s1} \end{pmatrix} = \frac{V_w v_i}{V_i} \cdot \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \tag{57}$$

The average matter fluxes across the bases of cell are defined by the ordinary way:

$$\begin{aligned} \begin{pmatrix} J_V \\ J_e \\ J_s \end{pmatrix} &= \alpha \begin{pmatrix} j_{V1} \\ j_{e1} \\ j_{s1} \end{pmatrix} + (1-\alpha) \begin{pmatrix} j_{V2} \\ j_{e2} \\ j_{s2} \end{pmatrix} \\ &= (1-\alpha)(\mathbf{k}) \cdot \begin{pmatrix} \nabla_b p \\ \nabla_b \varphi \\ \nabla_b c_s \end{pmatrix} + \alpha \frac{V_w v_i}{V_i} \cdot \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \end{aligned} \tag{58}$$

Let us turn to the second problem defining the liquid pressure and the solution concentration at the inclusion surface.

Select a thin cylindrical layer Δr (Fig. 4) and write the transfer Eqs. (2)–(4) for the upper and lower fine-pored columns:

$$\begin{pmatrix} j_{V1} \\ j_{e1} \\ j_{s1} \end{pmatrix} = \frac{1}{h_2} (\mathbf{k}) \cdot \begin{pmatrix} p_1' - p_1 \\ \varphi_1' - \varphi_1 \\ c'_{s1} - c_{s1} \end{pmatrix}; \quad \begin{pmatrix} j_{V1} \\ j_{e1} \\ j_{s1} \end{pmatrix} = \frac{1}{h_2} (\mathbf{k}) \cdot \begin{pmatrix} p_2 - p_2' \\ \varphi_2 - \varphi_2' \\ c_{s2} - c'_{s2} \end{pmatrix} \tag{59}$$

The values of $p_1', p_2', c'_{s1}, c'_{s2}$ constitute the potentials of p_R and c_{sR} (Fig. 4). Multiplying Eq. (59) by the inverse matrix $(\bar{\mathbf{k}})$, taking into account of Eq. (57), and presenting the value h_2 in terms of R and θ gives the explicit form of the required potentials

$$p_R(\theta) = \begin{cases} p_2 - \frac{V_w}{V_i} \bar{k}_{pp} v_i R\left(\frac{1}{\beta} - \cos\theta\right), & 0 \leqslant \theta \leqslant \frac{\pi}{2} \\ p_1 + \frac{V_w}{V_i} \bar{k}_{pp} v_i R\left(\frac{1}{\beta} + \cos\theta\right), & \frac{\pi}{2} \leqslant \theta \leqslant \pi \end{cases} \tag{60}$$

$$c_{sR}(\theta) = \begin{cases} c_{s2} - \frac{V_w}{V_i} \bar{k}_{sp} v_i R\left(\frac{1}{\beta} - \cos\theta\right), & 0 \leqslant \theta \leqslant \frac{\pi}{2} \\ c_{s1} + \frac{V_w}{V_i} \bar{k}_{sp} v_i R\left(\frac{1}{\beta} + \cos\theta\right), & \frac{\pi}{2} \leqslant \theta \leqslant \pi \end{cases} \tag{61}$$

Calculation of the functional Θ_0 at the values of $p_R, c_{sR}, T_{R,}$, defined by Eqs. (60), (61) and (34), produces the following result:

$$\Theta_0(p_R) = \frac{R}{\beta}\left[\nabla_b p - \frac{V_w}{V_i} \bar{k}_{pp} v_i \left(1 - \frac{2}{3}\beta\right)\right] \tag{62}$$

$$\Theta_0(c_{sR}) = \frac{R}{\beta}\left[\nabla_b c_{sR} - \frac{V_w}{V_i} \bar{k}_{sp} v_i \left(1 - \frac{2}{3}\beta\right)\right] \tag{63}$$

$$\Theta_0(T_R) = \frac{\lambda_2}{\lambda_1} R\left[I_{3t} \nabla_b T - \frac{\kappa v_i}{V_i \lambda_2} (I_{3t} - \beta I_{4t})\right] \tag{64}$$

Substituting Eqs. (62)–(64) in the condition of the mechanical and thermodynamic equilibrium (31) gives the ice velocity v_i:

$$v_i = -\omega_{p0} \nabla_b p - \omega_{t0} \nabla_b T - \omega_{s0} \nabla_b c_s \tag{65}$$

where $\omega_{p0} = \frac{V_w}{V_i} \frac{1}{den_0}$; $\omega_{t0} = -\frac{\kappa \lambda_2}{T_0 V_i \lambda_1} \frac{\beta I_{3t}}{den_0}$; $\omega_{s0} = \frac{\gamma_w}{V_i} \frac{1}{den_0}$

$$\begin{aligned} den_0 = &-\left(\frac{V_w}{V_i}\right)^2 \left(1 - \frac{2}{3}\beta\right) \bar{k}_{pp} + \left(\frac{\kappa}{V_i}\right)^2 \frac{\beta(I_{3t} - \beta I_{4t})}{T_0 \lambda_1} \\ &- \frac{\gamma_w V_w \bar{k}_{sp}}{V_i^2} \left(1 - \frac{2}{3}\beta\right). \end{aligned}$$

Substitution of the value v_i (51) in Eqs. (35) and (58) produces the heat and mass flows across the basis of the cell in the form (54) with the C-coefficients, as follows:

$$\begin{aligned} &C^0_{pp} = (1-\alpha)k_{pp} - \alpha \frac{V_w}{V_i} \omega_{p0}, \quad C^0_{pe} = (1-\alpha)k_{pe}, \\ &C^0_{ps} = (1-\alpha)k_{ps} - \alpha \frac{V_w}{V_i} \omega_{s0}, \\ &C^0_{pq} = -\alpha \frac{V_w}{V_i} T_0 \omega_{t0}, \\ &C^0_{ep} = (1-\alpha)k_{ep}, \quad C^0_{ee} = (1-\alpha)k_{ee}, \quad C^0_{es} = (1-\alpha)k_{es}, \quad C^0_{eq} = 0, \\ &C^0_{sp} = (1-\alpha)k_{sp}, \quad C^0_{se} = (1-\alpha)k_{se}, \quad C^0_{ss} = (1-\alpha)k_{ss}, \quad C^0_{sq} = 0, \end{aligned} \tag{66}$$

$$\begin{aligned} &C^0_{qp} = \frac{\lambda_2 \kappa}{\lambda_1 V_i} \alpha\beta \cdot I_{3t} \omega_{p0}, \quad C^0_{qe} = 0, \quad C^0_{qs} = \frac{\lambda_2 \kappa}{\lambda_1 V_i} \alpha\beta \cdot I_{3t} \omega_{s0}, \\ &C^0_{qq} = \left(\frac{\lambda_2 \kappa}{\lambda_1 V_i} \alpha\beta \cdot I_{3t} \omega_{t0} - \lambda_2 I_\lambda\right) T_0, \end{aligned}$$

Those satisfy the Onsager reciprocal relations.

The problem of heat and mass transfer is solved by the "anisotropic conductivity" method. It was found the extreme transfer coefficients, those define an range of variable. The transfer coefficients of the cell with the isotropic elements fall into the range. The main postulate of non-equilibrium thermodynamics, namely, the Onsager reciprocity principle turns out to be valid for the porous media with phase transformations.

5. Results

In this section it is presented some properties of the model biporous medium with the ice inclusions. All values are received by two methods. The first method is given in details. Essence of the modified control volume method is presumed to publish elsewhere.

The elementary cell (Fig. 2) is a cube. The fine-pored medium E_2 is saturated by the aqueous solution of NaCl, that is supposed to be ideal. In this case it is valid the following relation: $\gamma_w = -iR_g T V_w$, i – isotonic factor, $i = \nu_1 + \nu_2$. The thermal conductivity of the elements E_1 and E_2 are $\lambda_1 = 2.2\ \mathrm{W\,m^{-1}\,K^{-1}}$, $\lambda_2 = 1.54\ \mathrm{W\,m^{-1}\,K^{-1}}$ and the typical values of the diffusion constants in the porous medium

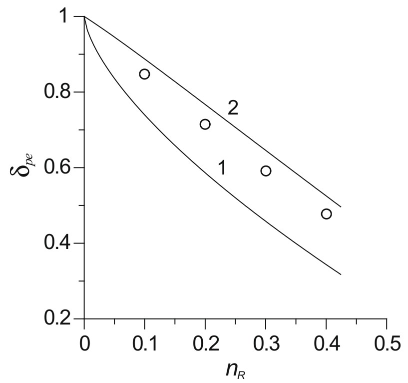

Fig. 5. The ratio coefficient δ_{pe} versus the volume fraction of ice n_R. Lines denote the cells with zero (1) and infinite (2) horizontal conductivity. Symbols are the numerical calculations.

are taken from the paper [8]: $D_{Na} = 4 \times 10^{-10}$ m^2 s^{-1} and $D_{Cl} = 6 \times 10^{-10}$ m^2 s^{-1}.

The coefficients of K_h, K_{os}, K_e in Eq. (16) are not independent. For example, the coefficient of K_e is practically equal to zero for the monodisperse soils with $K_h > 10^{-6}$ m^3 s kg^{-1}. With decreasing the soil hydroconductivity the value of K_e increases, reaches a maximum, and further, tends to zero [10]. In the region of the small values K_h that dependence of $K_e(K_h)$, constructed from data by H.W. Olsen [13] for kaolinite clay, has the following form:

$$K_e = \kappa_{eh}\sqrt{K_h}$$

where $\kappa_{eh} = \frac{1}{100}$ kg$^{\frac{1}{2}}$ m$^{\frac{1}{2}}$ V^{-1} s$^{-\frac{3}{2}}$.

Regarding the coefficient K_{os} it should be point out that the experiment gives the reflection or osmotic efficiency coefficient, σ [14–16]

$$\sigma = \left.\frac{\Delta p}{\Delta \pi}\right|_{\mathbf{j}_v = \mathbf{j}_e = 0} \tag{67}$$

where $\Delta\pi = iR_g T \Delta c_s$.

The value of σ for kaolinite clay is defined from the experimental data by H.W. Olsen [13] (Fig. 5). The experimental points is approximated the following function:

$$\sigma = \kappa_{es}/\sqrt{K_h}$$

where $\kappa_{es} = 10^{-8}$ m$^{\frac{3}{2}}$ s$^{\frac{1}{2}}$ kg$^{-\frac{1}{2}}$.

Express the coefficient of K_{os} in terms of the measured values. The equations of (2) and (3) at $X_q = 0$ and $\mathbf{j}_V = \mathbf{j}_e = 0$ lead to the following set:

$$k_{pp}\nabla p + k_{pe}\nabla\varphi + k_{ps}\nabla c_s = 0$$
$$k_{ep}\nabla p + k_{ee}\nabla\varphi + k_{es}\nabla c_s = 0$$

Eliminating the value $\nabla\varphi$ from the last set and using the explicit form of the k-coefficients (12), (13) with the definition (67) gives the following relation for the coefficient of K_{os}:

$$K_{os} = \frac{c_s \sigma i R_g T k_u K_h - k_D K_e}{c_s k_u + \frac{K_e^2}{K_h}}$$

In the present paper, all calculation results are received at the constant σ equal to 0.05.

5.1. Electroosmosis

Electroosmosis is the solution flow through the porous medium induced by the electrical field. The quantitative characteristic of the effect is the coefficient before the electrical potential gradient in Eq. (11). Appearing the ice changes the porous medium properties. Compare the electroosmotic properties of the fine-pored medium and the biporous medium with the ice inclusions. Define for that the following ratio:

$$\delta_{pe} = C_{pe}/k_{pe} \tag{68}$$

Substituting in Eq. (68) the C-coefficients from Eqs. (55) and (66) gives the explicit form of the value δ_{pe} for two cells:

- *zero horizontal conductivity:*

$$\delta_{pe} = 1 - \alpha$$

- *infinite horizontal conductivity:*

$$\delta_{pe} = f_w$$

The ice presence impairs the electroosmotic capability of the porous medium (Fig. 5). The ice is impermeable to foreign matter, immobile relative to the medium framework (see Eqs. (53), (65)), and, therefore, is a barrier to ion transfer.

5.2. Streaming potential

Streaming potential is electrical field in porous medium, produced by the liquid flow through the medium. Let us characterize the potential by the ratio μ between the induced potential difference and the pressure drop along the body at $J_e = \nabla_b c_s = X_q = 0$:

$$\Delta\varphi = \mu\Delta p$$

In according to the second equation of the set (54) the coefficient μ is expressed in terms of the C-coefficients;

$$\mu = C_{ep}/C_{ee}$$

Compare the streaming potentials of the fine-pored medium and the biporous medium with the ice inclusion by means of the nondimensional parameter of δ_μ:

$$\delta_\mu = \frac{C_{ep}k_{ee}}{C_{ee}k_{ep}} \tag{69}$$

Substituting the C-coefficients in Eq. (69) from the sets (55) and (66) gives the identical result for both cells:

$$\delta_\mu = 1$$

The numerical calculations confirm that result.

The presence of ice in porous medium has no effect on the value of the streaming potential. Though the ice moves relative to the fine-pored framework, but that does not take part in the ion transfer through the medium.

5.3. Thermoelectric polarization

Electrical polarization induced by the temperature gradient will be found for the closed cell ($J_V = J_s = J_e = 0$).

An equation set in three variables of $\nabla_b p, \nabla_b c_s, \nabla_b\varphi$ follows from the general relation of (54):

$$(\mathbf{C}^m)\begin{pmatrix}\nabla_b p \\ \nabla_b \varphi \\ \nabla_b c_s\end{pmatrix} = -X_q\begin{pmatrix}C_{pq} \\ C_{eq} \\ C_{sq}\end{pmatrix} \tag{70}$$

where $(\mathbf{C}^m) = \begin{pmatrix}C_{pp} & C_{pe} & C_{ps} \\ C_{ep} & C_{ee} & C_{es} \\ C_{sp} & C_{se} & C_{ss}\end{pmatrix}$.

Multiplying the expression (70) by the inverse matrix $(\overline{\mathbf{C}}^m)$ and taking into account of the equation $C_{eq} = C_{sq} = 0$ (see Eqs. (55) and (66)) gives the explicit form of the required gradients

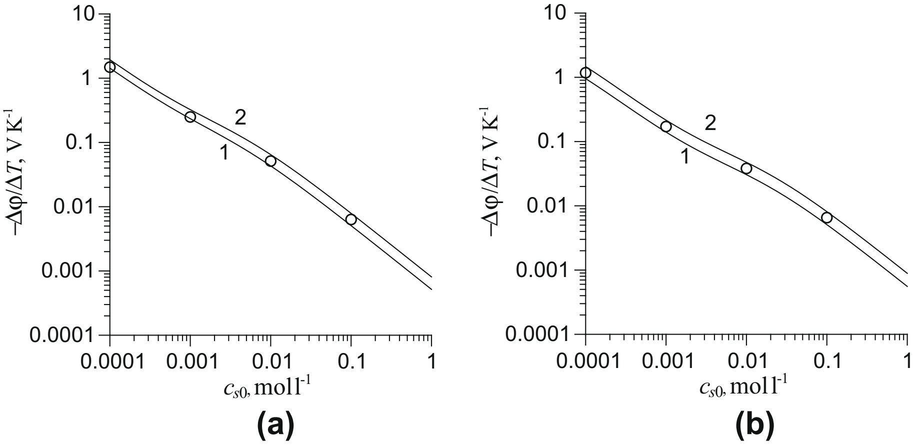

Fig. 6. Thermal polarization potential versus solution concentration c_{s0} at the volume fraction of ice $n_R = 0.4$ and different hydroconductivity coefficients K_h of element E_2 [m^3 s kg^{-1}]: a – 10^{-13}; b – 10^{-14} with zero (1) and infinite (2) horizontal conductivity. Symbols are the numerical calculations.

$$\begin{pmatrix} \nabla_b p \\ \nabla_b \varphi \\ \nabla_b c_s \end{pmatrix} = -C_{pq} X_q(\overline{\mathbf{C}}^m) \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \tag{71}$$

The value of the thermoelectric potential follows from Eq. (71):

$$\frac{\Delta\varphi}{\Delta T} = -\frac{C_{pq}\overline{C}^m_{ep}}{T_0} \tag{72}$$

The calculation results are presented in Fig. 6. The value of the potential increases with decreasing the solution concentration, depends weakly on the hydroconductivity of the fine-pored medium E_1, and reaches the value of 1 V/K at the solution concentration 10^{-4} mol l^{-1}.

If the fine-pored medium E_1 has not the osmotic and electroosmotic properties, than the potential value is under 250 mV/K [6]. The thermoelectric potential in the graphs of the referenced paper is a need to write with the negative sign. The double layer mechanism has the essential effect at the low concentration of the solution.

6. Conclusions

The model porous medium investigated in the present and other works [6,11,12] is a system with coupled phase transformations. The phase transformations intensify the cross effects in the systems. For example, the thermoelectric capacity of the medium may be increased more than an order in comparison with the porous body without phase transformations.

The role of the charge separation at the freezing boundary is not considered due to the thickness of the double electrical layer is less than 1 mm [17]. That mechanism must be taken into account if the magnitude of the ice inclusion is comparable with the double layer size. In this case the ice may transport ions, and in that way the mass transfer through the medium is taking new features.

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