International Journal of Heat and Mass Transfer 52 (2009) 1627–1634

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

journal homepage: www.elsevier.com/locate/ijhmt

Electrical cross effects in porous media with ice inclusions. 1. Diffusion mechanism

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ARTICLE INFO

Article history:
Received 13 June 2007
Received in revised form 9 September 2008
Available online 26 December 2008

Keywords:
Porous media
Aqueous solution
Ice
Coupled phase transition
Electrical cross effects

ABSTRACT

This paper is the first part of the theoretical work devoted to electrical cross effects in biporous media with ice inclusions. The fine-pored part of the medium is saturated by the electrolytic solution.

A heat and mass transfer problem is formulated for an elementary cell of the medium on basis of diffusion mechanism. An equation set is proposed for finding the temperature, pressure, concentration, and electric potential fields. All the heat and mass flows through the cell depend on the cross thermodynamical forces.

In the closed system the electric polarization induced by temperature gradient depends on the hydroconductivity of the fine-pored medium, the solution concentration and the ice content. At the low solution concentration and the high hydroconductivity the thermoelectric potential difference may be as great as 150 mV K^{-1}.

In the open system the ice presence has no effect on the diffusion potential difference induced by concentration gradient.

1. Introduction

It is commonly supposed that the formation of the dissipative structures in the thermodynamic system is realized far away from equilibrium state [1]. That condition, seemingly, is not necessary for the heterogeneous systems with the developed interface. In particular, the various structures appear in the dispersion medium with the coupled phase transformations at a small departure from the equilibrium [2]. Those systems frequently occur in nature, and therefore their investigation is essential to science and practice alike.

The freezing of the fine-grained saturated soils leads to transferring the moisture from the unfrozen soil to the phase transformation region, redistributing the soil components and increasing the ice content. Although the investigations of those systems have the long-standing history but the many problems are remaining unresolved. One of them is the role of ice in the transfer processes, and in particular the cross electrical effects.

The ice movement relative to the framework of the porous medium is accompanied by the coupled phase transformations of melting-freezing. The phase transitions may considerably intensify the cross-electrical effects. So the water freezing leads to the separation of the electrical charges (freezing potential) near the ice-water boundary. The freezing potential depends on the crystallization rate and reaches hundreds of volts [3]. And vice versa, the charges introduced in the metastable phase increase the rate of nucleation [4]. The heat transfer in the freezing soil initiates the mass transfer processes and formation of the ion accumulation domains [5]. The potential difference between the frozen and unfrozen soils is amounts up to 100 mV [6,7].

The cross-electrical properties of the ice-free soils have been investigated in details [8].

The experimental investigations with frozen soils show a correlation between their mechanical and electrical properties [9]. It is not improbable that the correlation is the result of the ice–water phase transition.

The presented paper is the first part of the theoretical work to determine the influence of the ice movement on the electrical properties of the systems with the coupled phase transformations. Certain of the resources of the cross-electrical effects are not considered in this paper.

When the electric current is absent, the solution flow through a porous body initiates appearing the electric potential difference (streaming potential) between the “input” and “output” boundaries of the sample.

The electric polarization of the ice-free porous medium is explained by the properties of the electric double layer at the interface of solution-mineral. The ions of the double layer are differently entrained by the solution flow. As result, the sample is polarized so that the potential difference between the body boundaries ensures equality of the inside and outside ion flows.

The value of the polarization depends directly on the volume of the double layer in porous space. That mechanism of the electric polarization is a major component of the induced polarization theory [10].

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doi:10.1016/j.ijheatmasstransfer.2008.09.023

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}], Eq. (25)
D_k	diffusion coefficient of k-ion [m^2 s^{-1}]
e	elementary charge, $e = 1.602 \cdot 10^{-19}$ $^\circ$C
F	Faraday constant, $F = 96484$[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, $k_B = 1.38 \cdot 10^{-23}$ 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]
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}]
v_i	velocity of ice [m s^{-1}]
X	thermodynamical force
z_k	charge number of k-ion
Greek symbols	
α	dimensionless parameter of the cell, $\pi R^2/S_a$
β	dimensionless parameter of the cell, $2R/b$
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}]
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
Other symbols	
∇	vector gradient operator
∇_b	difference gradient operator, Eq. (23)

If a porous body contents inclusions of ice, then the external gradients of the thermodynamic potentials causes the ice movement, the coupled phase transformations of "melting–freezing" and, as result, appearing the potential difference at the freezing boundary (Workman–Reynolds effect), and therefore in the biporous medium.

Those two mechanisms of the electrical cross effects don't considered in the presented work.

2. Problem statement

Consider a biporous body with the regular structure (Fig. 1), which includes the equal spherical cavities (E_1) and the fine-pored medium (E_2). The cavities are filled by ice and the medium E_2 is saturated by binary electrolyte. The system is under the thermodynamic conditions those forbid ice from melting and penetrating into the element E_2.

The heat and mass transfer is produced by the external gradients of temperature, liquid pressure, concentration and electric potential. The direction of all gradients coincides with Z-axis (Fig. 1). Fix the Cartesian co-ordinate system to the solid framework of the element E_2.

The steady-state problem of defining the fluxes through the medium reduces to the analogous problem for an elementary cell (Fig. 2). The thermodynamic potentials are specified on the bases of the cell, and the lateral faces are impenetrable for heat and matter.

The problem will be solved by the following way. First of all, the fields of temperature, pressure, concentration and electric potential will be found, and then the condition of the mechanical equilibrium of the ice inclusion will be bring in correspondence with the local phase equilibrium of ice and water. The term *local value* respect to the thermodynamic value in the element E_2 will be denoted the value averaged over a representative volume [11], the size of which is noticeably more than the heterogeneity size.

For simplicity assume that the elements E_1 and E_2 are homogeneous (1); ice is ideal dielectric, doesn't transmit fluid, and rejects all foreign matters (2); the framework of the element E_2 is rigid and inactive relate to chemical, ion-exchange, and other reactions (3); the element E_2 is saturated by strong electrolyte, is permeable for fluid, and hasn't osmotic and electroosmotic properties (4); in the solution it isn't occurred appearing gas (air or vapour) or solid (ice or solute crystals) phases (5), the system considered is near

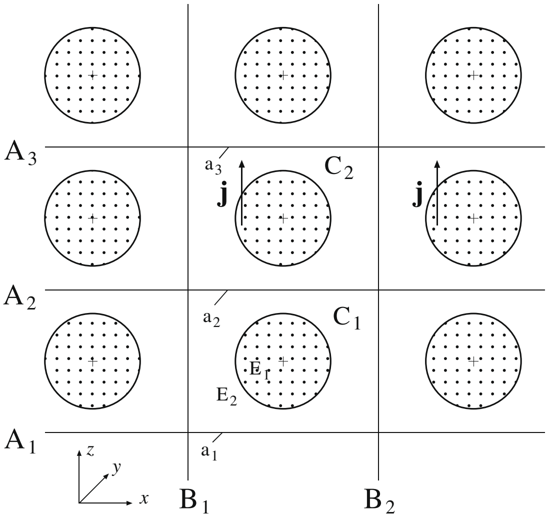

Fig. 1. A fragment of the model porous medium. E_1 – ice inclusion, E_2 – fine-pored medium.

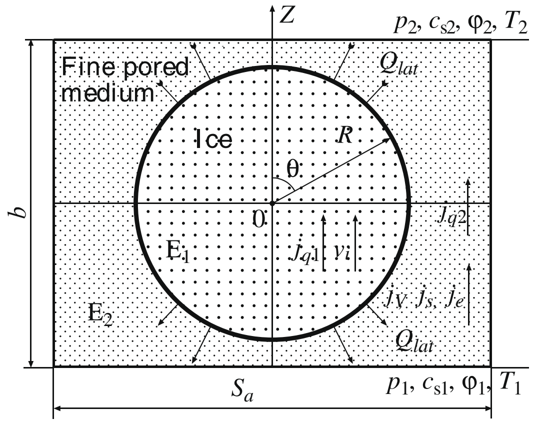

Fig. 2. Scheme of fluxes in an elementary cell. Q_{lat} is heat production at the phase transition surface.

equilibrium state (6). Also relative to electrolyte transfer in porous medium it will be accepted the properties as follow: in the interior of the elements of E_1 and E_2 (homogeneous media) the local electrical neutrality is realized (7); the solute transfer in E_2 is subjected to Fick's law (8); the nonzero electrical charge concentrates at the contact of elements E_1 and E_2 (9), the charge density depends on the value of the external electrostatic force and the rate of the transport processes (10), the thickness of the charged layer doesn't depends on the value of the external disturbance and equals the double layer thickness in accordance with Debye–Hückel theory (11); at the interface the total concentration of ions in the solution doesn't depend on the value of the charge and is defined by Fick's Eq. (12).The detailed substantiation of the given assumptions is carried out earlier [12].

The point (4) denotes that the transfer properties of the dissolved matter in the porous medium are the same as those in the bulk solution.

In the gradient field of the thermodynamic potentials the ice inclusion moves relative to the framework of the porous medium. The movement is accompanied by the couple phase transformations of freezing – melting, and changes the character of the heat and mass transfer through the medium. Defining the ice velocity generates a need for the solution of the thermal, filtration and diffusion problems. The equation set for defining temperature, liquid pressure, solution concentration and electric potential is presented in the third section. The boundary conditions are formulated in the fourth section.

3. Heat and mass transfer equations

Not counting the convective transport of heat the energy conservation law and a Fourier law gives Laplace's equation for temperature in the elements of E_1 and E_2:

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

The derivation of equations for finding the pressure, the concentration, and the electric potential will be given in more details.

Three constituents of the solution (anion, cation and water) are only transferred through the fine-pored medium E_2. Due to the accepted assumptions the volume flux is subjected to Darcy's law:

$$\mathbf{j}_V = -K_{\text{h}}\nabla p \tag{2}$$

The flux $\mathbf{j}_V$ is expressed in terms of the molar fluxes of the mixture components [13]:

$$\mathbf{j}_V = V_1\mathbf{j}_1 + V_2\mathbf{j}_2 + V_{\text{w}}\mathbf{j}_{\text{w}} \tag{3}$$

The ordered motion of ions is induced by the three causes: convective transport, diffusion and electric force. The molar fluxes of ions have the following form [14]:

$$\mathbf{j}_k = -c_k u_k \nabla\varphi - D_k\nabla c_k + c_k\mathbf{j}_V, k = 1,2 \tag{4}$$

The ion mobility u_k is connected with the diffusion coefficient D_k by the relation:

$$D_k = \frac{k_{\text{B}}Tu_k}{ez_k}.$$

where $z_k e$ – charge of k-ion (z_k is positive for a cation, and negative for an anion). Notice that the sign of the ion mobility is equal to the ion sign.

The local electrical neutrality of the element E_2

$$c_{\text{s}} = \frac{c_1}{v_1} = \frac{c_2}{v_2}$$

converts the Eq. (4) to the following form:

$$\mathbf{j}_k = -v_k c_{\text{s}} u_k \nabla\varphi - v_k D_k \nabla c_{\text{s}} + v_k c_{\text{s}}\mathbf{j}_V, k = 1,2 \tag{5}$$

Combine the fluxes $\mathbf{j}_k$ and introduce into consideration of the solute flux $\mathbf{j}_s$ and the current density $\mathbf{j}_e$:

$$\mathbf{j}_{\text{s}} = \chi_1\mathbf{j}_1 + \chi_2\mathbf{j}_2 \tag{6}$$

$$\mathbf{j}_e = \tilde{z}_1\mathbf{j}_1 + \tilde{z}_2\mathbf{j}_2 \tag{7}$$

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

Substituting (5) into (6) - (7) and having in view of neutrality of a solute molecule $z_1v_1 + z_2v_2 = 0$ gives

$$\mathbf{j}_{\text{s}} = -D_{\text{n}}\nabla c_{\text{s}} + c_{\text{s}}\mathbf{j}_V \tag{8}$$

$$\mathbf{j}_e = k_{\text{es}}\nabla c_{\text{s}} + k_{\text{ee}}\nabla\varphi \tag{9}$$

where
$D_{\text{n}} = \frac{(v_1+v_2)D_1D_2}{v_2D_1+v_1D_2}, k_{\text{es}} = -(\tilde{z}_1v_1D_1 + \tilde{z}_2v_2D_2); k_{\text{ee}} = -c_{\text{s}}(\tilde{z}_1v_1u_1 + \tilde{z}_2v_2u_2)$.

The conservation law of the matter (water and dissolved matter)

$$\nabla\cdot\mathbf{j}_V = 0; \nabla\cdot\mathbf{j}_{\text{s}} = 0; \nabla\cdot\mathbf{j}_e = 0 \tag{10}$$

with the transfer laws (2), (8), (9) gives the equations for finding the thermodynamic potentials in the element E_2:

- Laplace's equation for the liquid pressure p:

  $$\Delta p = 0 \tag{11}$$

- Fick's equation for the solution concentration c_{s}:

  $$\Delta c_{\text{s}} + \frac{K_{\text{h}}}{D_{\text{n}}}\nabla\cdot(c_{\text{s}}\nabla p) = 0 \tag{12}$$

- an equation for the electric potential φ:

  $$\nabla\cdot(c_{\text{s}}\nabla\varphi) - \frac{D_{\text{n}}}{D_e}\Delta c_{\text{s}} = 0 \tag{13}$$

  where $D_e = \frac{(v_1+v_2)u_1u_2}{v_1u_1+v_2u_2}$.

4. Boundary conditions

At the bases of the cell the values of temperature, liquid pressure, solution concentration and electric potential are fixed *at the bottom* ($z = -b/2$):

$$T = T_1, p = p_1, c_{\text{s}} = c_{\text{s}1}, \varphi = \varphi_1 \tag{14}$$

at the top ($z = b/2$):

$$T = T_2, p = p_2, c_{\text{s}} = c_{\text{s}2}, \varphi = \varphi_2 \tag{15}$$

Heat and mass transfer through lateral faces of the cell is absent:

$$\frac{dT}{dl}=0,\frac{dp}{dl}=0,\frac{dc_s}{dl}=0,\frac{d\varphi}{dl}=0 \tag{16}$$

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

At the inclusion surface (contact of ice with fine-pored medium) the boundary conditions are obtained from the following physical requirements: continuity of the thermodynamic potentials (temperature and electric potential), conservation of mass and energy (heat), heat and mass transfer laws (2) and (4), the properties (1)–(3) in Section 2. Since the symmetry of the boundary conditions (14)–(16) the direction of the ice velocity is the same as Z-axis, and therefore at the inclusion surface the thermodynamic potentials satisfy the following relations

- temperature T:

$$T|_{r=R-0}=T|_{r=R+0}\ \text{(temperature continuity)} \tag{17}$$

$$-\lambda_1\frac{\partial T}{\partial r}\bigg|_{r=R-0}-\left(-\lambda_2\frac{\partial T}{\partial r}\bigg|_{r=R+0}\right)=\kappa v_i\cos\theta/V_i\text{(heatbalance)} \tag{18}$$

- liquid pressure p:

$$\frac{\partial p}{\partial r}\bigg|_{r=R+0}=-\frac{V_w}{V_i}\frac{v_i\cos\ \theta}{K_h}\ \text{(solutionbalance)} \tag{19}$$

- solution concentration c_s:

$$\left(\frac{\partial c_s}{\partial r}-\frac{V_w v_i\cos\theta}{V_iD_n}c_s\right)\bigg|_{r=R+0}=0\ \text{(solute balance)} \tag{20}$$

- electric potential φ:

$$\frac{\partial\varphi}{\partial r}\bigg|_{r=R+0}=\frac{V_w v_i\cos\theta}{V_iD_e}\ \text{(charge and solute balance)} \tag{21}$$

The ice velocity v_i in the Eqs. (18)–(21) is found from the independent conditions of the mechanical equilibrium of the inclusion and the local phase equilibrium of ice and water at the inclusion surface. In absence of the external force fields these conditions give the desired equation [2]

$$\int_{S_R}\left(\frac{V_w}{V_i}p_R-\frac{\kappa T_R}{T_0V_i}+\frac{\gamma_w}{V_i}c_{sR}\right)\mathbf{n}dS=0 \tag{22}$$

where p_R, T_R, and c_{sR} is liquid pressure, temperature, and molar concentration of solution at the inclusion surface S_R; $\mathbf{n}$ is an unit vector perpendicular to dS; $\gamma_w=\frac{\partial\mu_w}{\partial c_s}$, μ_w – chemical potential of water in solution (for the ideal electrolyte solution $\gamma_w=-iR_gTV_w$, i – isotonic factor, $i=v_1+v_2$).

The equation set (14)–(22) is the boundary conditions for the heat and mass transfer problem, that includes the equation set for the temperature (1) in the elements E_1 and E_2, and also for the pressure (11), the concentration (12), and the electric potential (13) in the element E_2.

A problem consists in defining the flows of the heat, the solution and the solved matter across the bases of the cell (Fig. 2) at the boundary conditions (14)–(22).

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

5. Heat transfer, filtration and diffusion

Solution of the problem by "anisotropic conductivity" method was in detail described formerly [2]. Here, the final results are only presented, namely the fluxes through the bases of the cell.

5.1. Infinite horizontal conductivity

$$J_q=\lambda_2\left\{-\frac{\kappa v_i}{V_i\Delta\lambda_{21}}-\left[\nabla_bT-\frac{\kappa v_i}{V_i\Delta\lambda_{21}}\right]\cdot\frac{f_1}{\beta+f_1(1-\beta)}\right\} \tag{23}$$

$$J_V=\frac{V_w v_i}{V_i}-\left(K_h\nabla_bp+\frac{V_w v_i}{V_i}\right)\frac{f_2}{\beta+f_2(1-\beta)} \tag{24}$$

$$J_s=\frac{f_2}{\beta+(1-\beta)f_2}[-D_n\nabla_bc_s-c_{s0}K_h\nabla_bp] \tag{25}$$

where $\nabla_bT=\frac{T_2-T_1}{b}$; $\nabla_bp=\frac{p_2-p_1}{b}$; $\nabla_bc_s=\frac{c_{s2}-c_{s1}}{b}$; $c_{s0}=\frac{c_{s2}+c_{s1}}{2}$, $\Delta\lambda_{21}=\lambda_2-\lambda_1$ and β, ε_t, ε_p, f_1, f_2 are dimensionless parameters:

$$f_1=\begin{cases}\frac{2\varepsilon_t}{(1-\varepsilon_t^2)\ln\left|\frac{1+\varepsilon_t}{1-\varepsilon_t}\right|},\Delta\lambda_{21}<0\\ \frac{\varepsilon_t}{(1+\varepsilon_t^2)\text{arctg}\varepsilon_t},\Delta\lambda_{21}>0\end{cases},f_2=\frac{\varepsilon_p}{(1+\varepsilon_p^2)\text{arctg}\varepsilon_p},$$

$$\varepsilon_t^2=\frac{|\ \Delta\lambda_{21}\ |\ \pi R^2}{\lambda_2S_a-\Delta\lambda_{21}\pi R^2};\varepsilon_p^2=\frac{\pi R^2}{S_a-\pi R^2};$$

5.2. Zero horizontal conductivity

$$J_q=-\lambda_2I_\lambda\nabla_bT-\frac{\lambda_2\kappa\alpha\beta}{\lambda_1V_i}v_iI_{3t} \tag{26}$$

$$J_V=\frac{V_w}{V_i}\alpha v_i-(1-\alpha)K_h\nabla_bp \tag{27}$$

$$J_s=-(1-\alpha)(D_n\nabla_bc_s+c_{s0}K_h\nabla_bp) \tag{28}$$

where α, ε_{t0}, I_λ, I_{3t} are dimensionless parameters:

$$\varepsilon_{t0}=\beta\left(\frac{\lambda_2}{\lambda_1}-1\right),I_\lambda=(1-\alpha)+\frac{2\alpha}{\varepsilon_{t0}^2}[\varepsilon_{t0}-\ln(1+\varepsilon_{t0})];$$

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

6. Electroconductivity problem

The problem consists in defining the electric flux through the bases of the cell. That requires solving the Eq. (13) for electric potential at the boundary conditions (14), (15), (16), and (21). A dissolved matter distribution (concentration c_s) in the element E_2 must be found previously.

In this section the electroconductivity problem will be solved by the anisotropic conductivity method for two cells with the infinite and zero horizontal conductivities. Since the system is near the equilibrium state it will be supposed that the coefficient k_{ee} is constant: $k_{ee}=-c_{s0}(\tilde{z}_1v_1u_1+\tilde{z}_2v_2u_2)$. In consequence of the accepted properties of ice (Section 2) the ions are only transferred in the element E_2. The transfer law (13) and the law of conservation of matter is a foundation for the solution of the problem.

6.1. Infinite horizontal conductivity

The current density connects with the concentration and electric potential gradients by Eq. (9). The z components of the gradients don't depend on co-ordinate z due to accepted anisotropy.

In the range of z $[-b/2,-R]$ and $[R,b/2]$ the medium homogeneous (Fig. 3). In direction of z-axis the current density j_e is constant and equal to the value of the flux J_e through the bases of the cell. Writing the Eq. (9) in the difference form gives

$$J_e=k_{es}\frac{c'_{s1}-c_{s1}}{b/2-R}+k_{ee}\frac{\varphi'_1-\varphi_1}{b/2-R} \tag{29}$$

$$J_e=k_{es}\frac{c_{s2}-c'_{s2}}{b/2-R}+k_{ee}\frac{\varphi_2-\varphi'_2}{b/2-R} \tag{30}$$

where $(p'_1,c'_{s1},\varphi'_1)$ and $(p'_2,c'_{s2},\varphi'_2)$ is pressure, concentration and electric potential in sections $z=-R$ and $z=R$ accordingly. Summing Eqs. (29) and (30) produces the following relation

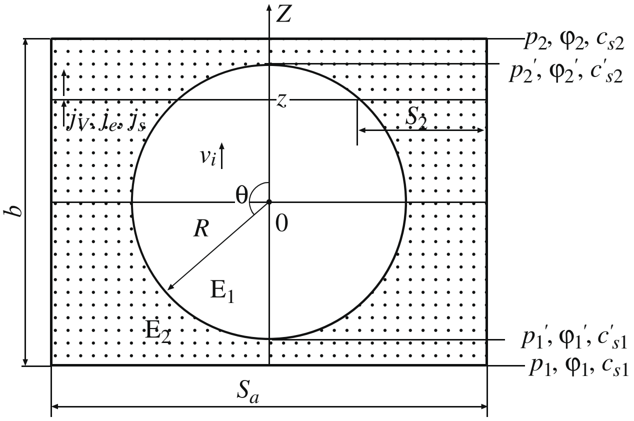

Fig. 3. Scheme of matter fluxes through the cell with infinite horizontal conductivity.

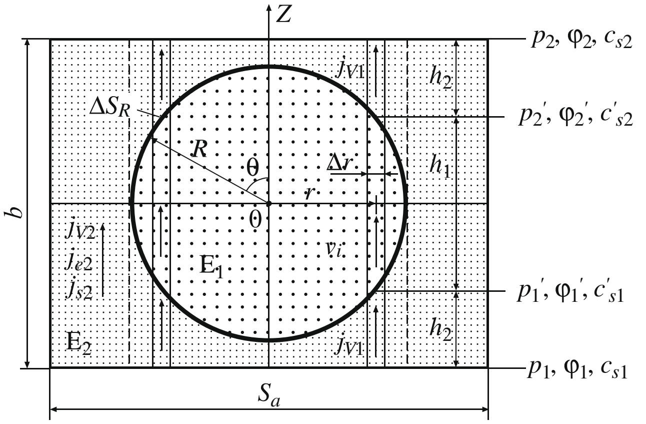

Fig. 4. Scheme of mass fluxes through the cell at zero horizontal conductivity.

$$J_e(1-\beta) = k_{\mathrm{es}}(\nabla_b c_{\mathrm{s}} - \nabla_b c'_{\mathrm{s}}) + k_{\mathrm{ee}}(\nabla_b \varphi - \nabla_b \varphi') \tag{31}$$

In the region of $z\epsilon[-R, R]$ the conservation law of the charge gives the following relation:

$$j_e S_2(z) = J_e S_a \tag{32}$$

where j_e is z-component of the current density $\mathbf{j}_e$, S_2 is area of the element E_2 in the horizontal section z: $S_2(z) = S_a - \pi(R^2 - z^2)$. Substituting j_e in (32) from the relation (9) gives an simple differential equation for defining the electric potential φ

$$k_{\mathrm{es}}\frac{\mathrm{d}c_{\mathrm{s}}}{\mathrm{d}z} + k_{\mathrm{ee}}\frac{\mathrm{d}\varphi}{\mathrm{d}z} = \frac{J_e S_a}{S_2(z)} \tag{33}$$

In general case a function c_{s} must be found previously from the solution of the diffusion problem. Integrating Eq. (33) with respect to z from $-R$ to R gives

$$k_{\mathrm{es}}\nabla_b c'_{\mathrm{s}} + k_{\mathrm{ee}}\nabla_b \varphi' = \frac{J_e \beta}{f_2} \tag{34}$$

Eliminating the parameters $\nabla_b c'_{\mathrm{s}}$ and $\nabla_b \varphi'$ from Eqs. (31) and (34) gives an expression for the current density J_e:

$$J_e = f_{\mathrm{w}}(k_{\mathrm{es}}\nabla_b c_{\mathrm{s}} + k_{\mathrm{ee}}\nabla_b \varphi) \tag{35}$$

where $f_{\mathrm{w}} = \frac{f_2}{\beta + (1-\beta) f_2}$.

6.2. Zero horizontal conductivity

In the region of $r < R$ the vertical ion flows are equal to zero ($j_{e1} = 0$) because of impearmeable of ice for the foreign matter. The ion transport in the cell is only realized in the region of $r > R$ (Fig. 4). The average current density J_e through the bases of the cell connects with the current density j_{e2} in the second region: $J_e = (1-\alpha) j_{e2}$. Writing Eq. (9) in the difference form and substituting j_{e2} from the last relation gives

$$J_e = (1-\alpha)[k_{\mathrm{es}}\nabla_b c_{\mathrm{s}} + k_{\mathrm{ee}}\nabla_b \varphi] \tag{36}$$

7. Transfer equations and transport coefficients

The transfer equations content the ice velocity v_i, which depends linearly on the temperature, pressure, and concentration gradients. The expression for the values v_i was obtained earlier using the boundary condition (22) [2]. Here, it is only presented the final result.

7.1. Infinite horizontal conductivity

Substituting the value of v_i:

$$v_i = -\omega_{\mathrm{p1}}\nabla_b p - \omega_{\mathrm{t1}}\nabla_b T - \omega_{\mathrm{s1}}\nabla_b c_{\mathrm{s}}$$

where $\omega_{\mathrm{p1}} = \frac{V_{\mathrm{w}}}{V_i}\frac{f_{\mathrm{p}}}{den_1}$; $\omega_{\mathrm{t1}} = -\frac{\kappa}{T_0 V_i}\frac{f_{\mathrm{t}}}{den_1}$; $\omega_{\mathrm{s1}} = \frac{\gamma_{\mathrm{w}}}{V_i}\frac{f_{\mathrm{p}}}{den_1}$

$$den_1 = \left(\frac{V_{\mathrm{w}}}{V_i}\right)^2\left(f_{\mathrm{p}} - \frac{2}{3}\right)\frac{1}{K_{\mathrm{h}}} + \left(\frac{\kappa}{V_i}\right)^2\frac{(f_{\mathrm{t}} - 2/3)}{T_0\Delta\lambda_{21}} - \frac{\gamma_{\mathrm{w}} V_{\mathrm{w}} c_{\mathrm{s0}}}{V_i^2 D_{\mathrm{n}}}\left(f_{\mathrm{p}} - \frac{2}{3}\right),$$

$$f_{\mathrm{t}} = \begin{cases} \frac{(1-f_1)}{[\beta+(1-\beta)f_1]}\cdot\frac{(\varepsilon_{\mathrm{t}}^2-1)}{\varepsilon_{\mathrm{t}}^2}, \Delta\lambda_{21} < 0 \\ \frac{(1-f_1)}{[\beta+(1-\beta)f_1]}\cdot\frac{(\varepsilon_{\mathrm{t}}^2+1)}{\varepsilon_{\mathrm{t}}^2}, \Delta\lambda_{21} > 0 \end{cases}$$

in (23) and (25) having in view (25) and (35) gives the required expression for the fluxes:

$$J_V = C_{\mathrm{pp}}\nabla_b p + C_{\mathrm{ps}}\nabla_b c_{\mathrm{s}} + C_{pe}\nabla_b \varphi + C_{\mathrm{pq}}\nabla_b T/T_0 \tag{37}$$

$$J_{\mathrm{s}} = C_{sp}\nabla_b p + C_{ss}\nabla_b c_{\mathrm{s}} + C_{\mathrm{se}}\nabla_b \varphi + C_{sq}\nabla_b T/T_0 \tag{38}$$

$$J_e = C_{\mathrm{ep}}\nabla_b p + C_{\mathrm{es}}\nabla_b c_{\mathrm{s}} + C_{\mathrm{ee}}\nabla_b \varphi + C_{eq}\nabla_b T/T_0 \tag{39}$$

$$J_{\mathrm{q}} = C_{\mathrm{qp}}\nabla_b p + C_{qs}\nabla_b c_{\mathrm{s}} + C_{qe}\nabla_b \varphi + C_{qq}\nabla_b T/T_0 \tag{40}$$

where $C_{\mathrm{pp}} = -\left[K_{\mathrm{h}} f_{\mathrm{w}} + \frac{V_{\mathrm{w}}}{V_i}\alpha\beta f_{\mathrm{p}}\omega_{\mathrm{p1}}\right], C_{\mathrm{ps}} = -\frac{V_{\mathrm{w}}}{V_i}\alpha\beta f_{\mathrm{p}}\omega_{\mathrm{s1}}, C_{pe} = 0, C_{\mathrm{pq}} = -\frac{V_{\mathrm{w}}}{V_i}\alpha\beta f_{\mathrm{p}}\omega_{\mathrm{t1}} T_0,$

$$\begin{aligned} &C_{sp} = -c_{\mathrm{s0}} K_{\mathrm{h}} f_{\mathrm{w}}, \quad C_{ss} = -D_{\mathrm{n}} f_{\mathrm{w}}, \quad C_{\mathrm{se}} = 0, \quad C_{sq} = 0, \\ &C_{ep} = 0, \quad C_{\mathrm{es}} = k_{\mathrm{es}} f_{\mathrm{w}}, \quad C_{\mathrm{ee}} = k_{\mathrm{ee}} f_{\mathrm{w}}, \quad C_{eq} = 0, \\ &C_{\mathrm{qp}} = \frac{\kappa}{V_i}\cdot\alpha\beta f_{\mathrm{t}}\omega_{\mathrm{p1}}, \quad C_{qe} = 0, \quad C_{qs} = \frac{\kappa}{V_i}\cdot\alpha\beta f_{\mathrm{t}}\omega_{\mathrm{s1}}, \\ &C_{qq} = \left(\frac{\kappa}{V_i}\cdot\alpha\beta f_{\mathrm{t}}\omega_{\mathrm{t1}} - \lambda_2 f_{\mathrm{q}}\right) T_0 \end{aligned} \tag{41}$$

The thermodynamical forces X_V, X_{s}, X_e, which correspond to the fluxes J_V, J_{s}, J_e and ensure symmetry of the transport coefficients is expressed in the terms of the thermodynamical potential gradients as follow [15,12]

$$\begin{aligned} &X_V = \nabla p - \nabla\pi_{\mathrm{s}}, \ X_{\mathrm{s}} = \nabla\pi_{\mathrm{s}}/c_{\mathrm{s}}, \\ &X_e = \nabla\varphi + k_\pi\nabla\pi_{\mathrm{s}}, \\ &X_{\mathrm{q}} = \nabla T/T_0 \end{aligned} \tag{42}$$

where $\pi_{\mathrm{s}} = -\gamma_{\mathrm{w}} c_{\mathrm{s}}/V_{\mathrm{w}}$, $k_\pi = -\frac{V_{\mathrm{w}}(D_1 - D_2)}{c_{\mathrm{s}}\gamma_{\mathrm{w}}(u_1 - u_2)}$.

The symmetry of the standard coefficients gives the linear relations between C-coefficients:

$$\begin{aligned}
&c_{\mathrm{s}}\left(C_{\mathrm{pp}} - k_{\pi}C_{pe} - \frac{V_{\mathrm{w}}}{\gamma_{\mathrm{w}}}C_{\mathrm{ps}}\right) = C_{sp}\\
&C_{pe} = C_{ep}\\
&C_{\mathrm{pq}} = C_{\mathrm{qp}}\\
&C_{\mathrm{se}} = c_{\mathrm{s}}\left(C_{ep} - k_{\pi}C_{\mathrm{ee}} - \frac{V_{\mathrm{w}}}{\gamma_{\mathrm{w}}}C_{\mathrm{es}}\right)\\
&C_{sq} = c_{\mathrm{s}}\left(C_{\mathrm{qp}} - k_{\pi}C_{qe} - \frac{V_{\mathrm{w}}}{\gamma_{\mathrm{w}}}C_{qs}\right)\\
&C_{eq} = C_{qe}
\end{aligned} \tag{43}$$

The Eq. (43) are verified by the direct substitution of C-coefficients (41).

7.2. Zero horizontal conductivity

At zero horizontal conductivity the ice velocity is presented as follow

$$v_i = -\omega_{\mathrm{p0}}\nabla_b p - \omega_{\mathrm{t0}}\nabla_b T - \omega_{\mathrm{s0}}\nabla_b c_{\mathrm{s}}$$

where $\omega_{\mathrm{p0}} = \dfrac{V_{\mathrm{w}}}{V_i}\dfrac{1}{den_0}$;

$$\omega_{\mathrm{t0}} = -\frac{\kappa\lambda_2}{T_0V_i\lambda_1}\frac{\beta I_{3t}}{den_o}, \omega_{\mathrm{s0}} = \frac{\gamma_{\mathrm{w}}}{V_i}\frac{1}{den_0},$$

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

$$\begin{aligned}
den_0 = {}& \left(\frac{V_{\mathrm{w}}}{V_i}\right)^2\left(1 - \frac{2}{3}\beta\right)\frac{1}{K_{\mathrm{h}}} + \left(\frac{\kappa}{V_i}\right)^2\frac{\beta(I_{3t} - \beta I_{4t})}{T_0\lambda_1}\\
&- \frac{\gamma_{\mathrm{w}}V_{\mathrm{w}}c_{\mathrm{s0}}}{V_i^2D_{\mathrm{n}}}\left(1 - \frac{2}{3}\beta\right).
\end{aligned}$$

Substituting this expression for the velocity v_i in (26), (27) and taking into account of the relations (28) and (36) gives the transfer equations in the form (37)–(40) with the transport coefficients as follow

$$\begin{aligned}
&C^0_{\mathrm{pp}} = -\left[(1-\alpha)K_{\mathrm{h}} + \alpha\frac{V_{\mathrm{w}}}{V_i}\omega_{\mathrm{p0}}\right], C^0_{pe} = 0,\ C^0_{ps} = -\alpha\frac{V_{\mathrm{w}}}{V_i}\omega_{\mathrm{s0}},\\
&C^0_{\mathrm{pq}} = -\alpha\frac{V_{\mathrm{w}}}{V_i}T_0\omega_{\mathrm{t0}}, C^0_{sp} = -(1-\alpha)c_{\mathrm{s0}}K_{\mathrm{h}},\ C^0_{\mathrm{se}} = (1-\alpha)k_{\mathrm{se}},\\
&C^0_{ss} = (1-\alpha)k_{ss}, C^0_{sq} = 0, C^0_{\mathrm{ep}} = 0,\ C^0_{\mathrm{ee}} = (1-\alpha)k_{\mathrm{ee}},\\
&C^0_{\mathrm{es}} = (1-\alpha)k_{\mathrm{es}},\ C^0_{eq} = 0,\ C^0_{\mathrm{qp}} = \frac{\lambda_2\kappa}{\lambda_1V_i}\alpha\beta\cdot I_{3t}\omega_{\mathrm{p0}},\ C^0_{qe} = 0,\\
&C^0_{qs} = \frac{\lambda_2\kappa}{\lambda_1V_i}\alpha\beta\cdot I_{3t}\omega_{\mathrm{s0}}, C^0_{qq} = \left(\frac{\lambda_2\kappa}{\lambda_1V_i}\alpha\beta\cdot I_{3t}\omega_{\mathrm{t0}} - \lambda_2I_{\lambda}\right)T_0
\end{aligned} \tag{44}$$

where $I_{4t} = \frac{2}{3\varepsilon_{\mathrm{t0}}} - \frac{1}{\varepsilon_{\mathrm{t0}}^2} + \frac{2}{\varepsilon_{\mathrm{t0}}^3} - \frac{2}{\varepsilon_{\mathrm{t0}}^4}\ln(1+\varepsilon_{\mathrm{t0}})$. The direct check shows that the coefficients (44) satisfy the transformed Onsager reciprocal relations (43).

So the limits of variation have be found for the transport coefficients by the anisotropic conductivity method. The Eqs. (41) and (44) give the additional relations for transport coefficients: $C_{\mathrm{pe}} = 0$, $C_{\mathrm{sq}} = 0$, $C_{\mathrm{eq}} = 0$. Therefore, a number of the independent coefficients are equal to 7. It is not improbable that a detailed analysis of the system reduces this number.

8. Electrical properties of the medium

The electric conductivity of the medium considered doesn't depend on the ice velocity (see (35) - (36)), and so the cross-electrical properties of the cell will be presented in this section.

All calculations are made for the cubic cell. The fine-pored medium E_2 is saturated by the NaCl electrolyte that is supposed ideal (see (22)). The thermal conductivity of the elements E_1 and E_2 are $\lambda_1 = 2.2$ W m^{-1} K^{-1}, $\lambda_2 = 1.54$ W m^{-1} K^{-1} and the diffusion constants of ions in the porous medium [16] are $D_{\mathrm{Na}} = 4{\cdot}10^{-10}$ m^2 s^{-1} and $D_{\mathrm{Cl}} = 6{\cdot}10^{-10}$ m^2 s^{-1}.

8.1. Electric polarization induced by temperature gradient

In this section the calculation of thermoelectric polarization was made for the closed cell; i.e. the mass flows through the bases of the cell are equal to zero ($J_{\mathrm{V}} = J_{\mathrm{s}} = J_e = 0$). The thermal flow generates the difference of thermodynamical potentials: liquid pressure, solution concentration and electric potential. The equations for finding the potential difference follow from the set (37)–(39):

$$\begin{aligned}
&C_{\mathrm{pp}}\nabla_b p + C_{\mathrm{ps}}\nabla_b c_{\mathrm{s}} + C_{\mathrm{pq}}X_{\mathrm{q}} = 0\\
&C_{sp}\nabla_b p + C_{\mathrm{se}}\nabla_b\varphi + C_{ss}\nabla_b c_{\mathrm{s}} = 0\\
&C_{\mathrm{es}}\nabla_b c_{\mathrm{s}} + C_{\mathrm{ee}}\nabla_b\varphi = 0
\end{aligned} \tag{45}$$

Excluding the values of $\nabla_b p$ and $\nabla_b c_{\mathrm{s}}$ from Eqs. (45) gives the relationship for the thermal electromotive force:

$$\Delta\varphi = \frac{C_{\mathrm{pq}}C_{\mathrm{es}}C_{sp}}{C_{\mathrm{ps}}C_{\mathrm{ee}}C_{sp} + C_{\mathrm{pp}}(C_{\mathrm{se}}C_{\mathrm{es}} - C_{\mathrm{ee}}C_{ss})}\frac{\Delta T}{T_0}$$

Substituting in the last equation the coefficients C_{ee}, C_{es}, C_{se}, C_{ss} from Eqs. (41) and (44) gives the required value $\Delta\varphi$ for the cells at

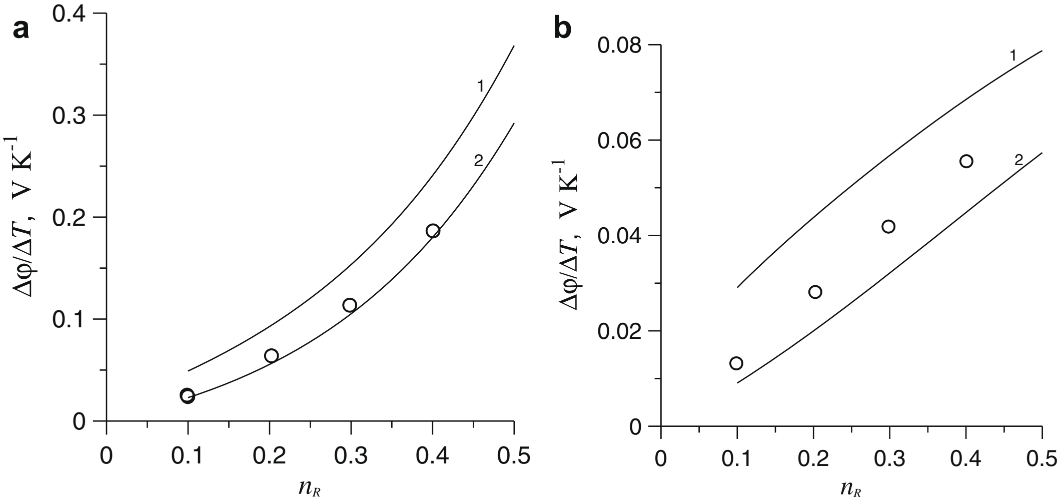

Fig. 5. Thermal polarization potential in closed system versus the volume fraction of ice at solution concentration c_{s0}=0.0001 mol l^{-1} and different hydroconductivity coefficients K_{h} of element E_2 [m^3 s kg^{-1}]: a – 10^{-13}; b – 10^{-14} with infinite (1) and zero (2) horizontal conductivity. Symbols are the numerical calculations with an accuracy of 0.025–0.05.

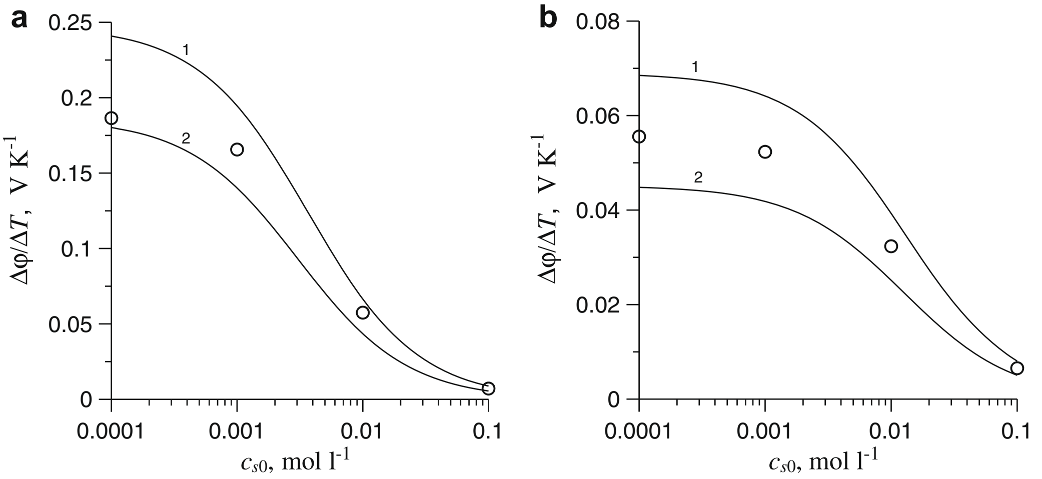

Fig. 6. Thermal polarization potential versus solution concentration c_{s0} at the volume fraction of ice $n_R = 0.4$ and different hydroconductivity coefficients K_h of element E_2 [$m^3\ s\ kg^{-1}$]: a – 10^{-13}; b – 10^{-14} with infinite (1) and zero (2) horizontal conductivity. Symbols are the numerical calculations with an accuracy of 0.025–0.05.

infinite horizontal conductivity:

$$\Delta\varphi_1 = -\frac{C_{pq}}{c_{s0}D_e\left(\frac{C_{ps}}{D_n} + \frac{C_{pp}f_w}{C_{sp}}\right)}\frac{\Delta T}{T_0}$$

zero horizontal conductivity:

$$\Delta\varphi_0 = -\frac{C^0_{pq}}{c_{s0}D_e\left(\frac{C^0_{ps}}{D_n} + \frac{C^0_{pp}(1-\alpha)}{C^0_{sp}}\right)}\frac{\Delta T}{T_0}$$

The dependence of the polarization potential on the fraction of the ice volume in the cell at the electrolyte concentration 0.0001 mol l^{-1} shows in Fig. 5. The polarization potential becomes appreciable (∼100 mV K^{-1}) when the volume fraction of ice in the cell n_R is greater than 0.3 and the hydroconductivity coefficient is more than $10^{-14}\ m^3\ s\ kg^{-1}$. At the low hydroconductivity ($K_h < 10^{-15}\ m^3\ s\ kg^{-1}$) the thermal polarization effect is very small (<10 mV K^{-1}).The influence of the average concentration of the solution at the fixed ice content ($n_R = 0.4$) is presented in Fig. 6. The value of the polarization potential decreases monotonically with increasing the solution concentration. At the sufficiently small concentration ∼0.0001 mol l^{-1} the dissolved matter begins to influence on the ice velocity, and therefore on the electrical properties of the cell. At the solution concentration ∼0.1 mol l^{-1} the polarization potential decreases more than one order of magnitude.

The calculation results show that the polarization effect of the medium becomes apparent at the high hydrocondictivity of porous media and the low concentration of solutions.

8.2. Electric polarization induced by concentration gradient

Find the sample polarization induced by the concentration difference along the height of the cell, when the electric current is equal to zero (J_e=0). Transforming Eq. (49) gives an expression for the electrical potential difference:

$$\Delta\varphi = -\frac{C_{es}}{C_{ee}}\Delta c_s$$

Substituting in the last equation the C-coefficients from Eqs. (41) and (44), and using explicit form for k-coefficients (see (9)) gives identical results for cells with zero and infinite horizontal conductivities:

$$\Delta\varphi = -\frac{(D_1 - D_2)}{c_{s0}(u_1 - u_2)}\Delta c_s, \tag{46}$$

The value of the potential difference doesn't depend on the ice content and therefore the electro-diffusion effect in the system considered is the same as in the macroporous media without ice. The electric potential difference generated by the concentration drop is named as the diffusion potential [13,17]. The value of the diffusion potential is found from Eq. (46). When the concentration difference is approximately equal to the average concentration ($\Delta c_s = c_{s0}$), the diffusion potential is equal to ∼10 mV.

9. Conclusions

In this paper the diffusion mechanism of electric polarization has only been studied. We exclude the electric double layer and freezing potential mechanisms from consideration.

In the closed system the electric potential difference is initiated by the external temperature gradient, which makes to move the ice inclusion and to produce the concentration gradient in the medium. The value of the effect is approximately so as for the freezing soils and the ice with the salt inclusions, and greater more than an order for the pure ice [18].

In the open system the ice movement hasn't an influence on the value of the diffusion potential.

In experiments with the freezing soils the electric potential difference between the frozen and unfrozen soil reaches several tens of millivolts [6,7]. It is not unlikely that the electric polarization is induced by the diffusion mechanism. In actual practice all the three mechanisms make one's contribution on the charge separation in the freezing soils. Clearing up the main source of that phenomenon is the subject matter of the further work.

Acknowledgements

This work was made within the framework of the integration program "Dangerous natural phenomena on land surface. Basic problems of functioning and existing of cryosphere in conditions of global change of natural environment" and was supported financially by Russian Foundation for Basic Research (Grant No. 05-05-64228).

We thank Dr. M.V. Kirov for an interest to our work, useful discussions, and remarks.

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