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Mathematical modeling of membrane polarization of rock

Valeriya Zadorozhnaya, Geophysical Unit, Council for Geoscience, Pretoria, South Africa

SUMMARY

Membrane polarization occurs in sediments with different surface area of capillaries (pore). Pore fluid (electrolyte) and double electrical layers (DEL) fill pore spaces. Obviously in large and in narrow capillaries the number of ions transporting an electrical current is different. In narrow capillaries part of the ions is adsorbed by DEL and do not transfer the electrical current. In large capillaries an amount of ions adsorbed by the DEL can be neglected.
Membrane polarization is based on diffusion processes occurring in the rock due to an applied electrical field. The heat equation is used for calculating the salinity distribution in pores. The models were developed from the simplest models containing three connected pores to models with complicated structure of pores space.
The polarization occurs in all types of rocks if the surface areas and transfer numbers are different for connected pores. The duration of the polarization process depends on two parameters: pore radii of connected capillaries and transfer numbers. However the influence of a large capillary occurs at the early times of the process. The longest processes are to be expected of narrow capillaries with small differences in transfer numbers. During the polarization process all contacts between pores of different transfer numbers will be blocked and electrical current flows through the rest canals. This is why the resistivity of sediments measured by constant electrical current very often does not correspond to the volume of pores space of sediments.

Keywords: polarization, resistivity, transfer number, diffusion, pore

INTRODUCTION

Polarization of rock upon the application of an electrical field presents as a separation of charges of different sign and in any volume of rock an electrical moment appears. Membrane polarization occurs in sediments with different surface area of capillaries (pore). Pore fluid (electrolyte) and double electrical layers (DEL) fill pore spaces. Obviously in large and in narrow capillaries the number of ions transporting an electrical current differs. In narrow capillaries part of the ions is adsorbed by the DEL and do not transfer the electrical current. In large capillaries an amount of ions adsorbed by the DEL can be neglected. In sediments with different surface areas of pores mobilities of ions and transform number are different. If an electrical field is spontaneously applied or vice versa if an electrical field is switched off, a transient decay of electrical field strength can be measured. This phenomenon forms the basis of the well known induced polarization (IP) method. Moreover polarization parameters measured in the laboratory to study physical properties of rocks usually include chargeability η and constant decay τ. As far as diffusion processes based on the phenomenon of membrane polarization are concerned, some problems were discussed by Keller G.V. (1960) and Anderson L.A and Keller (1964), Bokris J.O.M and Reddy A.K.N (1973). Using the heat equation they described the result of transient salinity in the simplest model – half limited tube at time off. For more than 40 years the study of the IP effect was directed at finding an analogy of electrical circuits.

THEORETICAL CONSIDERATIONS

Our aim is to provide modeling of membrane polarization in rocks with complicated structure of pores space. The primary model consists of three connected capillaries (fig.1). More complicated models containing much more connected pores of different size and transfer numbers were then used.
Let us consider the problem of salinity distribution of ions in a solution filling pores when a spontaneous electrical current is applied. Heat distribution in a bar, with controlled temperature (salinity) on its ends, can be used as a solution for this case (Koshlyakov *et al.,* 1970). The general heat equation is the following:

$$\frac{\partial u}{\partial t} = a^2 \frac{\partial^2 u}{\partial x^2}, \qquad (1)$$

where u is salinity of solution, $a^2 = D$ is a diffusion coefficient.

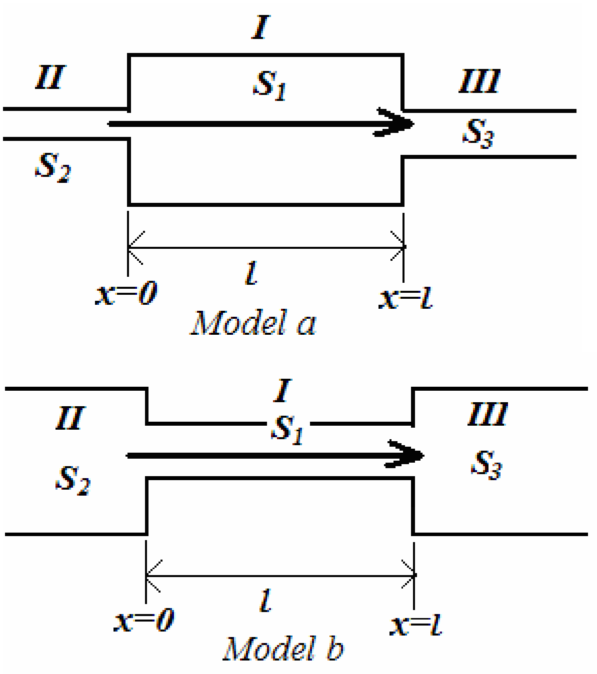

Fig.1. Models contain three connected capillaries. Arrow indicates the direction of current flow

The boundary conditions and initial conditions are:

$$u\big|_{x=0} = \psi_1(t), \quad u\big|_{x=l} = \psi_2(t) \text{ and}$$
$$u\big|_{t=0} = \varphi(t), \qquad (2)$$

where l is the length of the central pore. $\varphi(t)$ is constant and equal to salinity of cations and anions. Using the first Fick's, Kirchoff and Faraday laws it was shown that the boundary conditions can be written as follows:

$$u_0\big|_{t=0} = u_{0k} + u_{0a} = \varphi(x),$$
$$u_0\big|_{x=0} = u_{0k} + u_{\Delta 2k}(t) + u_{0a} + u_{\Delta 2a}(t) = \psi_1(t),$$
$$u_0\big|_{x=l} = u_{0k} + u_{\Delta 3k}(t) + u_{0a} + u_{\Delta 3a}(t) = \psi_2(t), \qquad (3)$$

where $u_{0k} = u_{0a} = u_0/2$,

$$u_{\Delta 2k}(t) = \frac{I_1^2 \mathrm{M}_{1k} t}{F z_k D S_1 S_2 \sigma_k}(n_{1k} - n_{2k}),$$
$$u_{\Delta 2a}(t) = \frac{I_1^2 \mathrm{M}_{1a} t}{F z_a D S_1 S_2 \sigma_a}(n_{2a} - n_{1a}),$$
$$u_{\Delta 3k}(t) = \frac{I_1^2 \mathrm{M}_{1k} t}{F z_k D S_1 S_3 \sigma_k}(n_{1k} - n_{3k}),$$
$$u_{\Delta 3a}(t) = \frac{I_1^2 \mathrm{M}_{1a} t}{F z_a D S_1 S_3 \sigma_a}(n_{3a} - n_{1a}). \qquad (4)$$

Subscripts k and a indicate cations and anions respectively, numerical subscript indicate the number of pores (I, II, III), u_0 is an initial salinity of solution, u_Δ is a excess of salinity at the boundary between pores, F – Faraday constant, z – valence, M is the mobility of ions in the central pore, σ is the conductance of ions, n is the transfer number of ions in pore, $n_k = \frac{\mathrm{M}_k}{\mathrm{M}_k + \mathrm{M}_a}$, $n_a = \frac{\mathrm{M}_a}{\mathrm{M}_k + \mathrm{M}_a}$, S is a surface area of pore, I_1 is an electrical current flowing in the pore I, t is time. Equations (4) show linear dependency of salinity on time at the boundaries between capillaries.
The solution of (1) can be found as the following series:

$$u(x,t) = \sum_{n=1}^{\infty} T_n(t) \sin\frac{n\pi x}{l}, \qquad (5)$$

where $T_n(t) = \exp(-At)\Big[C_n +$

$$+ \frac{2n\pi a^2}{l^2}\int_0^t \exp(-A\tau)\big(\psi_1(\tau) - (-1)^n \psi_2(\tau)\big)d\tau\Big],$$

$$A = \left(\frac{n\pi a}{l}\right)^2, \quad C_n = T_n(0).$$

Hence (4) are the linear function, $\psi_1(t)$ and $\psi_2(t)$ can can be written as:

$$\psi_1(t) = C_1 + C_{21}(t) = C_1 + K_{21} \cdot t,$$
$$\psi_2(t) = C_1 + C_{31}(t), = C_1 + K_{31} \cdot t, \qquad (6)$$

The difference of the functions $\psi_1(t) - (-1)^n \psi_2(t)$ can be written as:

$$\psi_1(t) - (-1)^n \psi_2(t) = Y = X \cdot t \qquad (7),$$

where $Y = \big(C_1(1 - (-1)^n\big)$, $X = (K_{12} - (-1)^n K_{31})$.

Now for salinity the solution can be written as definite integrals that provided very high accuracy of calculation:

$$u(x,t) = \sum_{n=1}^{\infty}\Bigg[C_n \cdot \exp(-At) + \frac{2n\pi a^2}{l^2}\Bigg(X\left[\frac{t}{A} - \frac{1}{A^2}\right] +$$

$$+\exp\left(-At\left[\frac{X}{A^2}-\frac{Y}{A}\right]\right)+\frac{Y}{A}\Bigg)\Bigg]\sin\frac{n\pi x}{l}. \qquad (8)$$

Software for calculating the salinity distribution in pores and potential difference caused by volume charge distributed in the pore has been created.

SALINITY ALONG THE PORE

Figure 2 demonstrates the salinity distribution along pores at selected time sequences for both models. The calculation shows the excess of salinity localized at the contacts of pores. The salinity decreases exponentially far away from contact in long pores. In short pores a linear dependence of excess of salinity has been observed even at earlier times.

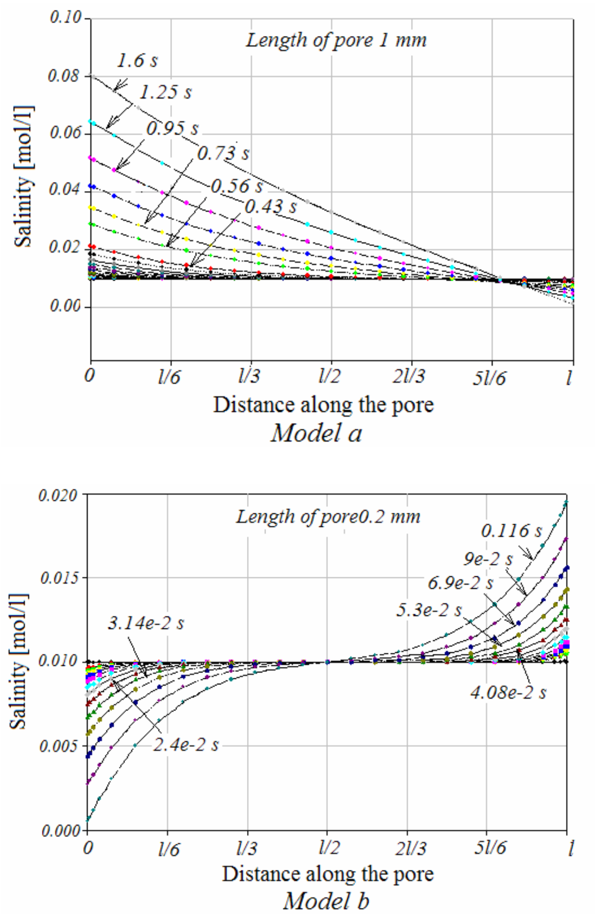

Fig.2. Salinity distribution in pore at selected time sequences. Total salinity of solution is 0.01 mol/l.

Model a. $l = 1$ mm, $r_1 = 0.02$ mm,

transfer numbers $n_{1k} = 0.5$, $n_{2k} = 0.64$, $n_{3k} = 0.53$.

Model b. $l = 0.2$ mm, $r_1 = 0.045$ mm,

transfer numbers $n_{1k} = 0.78$, $n_{2k} = 0.5$, $n_{3k} = 0.5$.

It is very important to note that if at one of the contacts i the salinity of solution is decreasing (when $n_i - n_1 < 0$), it can follow the situation when salinity at this contact will be equal to zero $\left(u_{\Delta i}(t) = -u_0\right)$. In this case it can be expected that disconnection of electrical circuit will occur. However the potential difference between the pore ends keeps stays constant. Let us name t_0 as the critical time of the polarization process. Then t_0 is equal to;

$$t_0 = -\frac{u_{0k} F z_k D S_1 S_2 \sigma_k}{I^2 \mathrm{M}_k \left(n_{1k} - n_{1i}\right)}. \qquad (9)$$

Now we come to an important conclusion: the effective time of the polarization process t_0 is controlled by the transfer numbers and radii of the connected pores. So the boundary conditions (4) for our problem exist up to time t_0, after which the rupture of the electrical circuit occurs and the potential difference between the pore ends becomes constant. It is also well known that the resistivity measured applying constant ρ_c and alternating ρ_a current are different due to polarization effect. So the value of resistivity depends on the transfer numbers of pores. In rocks containing large pores where the influence of the DEL can be neglected, or when transfer numbers of pores are the same even if the sediment contains very narrow pores, $\rho_c = \rho_a$. If transfer numbers are different, the pores with the biggest differences of transfer numbers will be blocked first, afterward all contacts between pores of different transfer numbers will be blocked and electrical current flows through the rest canals. This is why the resistivity of sediments measured by constant electrical current very often does not corresponding to volume of pores space of sediments.

POTENTIAL DIFFERENCE

The pore at switch-on time can be regarded as an extended charged body and a potential U intensity of electrical field E measured between two points of observation can be written as:

$$U = \frac{1}{4\pi\varepsilon_0 \varepsilon F z}\int_V \frac{u(x)}{r(x)}dv = \frac{S_1}{4\pi\varepsilon_0 \varepsilon F z}\int_v \frac{u_0 + u_{\Delta k,a}}{r(x)}dl, \qquad (10)$$

$$E = \frac{\Delta U}{\Delta r} = \frac{S_1}{4\pi\varepsilon\varepsilon_0 F z}\left(\int_V \frac{(u_0 + u_{\Delta k,a})}{r_1(x)}dl - \right.$$

$$- \int_V \frac{(u_0 + u_{\Delta k,a})}{r_2(x)} dl \Bigg), \qquad (11)$$

where $r_2(x)$ and $r_2(x)$ are the distances between the point of observation and points in pore, ε is a dielectric permeability, ε_0 is the electrical constant, Δr is a distance between points of observation. An example of calculating E for a rock sample of size 2.5x2.5x2.5 cm^3 with complicated pores space is shown on fig.3. This model contains pores of 16 sizes and demonstrates a typical curve of IP.

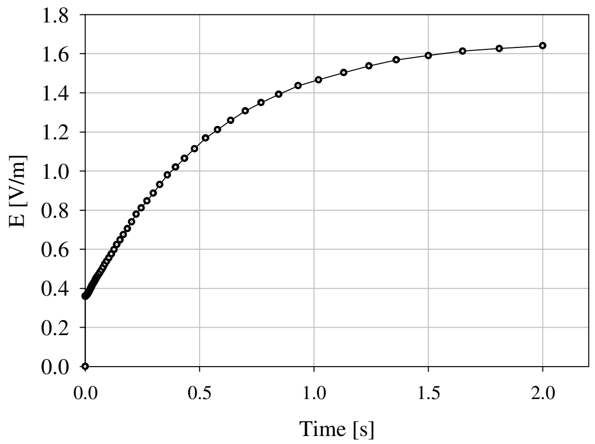

Fig. 3 Modeled intensity of electrical field in rock sample containing of pores of 16 sizes.

CONCLUSIONS

Numerous models have been calculated and the following conclusions were made:

The polarization occurs in all types of rocks if surface areas and transfer numbers are different for connected pores Duration of polarization process depends on two parameters: pore radii of connected capillaries and transfer numbers. However the influence of a large capillary occurs at the early times of process. If a large capillary is connected to a narrow capillary the duration of polarization process will be not longer than ten milliseconds. Usually this range of time is not recorded by standard IP instruments. If transfer numbers of connected large capillaries do not differ, a much longer polarization process can be recorded. The longest processes are to be expected of narrow capillaries with small differences in transfer numbers. It means the recordable time range of the IP effect corresponds to low porosity (high resistive) rocks with a small difference of transfer numbers at the contacts.

The amplitude of potential difference depends on many parameters that are constant for solutions filling pore spaces: ion mobility, diffusion coefficient, specific conductivity of solution, electrical current flowing in pores as well as volume of pores and difference of transfer numbers. However the amplitude of potential difference depends on the presence of large pores surrounded by narrow pores.

During the polarization process all contacts between pores of different transfer numbers will be blocked and electrical current flows through the rest canals. This is why the resistivity of sediments measured by constant electrical current very often does not correspond to volume of pores space of sediments.

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