Study on Microscopic Mechanism of Electrokinetic Coupling under Steady Condition

Xiaoqian Zhang*, Zheng Yan and Qi Guo

College of Emergency Management & Safety Engineering, China University of Mining and Technology (Beijing), Room 213, Zonghe Building, China University of Mining and Technology-Beijing, D11, Xueyuan Road, Haidian District, Beijing, People’s Republic of China

*Corresponding author e-mail: sdskszq@163.com

Abstract. The flow potential effects in oil-saturated pore medium are widely present in seismic exploration and electrokinetic logging, and the measurement of flow potential effects can be used to evaluate the properties of formations and fluids. In this paper, the momentum equation and current continuity equation that describe fluids in pore medium are adopted, and with the electric double layer theory of oil-water pore medium is combined with. In the capillary model considering the wettability of porous media, the expressions of the electrokinetic coupling relationship of oil-water saturated pore medium under steady conditions are derived, and the influence of electrochemical parameters of oil-water saturated pore medium on the flow potential effect under steady conditions is discussed.

1. Introduction

Reservoir rocks are complex pore medium containing formation water, crude oil and natural gas. Due to the existence of the double-layer structure at the solid-liquid interface, the residual cations in the solution migrate under the excitation of field sources such as pressure and electric field, so that the reservoir rocks exhibit different electrochemical characteristics, such as, the flow potential effect, the seismoelectric effect, and the like. In 1994, Sprunt [1] et al. conducted a core experiment to study the surge phenomenon of the flow potential, and measured the value of the flow potential when the different concentrations of the solution flow through the core under the condition that the other parameters such as the pressure difference were constant. In 2003, in the drainage experiment, Guichet [2] injected inert gas into the sandstone, and measured the flow potential under different water saturation for the first time. It was found that the flow potential decreased with the decrease of water saturation. From 2008 to 2013, Sherwood [3-5] studied the flow potential in a single capillary tube using bubble-containing capillary model theory, and considered that the bubble inside the capillary tube increased the resistance in the channel, thereby increasing the flow potential in the capillary tube. In 2006, Wu Jiankang [6] studied the electroosmotic effect in the dispersion state. He used the plate model theory to study the periodic electroosmotic flow effect in the biochip microchannel.

The flow potential effects in oil-saturated pore medium are widely present in seismic exploration and electrokinetic logging, and the measurement of flow potential effects can be used to evaluate the properties of formations and fluids. In this paper, the momentum equation and current continuity
equation that describe fluids in porous media are adopted, and with the electric double layer theory of oil-water pore medium is combined with. In the capillary model considering the wettability of pore medium, the expressions of the electrokinetic coupling relationship of oil-water saturated pore medium under steady conditions are derived, and the influence of electrochemical parameters of oil-water saturated pore medium on the flow potential effect under steady conditions is discussed.

2. Electrokinetic coupling model of reservoir rocks

2.1. Water wetting capillary model of reservoir rocks

According to the pore type and fluid distribution in the rock, the capillary bundle can be divided into four categories: the first type of capillary is a connected pore, which is an effective pore, and the saturated wetting phase fluid can flow freely; the second type of capillary is an effective pore in which the saturated non-wetting phase fluid can flow freely; the third type of capillary represents a dead end pore, a microcapillary pore and an isolated pore, which are non-effective pores in which a wetting phase fluid is distributed and cannot flow; the fourth type of capillary is also an ineffective pore, and the non-wetting fluid within it cannot flow. In addition, considering the influence of rock wettability, the inner walls of the four types of capillary bundles absorb a layer of wetting phase fluid by molecular gravitation, and its thickness is \( \delta_{wp} \). The capillary model thus established is shown in Fig. 1. The number of capillary per unit area of the \( i \) type of capillary is \( n_i (i = 1, 2, 3, 4) \), the radius of all capillary are \( r_i \), and the total number of capillary per unit area is \( n_0 \), and \( n_0 = n_1 + n_2 + n_3 + n_4 \).

![Figure 1. Capillary model of water wetting reservoir rock](image)

According to the definition of fluid saturation in reservoir rock, it is easy to obtain the macroscopic parameters of the rock—the saturation of wetting phase fluid, non-wetting phase fluid, wetting phase bound fluid and non-wetting phase residual are respectively \( S_{wp} \), \( S_{nwp} \), \( S_{wp} \) and \( S_{nwp} \), and their relationship with the microscopic parameters of the capillary are

\[
S_{wp} = \frac{n_1 \pi (r_0 - \delta_{wp})^2}{n_0 \pi r_0^2} + \frac{n_3 \pi (r_0 - \delta_{wp})^2}{n_0 \pi r_0^2} + \frac{\pi r_0^2 - \pi (r_0 - \delta_{wp})^2}{n_0 \pi r_0^2} \tag{1}
\]
In the formulas (1) to (4), the macroscopic parameters $S_{wp}$, $nwp$, $wpi$ and $nwpr$ can be obtained experimentally. The capillary radius and the total number of capillary per unit area can be estimated by the Kozeny formula, and the above four equations can be connected to obtain the expression of micro parameters of established model:

\[
S_{wpp} = \frac{n_w \pi (r_0 - \delta_{wp})^2}{n_0 \pi r_0^2} + \frac{n_w \pi (r_0 - \delta_{wp})^2}{\pi r_0^2}
\]  

(2)

\[
S_{wp} = \frac{n_w \pi (r_0 - \delta_{wp})^2}{n_0 \pi r_0^2} + \frac{\pi r_0^2 - \pi (r_0 - \delta_{wp})^2}{\pi r_0^2}
\]  

(3)

\[
S_{wp} = \frac{n_w \pi (r_0 - \delta_{wp})^2}{n_0 \pi r_0^2} 
\]  

(4)

In the formulas (1) to (4), the macroscopic parameters $S_{wp}$, $nwp$, $wpi$ and $nwpr$ can be obtained experimentally. The capillary radius and the total number of capillary per unit area can be estimated by the Kozeny formula, and the above four equations can be connected to obtain the expression of micro parameters of established model:

\[
n_1 = \frac{(S_{wp} - S_{wpp}) r_0^2}{(r_0 - \delta_{wp})^2} - n_0; n_2 = \frac{(S_{wp} - S_{wpp}) r_0^2}{(r_0 - \delta_{wp})^2} - n_0; n_3 = \frac{S_{wp} r_0^2 - r_0^2 + (r_0 - \delta_{wp})^2}{(r_0 - \delta_{wp})^2} - n_0; n_4 = \frac{S_{wp} r_0^2}{(r_0 - \delta_{wp})^2} - n_0
\]

2.2. Flow potential of water phase wetting pore medium

2.2.1. Ohm's law of current density in the water phase wetting capillary. The fluid in the first type of capillary is water, and only the solid-liquid interface can produce the electric double layer structure. Generally, the thickness $\lambda_D$ of the electric double layer in the pores of the rock is much smaller than the radius $r_0$ of the capillary, and the potential of first type of capillary is

\[
\psi = \xi_{s-w} \exp \left( -\frac{r_0 - r}{\lambda_D} \right)
\]  

(5)

In the formula, $\lambda_D = \frac{\varepsilon RT}{\sqrt{2F^2Z^2C_0}}$

Therefore, the ion concentration of the first type of wetting capillary can be expressed as

\[
C_i = C_o \exp \left( -\frac{ZF\psi}{RT} \right) = C_o \left[ 1 + \sum_{n=1}^{\infty} \left( -\frac{ZF\xi_{s-w}}{RT} \right)^n \frac{n!}{n!} \exp \left( -\frac{n(r_0 - r)}{\lambda_D} \right) \right]
\]  

(6)

The fluid in the first type of capillary is water, the gravity of the capillary is ignored, and the capillary flow with no inertia is assumed, thus the momentum equation of the capillary is

\[
\mu \nabla^2 u_{w1} = \nabla P + \rho \nabla U + RT \nabla \sum_i C_{iw} 
\]  

(7)

In the formula, $P$ is the fluid pressure; $u_{w1}$ is the fluid flow rate; $\mu$ is the fluid viscosity; $U$ is the applied electric field potential.

Using the flow rate boundary conditions: ① when $r = 0$, $u(r)_{w1}$ is the finite value; ② when $r = r_0 - \delta_{w}$, $u(r)_{w1} = 0$. The flow rate of the first type of capillary model is:
According to the theory of electrochemical mass transfer kinetics, the molar flux of the \( i \) component of the capillary solution can be obtained by linear superposition of the contribution of migration, diffusion and convection flux in the capillary.

\[
q_i = -v_i Z F C_i \frac{\partial U}{\partial x} - D_i \frac{\partial C_{ni}}{\partial x} + C_n u(r)_{ci}
\]  

Substituting formula (8) into formula (9) and integrating along the pore cross section. The ion flow rate component I of the pore capillary is as follows.

\[
w_{w,i} = -v_i Z F C_i \left[ \frac{1 + 2 \sum \left( \frac{-Z F C_i}{(RT)^n} \cdot \frac{\partial n}{\partial x} \cdot \left( \frac{\partial C}{\partial n} \cdot \varepsilon \right) \right]}{\varepsilon} \right] \frac{\partial U}{\partial x}
\]

\[
+ 2 \sum \left( \frac{-Z F C_i}{(RT)^n} \cdot \frac{\partial n}{\partial x} \cdot \left( \frac{\partial C}{\partial n} \cdot \varepsilon \right) \right) \int \frac{\partial U}{\partial x}
\]

\[
+ \frac{C_n u(r)_{ci}}{k_i n_c} \left[ \frac{1}{K_n \cdot (n+1) \cdot (n+1)} \cdot \left( \frac{\partial U}{\partial x} \right) \right] \int \frac{\partial U}{\partial x}
\]

The current density in the capillary can be obtained from the definition of current density.

\[
i = \sum_i F Z q_i = FZ \left( w_{w,i} - w_{w,i} \right) = P_n \frac{\partial P}{\partial x} + P_{w,22} \frac{\partial U}{\partial x} + P_{w,23} \frac{\partial C_{w}}{\partial x}
\]  

2.2.2. The second type of capillary model of water wetting porous medium. The electric double layer in the second type of capillary includes the electric double layer generated at the interface between the rock and the formation water and the electric double layer on the oil-water interface. Since the thickness of the water film is very thin, the potential in the water film can be approximated as a superposition of the electric double layer potentials of two interfaces, that is,

\[
\psi = \zeta_{w,2} \exp \left( -\frac{r_0 - r}{\lambda_d} \right) + \zeta_{w,3} \exp \left( -\frac{r - r_0 + \delta_d}{\lambda_d} \right)
\]  

The current intensity formed in the second type of capillary is

\[
I_{w,2} = FZ \left( w_{w,2} - w_{w,2} \right) = L_{w,22} \frac{\partial U}{\partial x} + L_{w,23} \frac{\partial C_{w}}{\partial x}
\]  

2.2.3. The third type of capillary model of water wetting pore medium. The third type of capillary represents dead pores, because the bound water in the capillary cannot flow, so no flow current can be generated in the capillary, but the water phase in the capillary can be electrically conductive, and the
structure of electric double layer is the same as that of the first type of capillary. Therefore, the current in this type of capillary is

\[
I_{w-1} = FZ (w_r - w_i) = L_{w-22} \frac{\partial U}{\partial x} + L_{w-23} \frac{\partial C_0}{\partial x} \tag{14}
\]

2.2.4. The fourth type of capillary model of water wetting pore medium. The fourth type of capillary means dead pores, the internal fluid does not flow, and the structure of electric double layer is the same as that of the second type of capillary, and only the conduction current can be formed in the capillary, and the size is the same as that of the second type of capillary, so

\[
I_{w-4} = L_{w-22}^{4} \frac{\partial U}{\partial x} + L_{w-23}^{4} \frac{\partial C_0}{\partial x} \tag{15}
\]

2.2.5. Calculation method of flow potential of water wetting pore medium. Through the established capillary model, the current intensity \( j \) per unit area in the oil-water saturated pore medium can be obtained as

\[
j = n_1 I_{w-1} + n_2 I_{w-2} + n_3 I_{w-3} + n_4 I_{w-4} \\
= n_1 L_{w-21}^{1} \frac{\partial P}{\partial x} + (n_1 L_{w-22}^{1} + n_2 L_{w-22}^{2} + n_3 L_{w-22}^{3} + n_4 L_{w-22}^{4}) \frac{\partial U}{\partial x} + (n_1 L_{w-23}^{1} + n_2 L_{w-23}^{2} + n_3 L_{w-23}^{3} + n_4 L_{w-23}^{4}) \frac{\partial C_0}{\partial x} \tag{16}
\]

In the formula,

\[
L_{n-21} = n_1 L_{n-21}^{1}, L_{n-22} = n_1 L_{n-22}^{1} + n_2 L_{n-22}^{2} + n_3 L_{n-22}^{3} + n_4 L_{n-22}^{4}, L_{n-23} = n_1 L_{n-23}^{1} + n_2 L_{n-23}^{2} + n_3 L_{n-23}^{3} + n_4 L_{n-23}^{4}
\]

3. Calculation Examples

Assuming the flow potential coupling coefficient \( \eta = \frac{\Delta U}{\Delta P} \) of water wetting pore medium, so the expression is

\[
\eta = \frac{\Delta U}{\Delta P} = \frac{L_{w-21}}{L_{w-22}} \frac{L_{w-23} \frac{\partial C_0}{\partial x}}{L_{w-22} \frac{\partial C_0}{\partial x}} \tag{17}
\]

In the simulation calculation, a set of data of macroscopic reservoir permeability parameters of the reservoir rock is needed to determine the microscopic parameters in the capillary model. Assuming that the formation water is a NaCl solution, the macro parameters selected are shown in Table 1.

| Parameter                          | Numerical value | Parameter                          | Numerical value |
|------------------------------------|-----------------|------------------------------------|-----------------|
| Porosity \( \phi \)                | 1.2             | Cation exchange capacity \( q_+ \) (mol·L⁻¹) | 1.0             |
| Formation water salinity \( C_+ \) (mg·L⁻¹) | 1500            | Na⁺ Mobility \( \nu_+ (10^{-10} \text{mol·S·kg}⁻¹) \) | 5.01            |
| Solution properties \( \text{NaCl} \) | \( \rho_\text{f} \) (g·cm⁻³) | CT Mobility \( \nu_+ (10^{-10} \text{mol·S·kg}⁻¹) \) | 7.62            |
| Formation water density \( \rho_\text{f} \) (g·cm⁻³) | 1.0             | Formation water viscosity \( \mu \) (mPa·s) | 1.0             |
3.1. Influence of water saturation and porosity on the dispersion characteristics of flow potential coupling coefficient

By changing the value of water saturation, the relationship curve between the flow potential coupling coefficient and the water saturation in the water wetting frequency domain can be obtained, as shown in Fig. 2(a). The values of different water saturations are obtained. The relationship between the coupling coefficient of flow potential and the water saturation in water wetting porous media is numerically simulated. The relative coupling coefficient increases with the increase of water saturation. When the water saturation is lower, the flow potential is generated, resulting in the substantial coupling coefficient because the fluid cannot flow when it is completely present in the form of bound water. The relationship curve between the solution concentration and the flow potential coupling coefficient in the oil-water saturated pore medium is shown in Figure 2(b), where the modulus is porosity. It can be seen from the figure that as the concentration of the solution increases, the absolute value of the flow potential coupling coefficient in the oil-water saturated pore medium decreases. This is because the electric double layer function of the pore solid-liquid interface decreases with the increase of concentration in the oil-water saturated pore medium solution, so that the electrochemical interaction between the oil-water interface becomes smaller, thereby weakening the absolute value of the flow potential coupling coefficient.

### Figure 2.

(a) Relationship between streaming potential coupling coefficient and water saturation, concentration  
(b) Relationship between streaming potential coupling coefficient and concentration

3.2. Influence of cation exchange capacity and porosity on dispersion characteristics of coupling coefficient of flow potential

While other parameters remain unchanged, the amount of cation exchange is changed, and the coupling coefficient of the flow potential of the water wetting pore medium and its variation are obtained, as shown in Figure 3(a). It can be seen from the figure that as the amount of cation exchange increases, the absolute value of the coupling coefficient of the flow potential in the oil-water saturated pore medium decreases. This indicates that the larger the cation exchange amount, the more ions are adsorbed on the solid-liquid interface of the oil-water saturated pores, and the larger the electric double layer potential on the solid-liquid interface, the more obvious the obstruction effect of the electric field generated on the fluid flow, namely, the absolute value of flow potential coupling coefficient becomes smaller. Under the same parameters, the permeability can be derived from the porosity. When the relationship between the coupling coefficient of flow potential and the porosity is obtained, we also obtain the relationship between the coupling coefficient of flow potential and the permeability, as shown in Figure 3(b). It can be seen from the figure that the absolute value of the coupling coefficient of the flow potential increases with the increase of the permeability, and the change trend is similar to the relationship between the
coupling coefficient of the flow potential and the porosity.

![Graph](image)

Figure 3. Relationship between streaming potential coupling coefficient and cation exchange capacity, porosity

4. Conclusion

By using Darcy's law, Fick's law and Ohm's law in the pore medium, the relationship between the seepage field, the current field and the ion flow field is established, and the formula for calculating the flow potential in the oil-water saturated pore medium is derived. The relationship between the flow potential and the physical parameters of the pore medium is analyzed, and the following conclusions are drawn:

As the water saturation increases, the absolute value of the coupling coefficient of the flow potential in the pore medium increases. When the water saturation is $S_w \leq 0.2$, the coupling coefficient of flow potential in the pore medium is substantially zero. At this time, the water in the capillary exists in the form of bound water, because the bound water cannot flow, and therefore the flow potential in the pore medium cannot be generated; With the increase of the concentration of the solution in the pore medium and the amount of cation exchange, the absolute value of the coupling coefficient of the flow potential decreases, and the coupling coefficient of the flow potential in the pore medium increases with the increase of porosity and permeability. The water film thickness has an influence on the coupling coefficient of flow potential and the oil film thickness has no effect on the coupling coefficient of flow potential.

References

[1] Sprunt E S, Mercer T B, Djabbarah N F, Streaming potential from multiphase flow [J]. Geophysics, 1994, 59: 707-711.
[2] Guichet X, Jouniaux L, Pozzi J P. Streaming potential of a sand column in partial saturation conditions [J]. Journal of Geophysical Research, 2003, 108 (B3): 2141
[3] Sherwood J D, Xie Y, A van den Berg, Eijkel J C T. Theoretical aspects of electrical power generation from two-phase flow streaming potentials [J]. Microfluid Nanofluid, 2013, DOI 10.1007/s10404-013-1151-7.
[4] Sherwood J D. Streaming potential generated by a drop moving along the centreline of a capillary [J]. J. Fluid Mech, 2009, 640: 55-77.
[5] Sherwood J D. Streaming Potential Generated by a Long Viscous Drop in a Capillary [J]. Langmuir, 2008, 24 (18): 10011-10018.
[6] Wang R J, Lin J Z. Numerical analysis on a passive chaotic micromixer with helical microchannel [J]. Journal of Nanoscience and Nanotechnology, 2006, 6 (1): 190-194.