Microscale Modelling of the Frequency Dependent Resistivity of Porous Media

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Abstract: The frequency dependent electrical impedance of porous media is studied by modelling the charge transport in the electrolyte filled pore space.

The corresponding experimental method, called Spectral Induced Polarization (or Impedance Spectroscopy), shows a frequency dependent phase shift between a measured electric current and an applied alternating voltage. It is caused by microscopic polarization effects depending on inner rock structure and electrolyte properties. To study these effects we use a membrane polarization model similar to a model proposed by Marshall and Madden (1959) with different ion-mobilities for cations and anions in smaller pores.

The governing equations and boundary conditions for a system of larger and smaller pores with apllied voltage are expressed in frequency domain using a time harmonic approach, the electric current is determined to obtain information about amplitude and phase of the complex resistivity.

The resulting resistivity-spectra show a frequency dependence as expected from experiments. Scaling up the pore sizes produces a shift of the characteristic curves.

Keywords: spectral induced polarization, porous media, pore scale,

1. Introduction

In geophysics frequency dependent complex resistivity measurements are called Spectral Induced Polarization (SIP). In other fields this method is known as Impedance Spectroscopy. In the last two decades many empirical relations were proposed which relate the frequency dependent electrical properties of water saturated rocks to structural properties such as pore radius, and inner surface area, or to hydraulic conductivity. Unfortunately, these relations are not universal; they apply only for specific rock types and water compositions. In order to

quantify the influence of inner rock structure (as well as of electrochemical water and rock properties) on the frequency dependent electrical properties we model the charge transport processes at the pore space.

In the frequency domain the effect of Induced Polarization (IP) is characterised by a phase shift between a measured electric current and an alternating voltage applied to the ground. A possible origin of this behaviour particularly for non-conducting rock minerals can be seen in the membrane polarization model as proposed by Marshall and Madden (1959). This model describes a system of electrolyte filled pores. Different mobilities of cations and anions in the small pores cause a membrane effect and thus an electrical polarization. This assumption is justified, as surface charges at the pore walls cause an electric double layer (EDL) in the electrolyte with different mobilities for different ions. In small pores the EDL dominates the charge transport while its effect can be neglected in large pores.

The influence of the microscopic pore structure on the frequency dependent electric behaviour is studied by numerical analysis. The pore space is assumed to be water saturated.

2. Equation System

2.1 Governing Equations (time domain)

The governing equations for charge transport in pore space according to Marshall and Madden (1959) are the continuity equations for the concentrations of cations \boldsymbol{C}_p and anions \boldsymbol{C}_n and Poisson's equation for the potential U:

$$\frac{\partial}{\partial t}C_{p} = D_{p}\Delta C_{p} + \nabla \left[\mu_{p}C_{p0}\nabla U\right],$$

$$\frac{\partial}{\partial t}C_{n} = D_{n}\Delta C_{n} - \nabla \left[\mu_{n}C_{n0}\nabla U\right],$$

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$$\Delta U = \frac{F}{\varepsilon} (C_n - C_p),$$

where D_p and D_n are the diffusion coefficients, μ_p and μ_n the mobilities of the ions, F Faraday's constant and ε the permittivity. The Einstein relation relates $D_{p/p}$ and $\mu_{p/p}$:

$$D_{p/n} = \frac{\mu_{p/n} k_B T}{e}$$

with Boltzmann's constant $k_{\scriptscriptstyle B}$, Temperature T and elementary charge e .

It is possible to examine the frequency dependent resistivity of pore systems by solving these equations time dependent for each frequency of alternating voltage (Blaschek and Hördt, 2007).

2.1 Governing Equations (frequency domain)

Since we are interested in frequency dependent effects if an alternating voltage ($\sim \sin(\omega t)$) is applied we choose a time-harmonic approach ($\sim \exp(i\omega t)$) for electric fields and excess concentrations in order to calculate the electrical properties more effectively.

The total concentrations of cations C_p and anions C_n of the electrolyte in the pore space are

$$C_p = c_{p0} + c_p \cdot e^{i\omega t}$$
 and $C_n = c_{n0} + c_n \cdot e^{i\omega t}$

with the constant concentrations \mathcal{C}_{p0} and \mathcal{C}_{n0} (concentrations of ions without applying voltage) and the complex amplitudes of the excess-concentrations \mathcal{C}_p and \mathcal{C}_n .

The electric potential is written in the form

$$U = u \cdot e^{i\omega t}$$
.

For small and time-harmonic electric fields $E = -\nabla U$ and excess-concentrations, the

governing equations for the complex amplitudes of the potential u and excess-concentrations c_p and c_n can be written in the form (Marshall and Madden, 1959):

(I)
$$i\omega c_p = D_p \Delta c_p + \nabla \left[\mu_p c_{p0} \nabla u \right],$$

(II)
$$i\omega c_n = D_n \Delta c_n - \nabla \left[\mu_n c_{n0} \nabla u \right],$$

(III)
$$\Delta u = \frac{F}{\varepsilon} (c_n - c_p).$$

The equations above are valid for monovalent ions with equal equilibrium concentrations $c_{p0} = c_{n0}$ (e.g. NaCl solution).

3. Model Properties

The equations (I)-(III) operate on a 2D axial symmetric geometry (verified by 3D-modelling) with small and large pores (Figure 1). For the basic model the small pores have a radius of $0.1\mu m$ and the large pores a radius of $1\mu m$ while the lengths of the pores are $1\mu m$ in both cases. According to Marshall and Madden (1959) we assume different ion mobilities $\mu_p \neq \mu_n$ in the small pores while the mobilities are equal in the large ones.

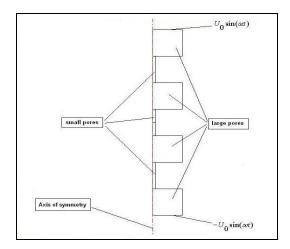


Figure 1. Pore system with applied alternating voltage.

A sinusoidal voltage is applied at the ends of the pore system by setting up boundary conditions for the complex amplitude of the time-harmonic voltage.

For equations (I) and (II) the "Electrokinetic Flow" application mode, for equation (III) the "Electrostatics" application mode (2D axial symmetry) is used.

As initial condition the electric potential and the excess-concentrations are equal to zero:

$$c_n(t_0) = c_n(t_0) = u(t_0) = 0$$

The system is solved parametrically for the frequency

$$f = (2\pi)^{-1}\omega$$
 ($f = 10^{-3}...10^{6}$ Hz).

4. Results

The ions concentrate at the ends of the smaller pores (Figure 2). Since there is a small difference in these excess-concentrations for the different types of ions the pore system shows the expected membrane polarization effect.

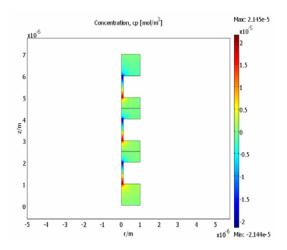


Figure 2. Excess-concentration of cations in the pore system at $\omega t = \frac{\pi}{2}$.

The electric current $I = |I| e^{i\varphi} e^{i\omega t}$ is determined by evaluating the surface integral of the complex current density for the cross-section of one pore. The complex resistivity R is given by the ratio of the applied voltage and this current. A first

result for the influence of the pore geometry on IP spectra is shown in figures 3 and 4. The resistivity amplitude (Figure 3) and phase (Figure 4) have a frequency-dependence as expected from laboratory experiments. Furthermore, there is a shift of the phase minima and the corresponding decrease of the resistivities from high to low frequencies when scaling the geometry (large pores with radius 1 μ m, small pores with radius 0.1 μ m, red curve) by a factor ten (blue curve) or hundred (green curve).

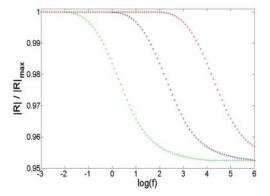


Figure 3. Frequency-dependence of the resistivity amplitude for a radius of 1 μ m (red), 10 μ m (blue), 100 μ m (green) of the larger pores. The aspect ratio between the small and the large pores remains constant (1:10).

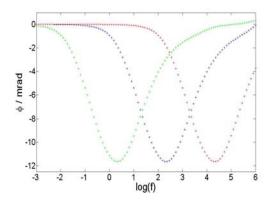


Figure 4. Frequency-dependence of the resistivity phase for a radius of 1 μ m (red), 10 μ m (blue), 100 μ m (green) of the larger pores The aspect ratio between the small and the large pores remains constant (1:10).

The dependence of the position of the phase minimum on the scale factor can be determined as a power law (Figure 5).

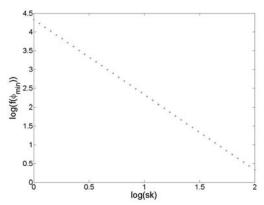


Figure 5. Scale factor dependence of the frequency of the phase minimum.

7. Conclusions

We are able to study the IP-Effect at the pore scale based on the membrane polarization model in frequency domain. The results of the numeric analysis are in agreement with those of experiments. The model can be applied to study the influence of pore sizes and pore structure as well as of electrolyte properties like ion mobilities and concentrations.

Furthermore we aim to find a more realistic way of modelling the membrane polarization effect than using the simple Marshall and Madden model. Since the electric double layer is caused by surface charges at the pore walls the origin of the Induced Polarization effect is located at the electrolyte rock interface. So modelling the EDL as a boundary effect would be probably more realistic than assuming a reduced anion mobility for the smaller pores as a whole.

8. References

- 1. Marshall, D.J. and Madden, T.K., Induced Polarization, a study of its causes, *Geophysics*, **24** (4), 790-816 (1959)
- 2. Blaschek, R. and Hördt, A., Numerical modeling of the IP-effect at the pore scale, 4th *International Symposium on Three-Dimensional Electromagnetics*, Freiberg, Germany, (September 27-30, 2007)