LOW FREQUENCY DIELECTRIC PROPERTIES OF SELECTED MOIST CLAYS

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ABSTRACT: *Recently the dielectric spectroscopy studies of clay soils has been extensively used for characterization of water content in these materials in order to better understand its electrical and mechanical properties. In this work we have performed the low frequency (100 Hz – 100 MHz) dielectric spectroscopy of selected kaolinitic clays at different water content raging from dry, over plastic to liquid limit. Specifically, the possible correlation between the dielectric properties of the chosen samples within the moisture regime where their mechanical shear modulus has been shown to exhibit a variation in magnitude has been investigated, however the results are found to be inconclusive. For all samples investigated, depending on the moisture content, the measured capacitance response reflects the anomalous behavior within the certain frequency region where the negative values of capacitance have been observed. Here we present a novel model based on the ions random drift in the presence of an absorbing barrier explaining the observed anomalies.*

1. INTRODUCTION

One of the most broadly used experimental methods for the investigation of the interfacial properties is the method of the capacitance spectroscopy. Most studies of this nature are concerned with the modification of classical capacitance arising due to various causes such as the occurrence of finite density of electronic states at the interface or electron tunneling through it. In this respect occasionally in the literature some very unusual results are reported. For instance, in the investigation of metal-semiconductor contacts it was observed that under forward bias some Schottky diodes manifest a »negative capacitance« in response to an AC signal. This effect was assigned to the impact-loss of electrons at the occupied interface states under high injection of hot electrons [1]. The recent investigation of the differential capacitance of quantum dots has shown that, providing the electron tunneling rates is external bias dependent and providing that only the limited number electron energy levels contribute to the electron transport in such a quantum dot, the negative differential capacitance is predicted [2]. On the other hand, the negative capacitance effect, but this time as a function of external AC signal frequency (at a given, but small, bias), has been found in the investigation of electroluminescent devices formed by the OC_1C_{10}-PPV organic polymer semiconductor/metal contacts. The solid semiconductor polymer is in general a dispersive medium as it was often observed that the charge carriers transit time, on account of the disorder, follows certain empirically established distribution density. An explanation of the negative capacitance in such samples has been offered by Kwok [3]. Using the Drude model for charge transport, he has introduced the complex mobility of charge carriers in order to incorporate the effect of time delay as caused by the dispersion of such medium. The capacitance of this system becomes negative if the carrier mobility possesses a negative imaginary component, what effectively represents the charge trapping in this dispersive medium. Physically this means that the damping (caused by collisions and traps) influences a direct negative impact on the polarization of the plasma, causing the capacitance to be lowered.

Recently, the capacitance spectroscopy of certain moist clay soils [4, 5] has resulted, at zero applied external bias, in the negative values of capacitance as measured within the large frequency interval of the external AC signal. Since the properties of moist soils and clays are of great practical importance (for the purpose of »in situ« electrical characterization of the soil contamination, the possibility of the rapid electrical determination of some of soil reological properties, etc.) a thorough understanding of their electrical properties is required. Since the »cause« of anomalous capacitance behavior of moist clays appears to be just the ordinary water acting as a solvent for various ionized salts (i.e. charge carriers) comprising the soil under investigation it appears this system to represent a simple physical model serving as a starting point in order to gain a thorough physical insight into the mechanism of negative capacitance formation. Surprisingly, it turns out that this problem in moist clays appears to be far more evolved than initially expected.

2. EXPERIMENT AND RESULTS

The electrical characteristics of the clay-water system were measured using the low frequency impedance analyzer at room temperature. The admittance of the sample placed in the measuring cell between two planparallel electrodes (area S=5,5 cm^2, distance L=4,5 – 5 mm) was determined from the linear response of the sample to the small oscillating bias on the electrodes of magnitude 10 mV. The real (conductance) and imaginary part (capacitance) of the admittance were measured in the frequency interval 100 Hz to 100 MHz. The soil sample used was kaolinitic clay. The frequency dependence of the conductance and capacitance was determined first for dry sample, and then for moist samples, with moisture content ranging from 36 % to 56 %. Moist samples were obtained with addition of distillated water to the clay. Figures 1 and 2 show typical measured capacitance and conductance of the moist clay sample. The frequency range for the capacitance in figure 1 shows the details of the part of the spectrum where the negative capacitance effect was observed.

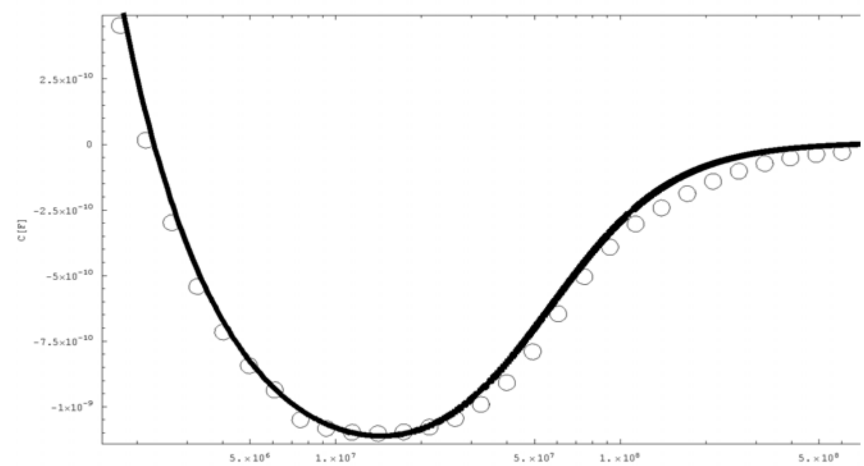

Figure 1: *Measured frequency dependence of capacitance of the moist kaolinitic clay. The moisture content was 32 %. The part of the spectrum exhibiting the negative capacitance effect is presented. The dot represent the measured values, while the solid line corresponds to the calculated values (see eq. 1).*

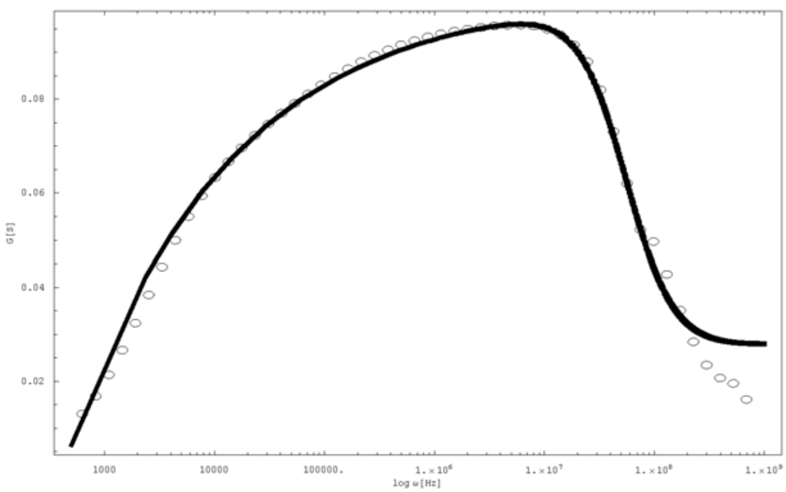

Figure 2: *Measured frequency dependence of the conductance of the moist kaolinitic clay. The moisture content was 32 %. The dot represent the measured values, while the solid line corresponds to the calculated values (see eq. 2).*

The solid lines in figures 1 and 2 are calculated from the following expressions for the frequency dependence of the capacitance C and conductance G of the moist clay soil:

$$C(\omega) = C_\infty \left(\varepsilon_\infty - \frac{b}{1+\omega^2\tau^2} + \frac{\varepsilon_s}{(\omega\tau)^{s+1}} \right), \tag{1}$$

where , and

$$G(\omega) = C_\infty \frac{b}{\tau}\left(\frac{1}{1+\omega^2\tau^2} - \frac{c_2}{(\omega\tau)^s} \right) + c_1 . \tag{2}$$

Here $C_\infty = \varepsilon_0 S / L$ is the geometric capacitance of the empty measuring cell. For the calculation of the solid lines shown in figs. 1 and 2 the following values of the parameters were used: b=950, c_1=0,029, τ=1,8 10^{-8} s, ε_s=15, $\varepsilon_\infty = 2$, c_2=0,04, s=0,3. The physical model and the arguments leading to expressions for the capacitance and conductance in eqs. 1 and 2 are given in some detail in the following. The model description of the measured data based on eqs. 1 and 2 for other moist clay samples yielded similar results with only slight changes of parameters values except in case of dry clay sample where the parameters b and c_1 are set to zero [5].

3. THEORETICAL CONSIDERATIONS AND DISCUSSION

In the experiment performed the admittance $Y(\omega)$ as a function of the frequency of the applied electric field was determined which measures the linear response of the soil-water system to the oscillating perturbation. In general is the current density at given moment a linear function of the values of the electric field at all previous moments [6] so the following relationship between the

Fourier transforms of one dimensional current density and electric field applies for the sample between two planparallel electrodes (area S, distance L):

$$j(\omega) = Y(\omega)E(\omega)L / S\ . \tag{3}$$

We regard the moist clay as an complex medium consisting of mobile ions in the water solution and the dielectric clay matrix. It was already emphasized [7] that the effect of mobile ions on the dielectric properties of soil-water system cannot be neglected when considering its dielectric response. From figs. 1 and 2 we can read off the main features of the measured soil-water dielectric spectrum. These are: the high values of the low frequency capacitance, the negative capacitance in the frequency interval from few kHz to 10 MHz, and the specific shape of the conductance spectrum with the increasing and decreasing part in the low and high frequency part of the spectrum respectively connected with the plateau.

The recent models [1, 3, 4] seem to represent a step forward in understanding the underlying principles of the negative capacitance effect. However, we must emphasize that the complete model should involve the description of both (real and imaginary, i.e. conductance and capacitance) components of the admittance since they are related through the dispersion (Kramers-Kronig) relations which give additional check on the physical soundness of the model. The same can be said on the presentation of the relevant measured data. On the other hand Ershow et. al [8] have connected the origin of negative capacitance effect with the properties of the transient currents in response to the small voltage step and have presented the model for the admittance based on the transient current Fourier transform.

We start from the Fourier transformed Maxwell equation (Maxwell-Ampere law) for the curl of the magnetic field:

$$\vec{\nabla} \times \vec{H} = \vec{j}(\vec{r},\omega) = \vec{j}_f(\vec{r},\omega) - i\omega\vec{D}(\vec{r},\omega), \tag{4}$$

where on the right hand side is the total current density comprising of the free current due to the mobile ions and the displacement current due to the dielectric response. We further divide the free current into the bulk and the transient part. This division can be substantiated with the following arguments. The water in soils is classified into adsorption, capillary, and free water [9]. We envisage that the motion of the water molecules and ions associated with the first two types is controlled by the surface of the soil particle, while this boundary has no impact on the water molecules and ions associated with the free water.

The bulk part of the current therefore originates from the unbound motion of the ions through the solution. The interaction of the ion with the surrounding solution is described with the relaxation time τ. The equation of motion in one dimension of the particle moving in the fluid under applied electric field is:

$$m\frac{dv}{dt} = -\frac{m}{\tau}v + qE, \tag{5}$$

where $-(m/\tau)v$ describes the hydrodynamic resistance causing the dissipation with the relaxation time τ. Using $j = qnv$ for the (averaged) macroscopic bulk current density we have (after Fourier transforming the above equation) the known expression for the Fourier component of the bulk current density:

$$j_b(\omega) = \frac{(q^2 n\tau / m)E(\omega)}{1 - i\omega\tau}, \tag{6}$$

The motion of the ions under applied electric field in the adsorbed and capillary water layer near the soil particle surface is here treated as a random walk of particles in the presence of an partially absorbing barrier. The standard approach to the transport problem for random walk motion of the particles focuses on the advection-dispersion equation which in absence of the drift velocity (or constant electric field in our case) simplifies to diffusion equation:

$$\frac{\partial w}{\partial t} = D\frac{\partial^2 w}{\partial x^2}. \tag{7}$$

The solution of this equation gives the probability density distribution w describing the particles motion. In our case we need to consider the following initial and boundary conditions:

$$w(x, x_0, t = 0) = \delta(x - x_0)\text{, and } \frac{\partial w}{\partial x}\Big|_{x=0} - hw(x, x', t)\Big|_{x=0} = 0. \tag{8}$$

The boundary condition describes the partially absorbing barrier where the parameter h is given as $h = (1 - p)/p\lambda\sqrt{2\pi}$, where p is the probability the particle impinging on the barrier is reflected, and λ is the mean free path of the particle. Solving the eq. 7 with the stated initial and boundary conditions it is shown [10] that the asymptotic behavior for the particle current density dN/dt when $\hat{h} = h\sqrt{Dt}$ >>1 is:

$$\frac{dN}{dt} \propto t^{-1/2}. \tag{9}$$

Complex systems often exhibit anomalous diffusion transport properties theoretically described by continuous time random walk [11] and time-fractional advection-diffusion equation [12], with the transient current density power-law time dependence: $j_{tr} \propto t^{s-1}$, $0<s<1$. The corresponding Fourier transform of such transient current, assuming non-local time dependence of the response to the applied electric field is:

$$j_{tr}(\omega) \propto \omega^{-s} E(\omega). \tag{10}$$

Taking the moist clay as macroscopically homogenous, the total current density in one dimensional case is:

$$j(\omega) = j_{tr}(\omega) + j_b(\omega) - i\omega\varepsilon(\omega)E(\omega), \tag{11}$$

where $\varepsilon(\omega)$ is the dielectric function of the soil. Using eqs. 6 and 10 in eq. 11 the functional form of the admittance of the moist clay as described with the model function in eqs. 1 and 2 is obtained. Furthermore we see that the parameter $b = e^2 n\tau^2 / m\varepsilon_0$ depends on the the particle density n. For the measured samples this turned out to be approximately 10^{21} m^{-3} [5]. The value of the parameter c_1 gives the dc conductivity of the sample which for example shown in figs. 1 and 2 equals 0,2 S/m. The value of the parameter $\varepsilon_\infty = 2$ gives the optical dielectric constant of the sample. The physical meaning of the parameters describing the microscopic mechanisms of the random motion in the presence of absorbing soil particle surface ε_s, c_2, and s remains at this moment unclear.

4. CONCLUSIONS

The dielectric spectrum of selected moist clay soils exhibited anomalous features in the certain frequency range, most prominently the negative capacitance effect. The measured capacitance and conductance frequency dependence of the selected samples where found to be reasonably well described by the model based on two different particle transport mechanisms in the soil-water solution system. While the parameters describing the bulk current due to the unbound ion motion in free water layer of the moist soil can be given suitable physical background, the microscopic origin of the parameters describing the transient current due to anomalous diffusion transport in the presence of partially absorbing clay particle surface remain unclear at this moment.

5. ACKNOWLEDGEMENT

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6. REFERENCES

[1] X. Wu, E. S. Yang, and H. L. Evans, J. Appl. Phys. **68**, 2845 (1990).
[2] S. D. Wang, Z. Z. Sun, N. Cue, H. Q. Xu, and X. R. Wang, Phys. Rev B, **65**, 125307-3 (2002).
[3] H. L. Kwok, Solid-State Electronics, **47**, 1089 (2003).
[4] M. Carrier, K. Soga, Eng. Geology **53**, 115 (1999).
[5] J. Kramer, Raziskave možne soodvisnosti nekaterih mehanskih (nedrenirane strižne trdnosti v območju plastičnosti) in dielektričnih svojstev izbranih vezljivih zemljin, Univerza v Mariboru, Fakulteta za gradbeništvo, Diplomsko delo 2003.
[6] L. D. Landau, E. M. Lifshitz and L. P. Pitaevskii, *Electrodynamics of Continuous Media*, 2nd ed., Pergamon Press, 1984.
[7] A. Kaya and H.-Y. Fang, J. Env. Eng. **123**, 169 (1997).
[8] M. Ershov, H. C. Liu, M. Buchanan, Z. R. Wasilewski, and A. K. Jonsher, IEEE Trans. Elec. Dev. **45**, 2196 (1998).
[9] T. Saarenketo, J. Appl. Geophysics **40**, 73 (1998).
[10] A. S. Usenko and A. G. Zagorodny, Mol. Phys. **61**, 1213 (1987).
[11] H. Scher and E. W. Montroll, Phys. Rev. B **12**, 2455 (1975).
[12] R. Metzler and J. Klafter, Phys. Rep. **339**, 1 (2000).