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## **Dielectric Response of Fluid Radioactive Waste Contaminated Soils**

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### **ABSTRACT**

In this work we give the analysis of the low frequency (100 Hz – 100 MHz) dielectric response of selected kaolinitic clays at different water content ranging from dry, over plastic to liquid limit. For all samples investigated, depending on the moisture content, the real part of the dielectric function reflects the abnormal behaviour within the certain frequency region where the negative values of capacitance have been observed. The anomalies are explained within a generalized conductivity model based on the clay-water electrolyte ions free motion in pore water and their restricted motion near the clay particle surface. The results indicate that the dynamics of the ions in moist clay is in part governed by anomalous diffusion.

### **1 INTRODUCTION**

Low and intermedium radioactive waste (LILW) are deposited in surface or underground repositories. The release of radionuclides from the repository into biosphere is prevented using artificial barriers such as concrete containers or concrete walls, and natural barriers such as soil, clay and rock surrounding the repository. Monitoring of radionuclide concentrations in the repository surrounding soil is one of the key safety issues. Often, geophysical methods such as GPR (ground penetrating radar) methods are used in monitoring radionuclide concentration in the vicinity of the repository. For more accurate determination of the contamination the geophysical methods need to be calibrated with in-situ measurements of the soil samples.

Safety and environmental issues are crucial for the present efforts for determination of radioactive waste repository site in Republic of Slovenia [1]. The soil in the vicinity of the repository site can become contaminated through transport of moist in soil and migration of radionuclides through porous soil [2], so the knowledge and application of complementary experimental methods of contamination detection is of paramount importance [3, 4]. The dielectric spectroscopy of selected soil samples offers a possibility for monitoring the contamination of the soil in the vicinity of the repository. However, the complex dielectric characteristics of moist soil [5-8] which includes several relaxation mechanisms and often anomalous features of the underlying transport mechanisms does not allow simple analysis and correlation between the dielectric properties and degree of contamination [9, 10].

The aim of this work is to contribute to better understanding of the key physical processes involved in the dielectric response of moist soils and to identify key physical parameters that determine the linear response of the clean and contaminated moist soil. Here we concentrate on the very simple noncontaminated system consisting of selected kaolinitic clay and water but which already exhibits surprisingly complex behaviour [11].

## 2 EXPERIMENTAL DETAILS AND RESULTS OF MEASUREMENTS

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  $S=5,5 \text{ cm}^2$ , distance  $L=4,5 - 5 \text{ mm}$ ) 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 distilled water to the clay.

The results of the measured conductance of the dry and of the moist samples with lowest and highest moisture content are shown on figures 1 and 2. The common feature of all capacitance spectra are the increasing capacitance with diminishing frequency. Additionally, moist samples exhibit negative capacitance effect in the bounded frequency region as shown in figure 3. Notice that the conductance spectra of the dry and moist samples exhibit completely different dependence on the frequency (figs. 1 and 2).

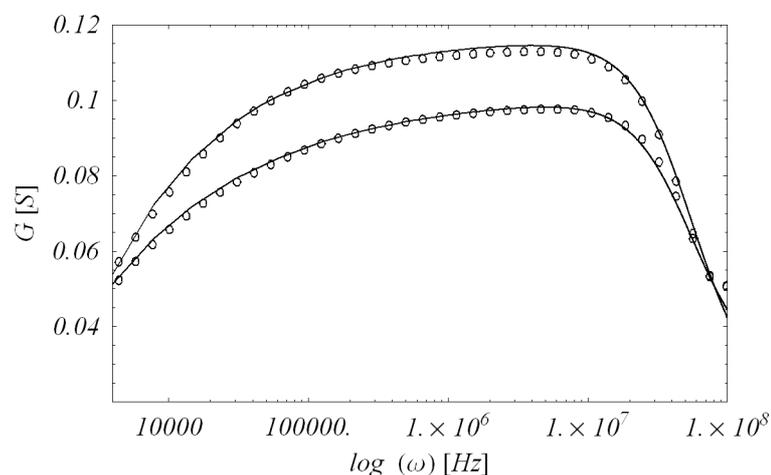


Figure 1: Measured conductance dependence on frequency for moist kaolinitic clay at 56 % (upper dots and curve) and 36 % (lower dots and curve) moisture content. The solid curves are calculated from the model described in the text.

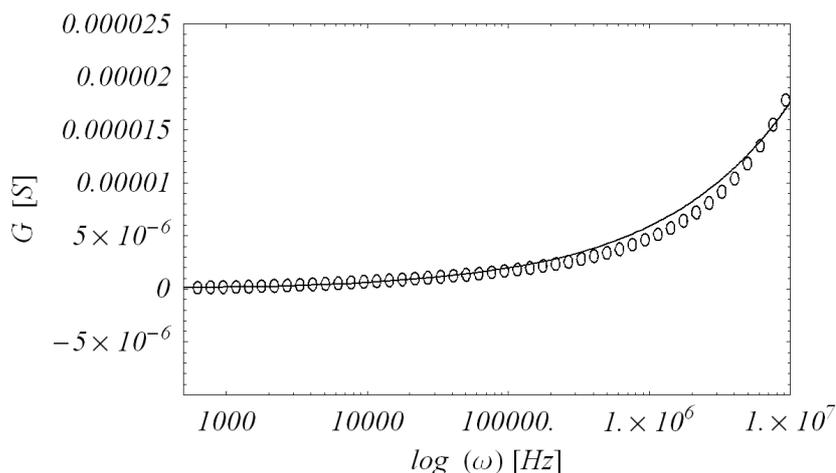


Figure 2: Measured conductance dependence on frequency for dry kaolinitic clay. Empty dots represent measured values and the solid curves is calculated from the model described in the text

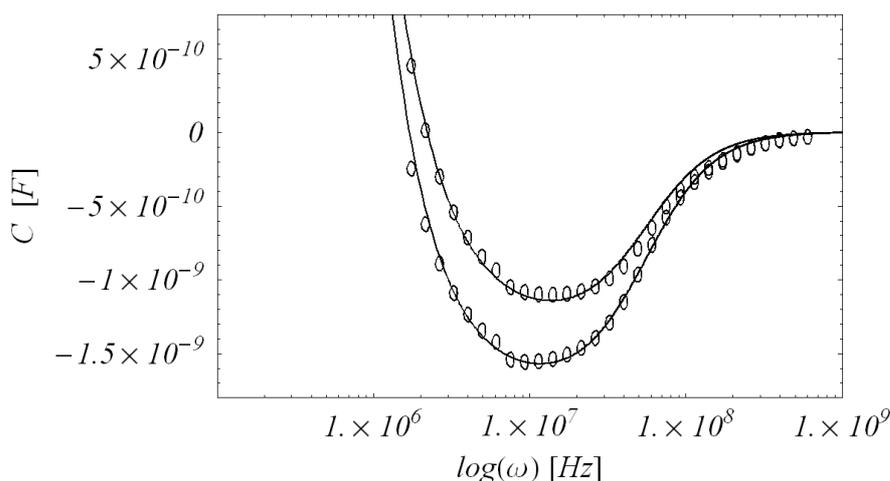


Figure 3: Measured capacitance dependence on frequency for moist kaolinitic clay at 56 % (upper dots and curve) and 36 % (lower dots and curve) moisture content. The frequency interval on this figure is chosen such to best demonstrate the observed negative capacitance effect. The solid curves are calculated from the model described in the text.

### 3 THEORETICAL MODEL

The water in soils is classified into adsorption, capillary, and free water [5]. We envisage that the motion of 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 response of the clay-water system to oscillating electrical field then consists of two parts, so the generalized conductivity of clay-water system is the sum of the bulk conductivity from ions in free water and diffusion conductivity from ions in

diffusive layer near the clay particle surface. The model for the real part of the frequency dependent conductivity which matches the measured linear response spectra of our clay-water samples (figs. 1-3) is:

$$\operatorname{Re}[\sigma(\omega)] = \frac{\sigma_b}{1 + (\omega\tau)^2} + \sigma_{s,\alpha} (\omega\tau)^\alpha + \sigma_{dc}. \quad (1)$$

Here,  $\alpha$  describes type of diffusion and is in the range  $-1 < \alpha < 1$ ,  $\tau$  is the typical relaxation time of the processes, and  $\sigma_b, \sigma_{s,\alpha}, \sigma_{dc}$  are the bulk, surface layer and frequency independent conductivities, respectively.

Let us explain briefly the origin of particular terms of eq. (1). Generalized conductivity, given by Kubo formula [12], is determined with the velocity autocorrelation function of the particles  $C_v(t) = \langle v(t)v(0) \rangle$ :

$$\sigma(\omega) = \frac{q^2 n}{kT} \int_0^\infty \langle v(t)v(0) \rangle \exp(i\omega t) dt. \quad (2)$$

It has been demonstrated recently [13, 14] that the velocity autocorrelation function for a anomalously diffusing particles is:

$$C_v(t) = \frac{kT}{m} E_{2-p} \left( -(t/\tau)^{2-p} \right), \quad (3)$$

where  $E_p(t) = \sum_{n=0}^\infty t^n / \Gamma(pn+1)$  is the Mittag-Leffler function which reduces to exponential function when  $p=1$  corresponding to normal diffusion. The autocorrelation function describes subdiffusion for  $0 < p < 1$  and superdiffusion for  $1 < p < 2$  [13, 14]. The first term of eq. (1) representing the conductivity of the particles in free water is obtained from generalized conductivity for  $p=1$ , while the second term representing the conductivity of the particles in the diffusive layer near the clay particle exhibits anomalous diffusion dynamics with  $\alpha = 1 - p$ .

The value of bulk conductivity depends on the density of particles, relaxation time and mass of the particle:  $\sigma_b = q^2 n_b \tau / m$ . The surface diffusion conductivity coefficient can be expressed, using Einstein relations, as a function of the density of the ions near the surface of the clay particle, effective diffusion constant and temperature:  $\sigma_{s,\alpha} = \operatorname{sgn}(\alpha) q^2 n_s D_{\text{eff}} / kT$ . The dependence on the sign of parameter  $\alpha$  indicates that in case of superdiffusing particles the surface diffusion term conductivity may become negative leading to a situation where the energy flow in the system will increase instead of being dissipated. We must here emphasize two points: firstly the *total* conductivity of our system in the given frequency interval is always positive, and secondly, for a system under nonequilibrium conditions it is possible to exhibit negative conductivity, well known examples include certain kind of semiconductor and superconductor devices, and electrical networks with nonequilibrium elements. Negative conductivity has also been suggested for interacting classical Brownian particles and even single Brownian particle [15, 16].

The dynamics of ions in the free pore electrolyte (bulk conductivity) and near the clay particle surface is governed by different timescales. In the diffusive surface layer it is characterized with the time constant [17]:

$$\tau_s = \frac{a^2}{2D_{eff}}. \quad (4)$$

Here,  $a$  is the radius of the clay particle, and  $D_{eff}$  is the effective diffusion constant. The motion of the ions in the free pore water is characterized with the following time constant based on interface polarization effect in heterogenous dielectrics [18, 19]:

$$\tau_b = \frac{\varepsilon_0(2\varepsilon_w + \varepsilon_{clay})}{\sigma_{dc,eff}}, \quad (5)$$

where  $\varepsilon_w, \varepsilon_{clay}$  are the bulk static dielectric constants of water and clay, and  $\sigma_{dc,eff}$  is the effective dc conductivity. Since there is no sharp boundary between the ions in the diffusive layer and the ions in the free pore water the coupling of the two transport mechanisms in case of significant water content is here considered using an approximate time constant:

$$\tau^{-1} = \tau_b^{-1} + \tau_s^{-1}. \quad (6)$$

In the dielectric spectroscopy experiment the admittance as a function of frequency of the sample is measured from which the complex dielectric function  $\varepsilon = \varepsilon' + i\varepsilon''$  is then deduced. The measured capacitance and conductance of the sample give the real and imaginary part of the dielectric function:

$$C(\omega) = \varepsilon' C_0, \quad G(\omega) = \varepsilon'' \omega C_0. \quad (7)$$

Here,  $C_0$  is the capacitance of the empty measuring cell.

To compare the theoretical model for the conductivity of the clay-water system with the measured data, the conductance as a function of frequency is explicitly written:

$$G(\omega) = \text{Re}[\sigma(\omega)] \frac{C_0}{\varepsilon_0} = \frac{C_0 b}{\tau} \left( \frac{1}{1 + (\omega\tau)^2} + \text{sgn}(\alpha) c (\omega\tau)^\alpha \right) + \sigma_{dc} \frac{C_0}{\varepsilon_0}. \quad (8)$$

Here, nondimensional parameters  $b$  and  $c$  have been introduced with:  $\varepsilon_0 b / \tau = \sigma_b$  and  $\varepsilon_0 b c / \tau = \sigma_s$ .

The real and imaginary part of the dielectric function are not independent functions but are connected through Kramers-Kronig relations [20]:

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{2}{\pi} \text{P} \int_0^\infty \frac{x \varepsilon''(x)}{x^2 - \omega^2} dx. \quad (10)$$

Using this we can compute the real part of the dielectric function from eqs. (8) of the model and compare it to the measured capacitance data using eqs. (9) and (7). A large discrepancy between the calculated and measured capacitance would indicate to the

inconsistencies in the proposed model for the conductivity (eq. (1)) which in our case was not observed.

The results of the calculated conductance and capacitance for the chosen set of parameters are presented on figs. 1-3 as solid lines. The values of the parameters obtained by fitting to the measured sets of data are given in table 1.

Table 1: Values of the parameters obtained by fitting the expression for the conductance and capacitance (eq. (9)) to the measured data.

	$p=36\%$	$p=56\%$	dry clay
$\epsilon_\infty$	2,5	2,5	2,5
$\tau$ [s]	$1,8 \times 10^{-8}$	$1,8 \times 10^{-8}$	$2,9 \times 10^{-4}$
$b$	950	1250	$10^{-3}$
$c$	0,015	0,005	$8,6 \cdot 10^4$
$\sigma_{dc}$ [S/m]	0,18	0,13	$-4,1 \cdot 10^{-7}$
$\alpha$	-0,4	-0,51	0,47

#### 4 DISCUSSION

Looking at results in table 1 we immediately notice very different values of parameters in cases of dry and moist clay. In dry clay the dielectric response of the sample originates from motion of ions near the clay particle surface in the bound water (adsorption and capillary) layer while in moist samples the free water electrolyte fills the space between the clay particles so bulk conductivity adds to transport mechanisms. We can estimate typical time constants for these two processes using eqs. (4) and (5). Taking typical values for diffusion constant ( $D_{eff} \approx 5 \times 10^{-10} \text{ m}^2/\text{s}$ ) of ions in clay-water electrolyte, typical radius of clay particles in kaolinite ( $a = 0,510^{-6} \text{ m}$ ), dielectric constants for water and dry clay ( $\epsilon_w = 80, \epsilon_{cl} = 2,5$ ), and typical dc conductivity for moist clay ( $\sigma_{dc} = 0,05 \text{ S/m}$ ), we obtain:  $\tau_b \approx 1,5 \times 10^{-8} \text{ s}$  and  $\tau_s \approx 5 \times 10^{-4} \text{ s}$  which agree with the values in table 1. The change in the transport mechanisms of ions in dry and moist samples is additionally signalled by the sign reversal of the parameter  $\alpha$  from positive to negative respectively suggesting the crossover from sub- to superdiffusive regime with increasing water content.

The microscopic properties of diffusion transport of ions in clayey soils has recently become an important issue in electromigration studies of radionuclides in moist soil for soil decontamination and engineering nuclear waste repository natural barriers [2, 21-25]. The importance of the effective diffusion constant was emphasized in ref. [2], where the diffusion coefficients for  $^{85}\text{Sr}$ ,  $^{131}\text{I}$  and HTO were obtained, while the dependence of the diffusion coefficient on the distance from the clay-water interface was studied in ref. [21] showing the increase in diffusion coefficient near the interface with respect to its value in the bulk as much as ten times. This leads to the suggestion that by detailed analysis of the dielectric response from contaminated and noncontaminated samples it is possible to obtain additional information on transport properties of contaminants in moist clayey soils.

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## REFERENCES

- [1] Strategija ravnanja z NSRAO, ARAO T-1119/00-1, May 2000 (in slovenian).
- [2] N. Maes, H. Moors, A. Dierckx, P. De Canniere, M. Put, “The assessment of electromigration as a new technique to study diffusion of radionuclides in clayey soils”, *Journal of Contaminant Hydrology*, **36**, 1999, 231-247.
- [3] Siting of Geological Disposal Facilities - A Safety Guide, IAEA Safety Series No. 111-G-4.1, IAEA - International Atomic Energy Agency, Vienna, 1994
- [4] The Principles of Radioactive Waste Management, IAEA Safety Series No. 111 - F, IAEA - International Atomic Energy Agency, Vienna, 1995.
- [5] T. Saarenketo, »Electrical properties of water in clay and silty soils«, *Journal of Applied Geophysics* **40**, 1998, 73-88.
- [6] M. C. Dobson, F. T. Ulaby, M. T. Hallikainen, M. A. El-Rayes, »Microwave dielectric behaviour of wet soil«, *IEEE Trans. Geosci. Remote Sensing* **1**, 1985, 35-46.
- [7] A. Kaya, H. Y. Fang, »Identification of contaminated soils by dielectric constant and electrical conductivity«, *Journal of environmental engineering* **123**, 1997, 169-176.
- [8] M. Carrier, K. Soga, »A four terminal measurement system for measuring the dielectric properties of clay at low frequencies«, *Engineering Geology* **53**, 1999, 115-123.
- [9] R.K. Rowe, J.Q. Shang, and Y. Xie, “Effect of permaeting solutions on complex permittivity of compacted clay”, *Can. Geotech. J.* **39**, 2002, 1016-1025.
- [10] S. Darayan, C. Liu, L.C. Shen and D. Shattuck, “Measurement of electrical properties of contaminated soil”, *Geophysical Prospecting* **46**, 1998, 477-488.
- [11] J. Kramer, D. Korošak, B. Cvikl, M. Pinterič, »Low frequency dielectric properties of selected moist clays«, *Proceedings of 39th International Conference on Microelectronics, Devices and Materials, MIDEM 2003*, 1. – 3. 10. 2003, Ptuj, Slovenija, pp. 411-416.
- [12] R. Kubo, »The fluctuation-dissipation theorem”, *Rep. Prog. Phys.* **29**, 1999, 255-284.
- [13] E. Lutz, »Fractional Langevin equation«, *Phys. Rev. E* **64**, 2001, 051106.
- [14] N. Pottier, »Aging properties of an anomalously diffusing particle«, *Physica A* **317**, 2003, 371-382.
- [15] B. Cleuren and C. Van den Broeck, “Brownian motion with absolute negative mobility”, *Phys. Rev. E* **67**, 2003, 055101.

- [16] Ralf Eichhorn and Peter Reimann, "Paradoxical motion of a single Brownian particle: Absolute negative mobility", *Phys. Rev. E* **66**, 2002, 066132.
- [17] S. S. Dukhin, V. N. Shilov, *Dielectric phenomena and the double layer in disperse systems and polyelectrolytes*, John Wiley&Sons, New York, 1974.
- [18] C. T. O'Konsky, »Electrical properties of macromolecules«, *J. Phys. Chem.* **64**, 1960, 605-619.
- [19] A. R. von Hippel, *Dielectrics and waves*, John Wiley & Sons, New York, 1954.
- [20] L. D. Landau, E. M. Lifshitz, L. P. Pitaevskii, *Electrodynamics of continuous media* 2nd Ed. (course of theoretical physics; vol. 8), Butterworth-Heinemann, Oxford, 1984.
- [21] I. R. Yukhnovskii, M. V. Tokarchuk, I. P. Omelyan, R. I. Zhelem, "Statistical theory for diffusion of radionuclides in ground and subterranean water", *Rad. Phys. Chem.* **59**, 2000, 361-375.
- [22] T. Kozaki, K. Inada, S. Sato, H. Ohashi, "Diffusion mechanisms of chloride ions in sodium montmorillonite", *J. Cont. Hyd.* **47**, 2001, 159-170.
- [23] J.-W. Yu, I. Neretnieks, "Theoretical evaluation of a technique for electrokinetic decontamination of soils", *J. Cont. Hyd.* **26**, 1997, 291-299.
- [24] Y. I. Kharkats, "Theoretical model of radionuclide extraction from soils by the mechanism of ionic electromigration", *J. Electroanal. Chem.* **450**, 1998, 27-35.
- [25] E. Simoni, "Radionuclides retention: from macroscopic to microscopic", *C. R. Physique* **3**, 2002, 987-997.