Dielectric Permittivity of Soils Mixed with Organic and Inorganic Fluids (0.02 GHz to 1.30 GHz)

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ABSTRACT

Changes in the characteristics of the pore fluid in soils, such as concentration, valence, and permittivity, affect the electrical properties of the bulk fluid and the formation of double layers, causes volumetric changes and alters the fabric of the soil. The complex permittivity spectrum of a clay-fluid system reflects the polarizability of the phases and their interaction. This paper presents a review of polarization mechanisms, followed by high-frequency (MHz-GHz) experimental results involving two clays of very different specific surface, aqueous electrolytes with varied concentration and valence, and non-aqueous phase liquids NAPLs. Complex permittivity measurements reveal the effect of mixing order, both in the case of electrolytes and when the clay-fluid mixture includes organic liquids. The development of double layers is hindered when NAPLs reach clay surfaces before water. Various processes that influence the complex permittivity of geomaterials are identified. Results are relevant to the interpretation of field measurements with ground penetrating radar and time domain reflectometry.

Introduction

Organic and inorganic contaminants affect the engineering properties of soils. Indeed, the pore fluid influences the fabric, the volumetric stability and the strength of particulate materials. (See Fam and Santamarina, 1996, for a review of trueeffective stress, and Santamarina and Fam, 1995, for its effects on wave propagation.) In addition, fluid change can alter the hydraulic conductivity of clay layers, e.g., if a contaminant causes the reduction in double layer thickness, there is a corresponding increase in effective pore size (e.g., Fernandez and Quigley, 1991; van Olphen, 1977).

The presence of contaminants also affects the electrical properties of soil-fluid mixtures, e.g., high ionic concentration increases the DC conductivity, alters the polarizability of ionic clouds, and affects interphasial polarization. This is the foundation for techniques based on electromagnetic waves used to assess and to monitor the geo-environment. In this experimental study, complex permittivity measurements are used to evaluate changes in pore fluid. Emphasis is placed on the understanding of the interaction between electromagnetic waves and soil mixtures with organic and inorganic fluids; empirical relationships are not attempted; however, general trends are highlighted. The frequency range selected for this study covers common field applications, including ground penetrating radar GPR and time domain reflectometry TDR.

This paper starts with a brief introduction to the complex permittivity of materials and polarization mechanisms, followed by a presentation of a broad experimental study of organic fluids, inorganic fluids, and soil-fluid systems.

Dielectric permittivity - Polarization mechanisms

The measured or "effective" relative permittivity reflects the extent to which the electrical charge distribution in the material can be distorted or polarized by the application of an electric field. Permittivity is a complex parameter $\kappa^* = \kappa' \cdot i\kappa''$. The real part κ'_{meas} denotes the polarizability of the material and out-of-phase conduction σ^{cr} (Knoll, 1996). The measured imaginary part κ''_{meas} characterizes polarization losses κ'' and Ohmic conduction losses σ^{c}

$$\kappa'_{\text{meas}} = \kappa' + \frac{\sigma''}{2\pi f \epsilon_o} \tag{1}$$

$$\kappa''_{\text{meas}} = \kappa'' + \frac{\sigma'}{2\pi f \epsilon_o}$$
(2)

In these equations, f is frequency [Hz], σ is DC conductivity of the medium [S/m], and ε_0 is the permittivity of vacuum, $\varepsilon_0 = 8.86 \cdot 10^{-12}$ F/m. The spectral response of the material κ^* (f) captures the various polarization mechanisms. These mechanisms are reviewed next, starting with single-phase systems.

Single-phase, Homogeneous materials

The polarization of the electronic cloud around an atom (fig. 1a), the polarization of ions in a molecule (fig. 1b), and the orientational polarization of dipolar or polarized molecules (fig. 1c) are the main polarization mechanisms of homogeneous, single-phase materials, such as minerals or fluid.



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Figure 1. Polarization mechanisms. Typical values in relaxation time are shown for each mechanism (in general, values of τ are related to the size of the polarizing unit).

Mineral. Non-conductive minerals tend to have low real permittivity, often ranging between 4 and 15 (see Parkhomenko, 1967; Zhdanov and Keller, 1994). In most cases, the permittivity is constant and no spectral feature is observed for frequencies below the ionic polarization frequency ($f < 10^{12}$ Hz).

Water. Water molecules are permanent dipoles. Thermal agitation enforces a generally random orientation, even though

tetrahedral coordination with short residence time is expected due to H-bonds. When an electric field is applied, randomly oriented water molecules align with the field and produce a globally polarized medium. Debye (1929) mathematically described this type of polarization with single relaxation time. In the case of water at room temperature, the optical permittivity is $\kappa'_{\infty} \approx 4-6$, the static permittivity is $\kappa'_{0} \approx 78.5$, and the relaxation time is $\tau \approx 9.10_{.12}$ s. The real and imaginary parts of the complex permittivity vary with frequency.

Heterogeneous materials - Low Specific Surface

Single-phase materials show no significant spectral features at frequencies lower than the molecular relaxation frequency. For example, water has a constant permittivity $\kappa' \approx$ 78.5 for f <1 GHz. However, heterogeneous mixtures (e.g., soils) may exhibit dispersion or changes of κ^* with frequency. Interfacial polarization results from differences in polarizability and conductivity among components which are aligned in series in the direction of the field, thus producing a "diffuse" charge accumulation at interfaces, and a spatially polarized material (fig. 1d).

Mixture models are obtained from analytical solutions based on global and local electric fields, electrical circuit analogies, and empirical relations. Maxwell's solution applies to layered materials, while Wagner's solution corresponds to dispersed spherical inclusions. The Maxwell-Wagner relaxation is mathematically described as:

$$\kappa^{*} = \kappa'_{\infty} + \frac{\kappa'_{0} - \kappa'_{\infty}}{1 + i\omega\tau} - i\frac{\sigma_{eq}}{\omega\varepsilon_{0}}$$
(3)

This equation differs from Debye's equation in the equivalent conductivity term, σ_{eq} (Maxwell, 1892; Wagner, 1914; von Hippel, 1954). Other mixture models based on E-field analyses generally assume low concentration of inclusions (e.g., Wagner, 1914; Sillars, 1937; some cases solved by Fricke, 1953).

Concentration [M]		Conductivity ⁽¹⁾ [S/m]			
	NaCl	KCI	CaCl ₂	FeCl ₃	
0.01	0.12	0.14	0.24	<0.43	
0.1	1.06	1.29	2.05	≈2.40	
1.0	8.5	11.1	11.5	>8.50	
4.0	22.0	37.4	<23.3	<7.5	

Table 1a: Electrical conductivity of different electrolyte solutions.

⁽¹⁾ Values were compiled from CRC Handbook (1988) and Timmermans (1960). They were also corroborated with measurements conducted in this study.

Heterogeneous materials - High specific surface

Media are always altered at interphases. The interaction between phases and the formation of diffuse layers cannot be disregarded in particulate materials with high specific surface. Water molecules adsorbed onto surfaces experience relaxation behavior at frequencies between 1 to 100 MHz (de Loor, 1983). The orientation polarization of water molecules H-bonded to the clay particle is possible when the field varies parallel to the clay particle (fig. 1e). In this case, efficient proton conductivity may develop along the surfaces. However, this conduction-polarization mechanism does not take place when the electrical field varies normal to the clay particle.

The applied external field also displaces the center of the atmospheric charge from the center of the colloid; the polarization of the double layer with respect to the particle causes ionic diffusion (fig. 1f). As a result, the complex permittivity of colloidal suspensions can exceed $\kappa'=10^4$ at radio frequencies. O'Konski (1960), Schwarz (1962), Schurr (1964), Dukhin and Shilov (1974), Lyklema et al. (1983), among others, developed different models to explain the high permittivity values for colloidal suspensions (see also review by Mandel and Odijk, 1984).

The permittivity of a mixture with interacting phases (adsorbed or double layer) can be analyzed using physicsbased analytical solutions or semi-empirical equations. Dukhin and Shilov (1974) considered spherical inclusions in a DC electric field. They showed that the static dielectric permittivity of a soil due to double-layer polarization can be approximated by:

$$\kappa' \approx \mathsf{d}_{\mathsf{w}} \kappa_{\mathsf{w}}' + \frac{9}{4\mathsf{v}} \mathsf{d}_{\mathsf{s}} \kappa_{\mathsf{w}}' (3\mathsf{m} + 1)^2 \mathsf{e}^{\left(\frac{\mathsf{v} \mathsf{F} \phi_{\mathsf{d}}}{\mathsf{R}\mathsf{T}}\right)} \tag{4}$$

where $m = \varepsilon_o \kappa'_w (RT)^2 / 6\pi\eta D$, η is the viscosity of water (kg/ms), D is the diffusion coefficient of ions (m²/s); $m \approx 0.1$ for clay-water system; v is cation valence; d_w is the volumetric water content; d_s is volumetric solid content; ϕ_d is the Stern layer potential; R is the gas constant = 8.314 J/Kmole; T is temperature (°K); F is Faraday's constant = 9.648.10⁴ C/mole. The relaxation time can be estimated as the time required for ions to diffuse from one end of the particle to the other (Dukhin, 1971):

$$\tau \approx \frac{a^2}{2D} \tag{5}$$

where a is the particle size and D is the diffusion coefficient. Recent models consider charge movement in the diffuse double layer as well as in the Stern layer (dynamic Stern layer models; Rosen et al., 1993).

Measuring Device - Test Procedure

The complex permittivity was measured between 0.2 GHz and 1.30 GHz. All measurements were conducted with a computer-controlled HP-8752A network analyzer together with an HP-85070A dielectric probe. The system measures the amplitude and the phase of the electromagnetic wave that reflects from the tip of the probe in contact with the material. The complex reflection coefficient is used to calculate the complex permittivity of the medium. The measurement system was calibrated every time before use, including open and short measurements and water as a known material. The error in a given measurement is estimated to be less than 0.5%. Fluids were tested by filling a 20 mm deep container, and submerging the probe into the fluid keeping a minimum distance of 15 mm from the bottom of the cell. Soil specimens were prepared by thor-

lon	Radius of Hydrated Ion [nm] ⁽¹⁾	Hydration Number "N _h " ⁽²⁾	Estimated Bound Water at c=0.10 M [%] ⁽³⁾
Na ⁺	0.184	5±1	0.90
K+	0.125	4±2	0.72
Ca ²⁺	0.310	12±2	2.16
Fe ³⁺	> 0.440	>12	>2.16
CI	0.121	1±1	0.18

Table 1b: Ion size and hydration number.

⁽¹⁾ Approximate radii of hydrated ions estimated from Stoke's law (from Rieger 1987).

- $^{(2)}$ The hydration number is defined as the number of water molecules bound per ion. N_h Values presented in this table emphasize the primary hydration shell (from Conway 1981).
- ⁽³⁾ Calculated using Equation 7.



Figure 2. Spectral response of different electrolytes at 0.10 M and 1.0 M: (a) & (c) real permittivity, (b) & (d) imaginary permittivity. The spectral response of water is included for comparison.

oughly mixing the selected soil with a pre-specified amount of fluid. Soil-fluid mixtures were placed in small cylindrical cells and statically compacted using constant energy. Immediately after preparation, the dielectric probe was brought into contact with the specimen.

The Permittivity of Fluids

Electrolytes - Aqueous solutions

Figure 2 shows the measured permittivity spectra for 0.1 M and 1 M electrolyte solutions. The effect of concentration on the high-frequency complex permittivity of KCl solution is further investigated in fig. 3. Reported and estimated values of the DC electrical conductivity σ of solutions with different concentrations are presented in Table 1a. The measurement of conductivity σ (macro-parameter) allows for the determination of micro-parameters, e.g., ionic mobility ui [m²/s·V] of certain species i:

$$u_i = \frac{\sigma}{z_i c_i F} \tag{6}$$

where z_i and c_i are the valence and the concentration [mol/m³] of the species.

As expected, the imaginary permittivity increases with



Figure 3. Complex permittivity of KCl solutions at 1.30 GHz: the effect of concentration.



Figure 4. Spectral response of different organic fluids: (a) real permittivity, (b) imaginary permittivity. The spectral response of water is included for comparison.

the increase in concentration due to the increase in conductivity [Eq. (2)]. The electrical conductivity of low-concentration solutions, e.g., 0.1 M, are in agreement with the valence and the size of the corresponding ion (Table 1a: $Fe^{3+}>Ca^{2+}>K^+>Na^+$). At high concentrations, ionic mobility decreases due to ion-interaction and ion-complexing. The reduction in electrical conductivity of potassium chloride solutions with the increase in concentration is not as severe as with ferric chloride solutions. Indeed, the ferric chloride solution exhibits the lowest conductivity at 4.0 M relative to the other three salts (see Table 1a).

The Debye-Huckel theory predicts an increase in the static permittivity κ'_s with the square root of concentration. The real permittivity at low frequencies is influenced by other factors including ion complexion and ion pairing, where, some cations are attracted directly or indirectly to the neighboring anions and form permanent or temporary dipoles, increasing the dipole moment per unit volume (Pottel, 1973). The real permittivity at high frequencies, i.e., GHz, decreases with the increase in concentration (see data in Hasted, 1973). This is due to the attraction of water molecules around ions, reducing the number of free water molecules per unit volume (kinetic polarization deficiency; Hubbard et al., 1977). For a specific electrolyte, the percentage of bound water p can be estimated as:

$$\mathbf{p} = 0.018 \cdot \mathbf{c} \left(\alpha_{c} \mathbf{N}_{\mathbf{h}_{c}} + \alpha_{a} \mathbf{N}_{\mathbf{h}_{a}} \right) \times 100 \tag{7}$$

where c is the molar concentration [M], α is the stoichiometric coefficient of salt hydration, N_b is the hydration number of the



Figure 5. Spectral plot of the real and imaginary permittivity for kaolinite and bentonite at different water contents (volumetric water content estimated assuming saturation).

Soil Type	Kaolinite	Bentonite	
Source	Vanderbilt Co., LA	Saskatchewan	
Trade name	Peerless clay	Avonseal or Geoseal	
Color	Light Cream	Light Tan	
Specific Gravity, G ⁽¹⁾	2.6	2.55	
Liquid Limit (%) ⁽¹⁾	50	250	
Plastic Limit (%) ⁽¹⁾	35	50	
Main cation in pore fluid ⁽²⁾	Sodium	Sodium	
Main adsorbed cations ⁽³⁾	-	Sodium-Calcium	
Specific surface (m²/g)	10	400	
CEC (meq/100 g)	10-20	80-85	
pH value ⁽⁴⁾	4.8 (10% solids)	9.0 (5% solids)	
Conductivity ⁽⁴⁾ (mS/cm)	0.04 (10% solids)	1.12 (5% solids)	
Real permittivity of air-dry clay ⁽⁵⁾	≈ 2	≈ 8	

Table 3: Physical and chemical characteristics of the two soils

Values provided by suppliers unless specified

CEC: Cation Exchange Capacity

- (1) Standard ASTM procedure
- ⁽²⁾ Ion chromatography on extracted fluid (bentonite: centrifuge; kaolinite: filtration)
- ⁽³⁾ From Quigley (1984)
- ⁽⁴⁾ Solids in suspension
- ⁽⁵⁾ Measured at 1.30 GHz

ion, and subscripts c and a refer to cation and anion, respectively. Values for N_h for the first hydration shell are summarized in Table 1b.

Real permittivity data at 1.30 GHz for KCl solutions are presented in fig. 3; results are in agreement with the estimated partial fixation of water molecules around ions ($\alpha_a=1$, $\alpha_c=1$, $N_{h_a}=2$, $N_{h_c}=5$, and bound water permittivity $\kappa'_{bw}=6$). The probability of ion complexing in the tested solutions is quite low except in FeCl₃; however, temporary ion pairs may form and lead to similar dispersion. In this case, the critical frequency is related to the residence time of ion pairs. The orientational polarization relaxation time also changes with the increase in concentration: a spread in relaxation time develops, and the average relaxation time increases (Hasted, 1973). The low-frequency permittivity κ'_s of electrolytes is difficult to measure due to electrode effects (2T cells) or phase resolution (4T cells) which are enhanced at high concentrations (Klein and Santamarina, 1997). Organic Fluids

The contrast in complex permittivity between organic fluids and water encourages the use of electromagnetic waves to detect pools of hazardous organic wastes. The organic fluids selected in this study are: Benzene, Xylene, Toluene, Tetrachloroethylene, Trichloroethylene, and Chloro-benzene. Relevant properties for these fluids are compiled in Table 2.

Figure 4 shows the spectral response of the selected organic fluids; the spectral response of water is included for comparison. The real permittivity of organic fluids is constant with frequency, and κ'' is almost $\kappa'' \approx 0$. Results confirm the low polarizability of these organic fluids throughout the frequency range tested in this study. Measured real and imaginary permittivity values are in agreement with published data (Table 2 and fig. 4). In summary, non-aqueous phase liquids do not show any significant spectral feature in the MHz-GHz region; the real permittivity is low ($\kappa' = 2$ to 6) and the imaginary permittivity κ'' approaches zero.

Water molecules must re-orient around hydrophobic organic fluids to minimize the number of H-bonds facing the

Table 4: Summary of database

Soil	Frequency	Pore fluid	Concentration or	Water	No. of
	range [GHz]		fluid content ⁽¹⁾	content [%]	Tests
	0.20 - 1.30	Water, NaCl, KCl, CaCl ₂ , and FeCl ₃	0.01, 0.1, 1.0, and 4.5 M	≈ 40	16
	0.20 - 1.30	Water, NaCl, KCl, CaCl ₂ , and FeCl ₃	0.10 M	9 - 45	32
Kaolinite	0.20 - 1.30	Water	(de-ionized water)	0 - 100	22
	0.02 - 1.30	Benzene Xylene Toluene Tetrachloroethylene Trichloroethylene Chlorobenzene	W:O:C= 0.20: 0.42: 1.0 Three mixing orders	≈ 20	18
	0.20 - 1.30	Water, NaCl, KCl, CaCl ₂ , FeCl ₃	0.10 M	7 - 300	75
	0.20 - 1.30	Water	(de-ionized water)	0 - 400	20
Bentonite	0.02 - 1.30	Benzene Xylene Toluene Tetrachloroethylene Trichloroethylene	W:O:C= 0.42: 0.28: 1.0 Three mixing orders	≈ 42	18

(1) Relative weights of W = water, O = Organic fluid, and C = Clay, with respect to the weight of dry clay.

organic fluid. Indeed, Kaatze and Pottel (1992) measured the complex permittivity of mixtures with hydrophobic substances and concluded that the static permittivity is higher than that of bulk water.

The Permittivity of Soil-fluid Systems

Kaolinite and bentonite were selected for this study. These two clays span the range of most clays encountered in the field, from the low specific surface kaolinite to the highspecific surface bentonite. Table 3 summarizes the physical and chemical properties of the two clays. A broad set of soilfluid mixtures were tested. The database includes more than 200 tests designed to evaluate the effect of concentration, valence, amount of electrolyte, the effect of organic fluids, and the implications of mixing order. The experimental study is summarized in Table 4.

Soil - Water

Selected spectral plots for the real and the imaginary

permittivity of kaolinite and bentonite specimens with different water contents are presented in fig. 5. The measured permittivity of water is included for comparison. Bentonite data show a continuous decrease in the real and the imaginary permittivity with the increase in frequency for all water contents; on the high-frequency end, the orientation polarization losses of free water is overshadowed by the tail of RF-relaxations and the contribution of DC loss. On the other hand, the increase in water content in kaolinite produces a monotonic increase in the real permittivity, towards the permittivity of water. However, changes in imaginary permittivity depend on the frequency under consideration; in the high frequency GHz region, values of κ''_{meas} reflect the orientation relaxation of free water.

Altogether, results in fig. 5 reflect the superposition of interfacial, double-layer, free-water relaxations, and the clear differences in electrical properties among soils with different specific surface.

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Figure 6. Change in the complex permittivity of kaolinite at 0.20 GHz with fluid content (different electrolytes with molar concentration = 0.10 M): (a) real permittivity, (b) imaginary permittivity.

Soil-Electrolyte

The complex permittivity of kaolinite and bentonite mixed with different electrolytes is shown in figs. 6 and 7 (c = 0.10 M). The gravimetric fluid content was gradually increased, from dry conditions to approximately the liquid limit of each soil. The plotted data correspond to the low-frequency end, 0.2 GHz, to capture free-water polarization and the tail-end of RF polarizations. Permittivity is related to the number of dipole moments per unit volume. Therefore, it is recommended to plot permittivity versus volumetric water content (Selig and Manuskhani, 1975). Inconsistent measurements of mixture density in small specimen cups did not allow for proper evaluation of volumetric fluid content; hence, the gravimetric fluid content is reported. The densified mixtures are saturated at about the plastic limit (Table 3: kaolinite PL=35 and bentonite PL=50). Thus, volumetric relations can be readily computed above these fluid contents.

The complex permittivity of all clay-electrolyte mixtures shows three regions in the permittivity-water content plot (f = 0.2 GHz). Regions I & II indicate a low rate of increase in real permittivity due to the low polarizability of bound water, and restricted ionic mobility due to surface forces and discontinuous conduction paths. Therefore, the imaginary permittivity is not affected by cation valence. Region III shows the gradually prevailing effect of the free-fluid chemistry, and the effect of ion valence and size. The transition between regions is less abrupt in kaolinite than in bentonite.

The real permittivity at f=0.2 GHz and the values of the wc are not significantly affected by the valence of the cation. (Valence has a strong effect on the thickness of the double layers, hence, on the availability of free water in high specific surface materials such as bentonite.) The principal energy loss mechanism at 0.2 GHz in region III is DC-Ohmic loss in the fluid; this loss increases as the fluid content increases and the dry density decreases.

The increase in ionic concentration affects the polariz-



Figure 7. Change in the complex permittivity of bentonite at 0.20 GHz with fluid content (different electrolytes with molar concentration = 0.10 M): (a) real permittivity, (b) imaginary permittivity.



Figure 8. Change in the complex permittivity of kaolinite at 1.30 GHz with molar concentration for different electrolytes (fluid content = 60%): (a) real permittivity, (b) imaginary permittivity.

ability of electrolytes (as discussed earlier), reduces the thickness of double layers liberating free water, and increases the conductivity of the liquid phase. The compounded implications of these phenomena were studied with kaolinite at w = 40% (saturated). Measurements at 1.30 GHz are summarized in fig. 8. Note that mixtures with mono-valent cations show a peak in real permittivity at 0.1-1.0 M. Similar trends in real permittivity κ' were observed when bentonite was mixed with KCl solution at different concentrations. However, mixtures with di- and tri-valent cations exhibit a gradual decrease in mixture permittivity with the increase in concentration, showing the decrease in free fluid polarizability.

The imaginary permittivity increases with concentration reflecting the increase in electrical conductivity of the fluid (see Table 1a). The drop observed in fig. 8b, for the mixture of kaolinite with the Fe₂Cl₃ aqueous solution is also in agreement with the trends in conductivity for the solution itself. Furthermore, the imaginary permittivity at high concentration is higher

for mono-valent high mobility ions than for di-valent and trivalent ions, as predicted from trends shown in Table 1a and fig. 2. The data shows that it is very difficult to identify ion type using complex permittivity data. Yet, the sensitivity of the imaginary permittivity to concentration is most valuable for the development of electrical methods to monitor diffusion fronts. (A unique data set under volume controlled conditions can be found in Santamarina and Fam, 1995.)

Equivalent Clay Conductivity. The equivalent conductivity of wet soil particles c can be estimated using Archie's law, by measuring the conductivity of the clay-fluid mixture m and the conductivity of the fluid f (Ward, 1990). In the case of bentonite with high fluid content (i.e., 100% saturation), the computed equivalent conductivity of wet clay particles de-



Figure 9. Spectral response of bentonite specimen prepared with different mixing orders (fluid content = 220%, molar concentration = 0.10 M and 1.0 M NaCl): (a) real permittivity, (b) imaginary permittivity. Dry-mix: clay is mixed with the electrolyte. Wet-mix: clay is mixed with water and salt is added later.

Soil	Fluid	Mixing	κ'	κ'	κ"	κ"
		order	(0.2 GHz)	(1.30 GHz)	(0.2 GHz)	(1.30 GHz)
	Water	CW	23	22	4.0	1.7
ĺ	Chloro-	СО	7.3	6.9	0.33	0.3
	benzene	COW	15	14	1.8	1.0
		CWO	21	20	2.2	1.5
	Tetra-	CO	3.0	3.0	0.2	0.0
	chloroethylene	COW	15	14	2.2	0.9
		CWO	13	12	0.9	0.6
	Tri-	CO	4.3	4.3	0.2	0.04
	chloroethylene	COW	17	16	2	1.1
Kaolinite		CWO	22	21	2.3	1.6
	Xylene	CO	3.7	3.6	0.2	0.06
-		COW	13	12	1.6	0.8
		CWO	12	11	1.2	0.6
	Benzene	CO	4.4	4.2	0.3	0.1
		COW	16	15	2.3	0.9
		CWO	20	19	3.1	1.6
	Toluene	CO	2.2	2.2	0.07	0.0
		COW	15	14	2.0	0.9
		CWO	22	21	2.5	1.5
	Water	CW	54	29	60	17
	Chloro-	CO	9.5	4.9	2.9	0.5
	benzene	COW	33	20	50	12
		CWO	52	32	74	19
	Tetra-	CO	6.2	3.6	0.4	0.2
	chloroethylene	COW	33	20	55	13
		CWO	40	24	61	15
	Tri-	CO	10	4.3	2.5	0.7
Bentonite	chloroethylene	COW	39	24	66	15
		CWO	54	32	75	19
	Xylene	CO	9.5	4.6	4.4	0.6
		COW	29	18	41	10
		CWO	44	29	63	16
	Benzene	co	11	5.8	3.7	1.9
		cow	30	19	45	11
		CWO	44	29	71	17
	Toluene	со	9.8	4.2	2.1	0.5
		COW	32	19	51	12
		CWO	49	32	73	18

Table 5: Summary of permittivity results for clay-organic mixtures

Notes:

C = Clay, W = Water, O = Organic fluid

The water content for Kaolinite and Bentonite were 20 % and 42%, respectively.

COW and CWO mixtures tended to bleed when the probe was pressed against

the specimen (saturation is presumed)

Table 6.Summary of processes that influence the complex permittivityof particulate media

Medium	Processes and phenomena		
Electrolyte	Decrease mobility of bound water around ions.		
	 Ion-pairing and ion complexing. 		
	 Diminished ion mobility and conductivity at high 		
	concentration		
Organic fluid	Ionic, electronic, and some orientational polarization.		
	Presence of impurities		
Clay-salt-water	Low mobility of bound water.		
	Double layer formation (thickness) and polarization.		
	Conductivity pore fluid and Maxwell-Wagner spatial		
	polarization.		
	Mixing order - fabric		
	Volumetric changes (true effective stress)		
Clay-NAPL-water	Mixing order: Hindered ion hydration if NAPL wet		
	(adsorbed ions on clay surface shield electric field and		
	restrict double layer formation; reduced bulk fluid		
	conductivity)		
	Altered double layer polarization.		
	Altered Maxwell-Wagner relaxation		
	Hydrophobic interactions.		
	Altered polarizability of water near NAPLs		
	Spatial distribution of phases		
	Volumetric and fabric changes (true effective stress)		

Note: These effects manifest at different frequency ranges

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Figure 10. Spectral response of kaolinite-water-benzene mixtures (water content = 20%, benzene content = 42%) prepared with different mixing orders (C: clay, W: water, O: organic fluid): (a) real permittivity, (b) imaginary permittivity.

creases for $Na^+>K^+>Ca^{2+}>Fe^{3+}$. This is consistent with the theoretically predicted thickness of the double layer.

Mixtures and pH. Some salts used in this study produce solutions with pH different than 7.0 because of impurities. For example, pH decreased in NaCl solutions with the increase in concentration. The pH of electrolytes mixed with kaolinite or bentonite was also evaluated, showing that both soil slurries undergo a decrease in pH with the increase in pore fluid concentration (possible surface complexations). This change may become critical in the case of kaolinite, where pH controls the surface charge (lower pH values decrease the negative charge; edge charges become positive at pH < 5). Therefore, increasing the ionic concentration may decrease the double-layer thickness, change pH, increase hydrogen concentration (which affects some polarization mechanisms), and alter internal soil fabric.

Mixing Order: Hydration and Hysteresis. The effect of mixing salt, soil, and water in different orders was studied with the dielectric permittivity response of bentonite at w = 220%(saturated). The "dry-mix" specimen was prepared by dry mixing bentonite with NaCl crystals and then adding water; the "wet-mix" specimen was prepared by prehydrating the bentonite and then adding NaCl crystals. In both cases, the added salt was such that the solution would have a 0.10 M concentration. Measurements were conducted shortly after mixing. The study was repeated with a 1.0 M NaCl solution. In both cases, the "wet-mix" was clearly stiffer than the "dry-mix" for the same fluid content. (Similar observations were made with liquid limit determinations using fluids of increasing concentration; see also mixing order effects in soil-cement mixtures -Fam and Santamarina, 1996.) Figure 9 shows the effect of mixing order on the spectral response. The following observations can be made: (1) wet mixing leads to slightly higher κ''_{meas} at all frequencies; (2) mixing order is more relevant than concentration on the value of κ'_{meas} at GHz frequencies; this is a measure of available free water; and (3) concentration is more important than mixing order on the value of κ'_{max} at MHz frequencies; this is a measure of interfacial and double-layer polarization.

Hence, the formation of double layers and the solubilization of salts depend on the mixing order. Wet-mixing permits delamination of the clay mineral and full development of the double layer around each particle which must later shrink upon the addition of salt. On the other hand, particle aggregation in dry mixing and the development of a different soil-fabric is reflected as a decrease in the real permittivity.

Clay-Organic Fluid

The permittivity of soil-water mixtures decreases when water is displaced by a low-permittivity organic fluid. (See experimental data in Börner et al., 1993, and Alharthi et al., 1986.) Kaolinite and bentonite were mixed with water and with the selected non-aqueous phase liquids tested earlier; proportions are summarized in Table 4. Various mixtures were tested:

- · Clay is mixed with water CW
- Clay is mixed with organic fluid CO
- Clay is mixed first with organic fluid, and water is added later COW
- Clay is mixed first with water, and organic fluid is added afterwards CWO.

Specimens were densified to the same compaction effort. CW and CO mixtures remained unsaturated. However, COW and CWO mixtures approached saturation and started to drain fluids as the specimens were densified. The complex permittivity for mixtures with benzene (light non-aqueous phase liquid) is presented in figs. 10 and 11. Results for other fluids are similar



Figure 11. Spectral response of bentonite-water-benzene mixtures (water content = 42%, benzene content = 28%) prepared with different mixing orders (C: clay, W: water, O: organic fluid): (a) real permittivity, (b) imaginary permittivity.

and are summarized in Table 5. (This data set was obtained by the same individual. The variability in the data obtained by different individuals can be high, due to differences in sample preparation and test procedures.)

CO Mixtures. CO mixtures displayed the lowest permittivity. Small Maxwell-Wagner relaxation can develop in these mixtures (see data in Rinaldi and Redolfi, 1996). In addition, the electrostatic field of the clay surface can generate Coulombian forces that either induce dipole moments or enhance the polarity of fluids near the clay surface (Theng, 1974).

The difference between kaolinite and bentonite in the CO mixture may reflect thin monolayers of water (bentonite shows small relaxation). Tests were conducted with oven-dry clays. Nevertheless, it is expected that both clays can form thin monolayers of water by absorbing moisture from the atmosphere during mixing. The gravimetric water content w% required to coat soil particles with a uniform water layer of thickness tw can be estimated as:

$$\mathbf{w}\% = \left(\mathbf{S}_{s} \cdot \boldsymbol{\rho}_{w} \cdot \mathbf{t}_{w}\right) \times 100 \tag{8}$$

where S_s is the specific surface of the soil $[m^2/g]$ and w is the mass density of water [kg/m³]. Assuming one monolayer, t_w = 0.28 nm, kaolinite would have a water content w=0.5% while the water content of bentonite would have w=11%.

COW and CWO Mixtures. The preparation of these specimens is cumbersome because of the strong tendency of these soils to form granules in the presence of water. Therefore, one should not expect homogeneous specimens at fine scales, but specimens made of conglomerations of wet particles, surrounded by a second fluid. The internal fabric within conglomerates must be different in COW and CWO specimens. Fluid bleeding takes place when the probe is pressed onto the specimen, i.e., saturation and same volumetric fractions.

The permittivity is higher in CWO mixtures than in COW mixtures, in all the frequency range from 20 MHz and 1.3 GHz. The real and imaginary components of the effective permittivity are similar for CW and CWO mixtures. Values are similar between CW and CWO mixtures; apparently double layers are not altered by the presence of the organic fluid (hydrophilic nature of clay particles).

In the case of COW mixtures, organic fluids are adsorbed onto clay surfaces because of differences in free energy between the bulk fluid and the interface (Mingelgrin and Prost, 1989). This hinders the hydration of ions attracted to the surface of dry clay particles. The electric field from the particles is screened and the formation of double layers is hampered. The hydration of excess salts is also restricted; therefore, the conductivity of the bulk fluid is low, limiting interphasial polarization. (It is assumed in this discussion that there is no intercalation of the organic fluid into the bentonite mineral since nonpolar molecules are inadequate to penetrate clay layers, unless extensive periods are allowed [Theng, 1974]. Hydrophobic interactions result in adsorption of non-ionic compounds on surfaces. The decrease in hydration water surrounding an organic solute results in an increase in the entropy that leads to hydrophobic interactions [Curtis et al., 1986]).

Discussion

While there are small differences between some of these measurements, within the variability of the data, the changes are significant to support the development of wave-based techniques for process monitoring. Furthermore, field situations may trigger other phenomena not modeled in this study. For 50

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example, DeRyck (1994) showed that GPR can detect the change caused by the injection of kerosene, which displaces the water held by capillary forces above the water table, while the kerosene itself remains almost transparent. (See also Santamarina and Fam 1994.)

A three-phase network model was used to assess the effect of mixing order and spatial distribution of phases in COW and CWO mixtures. In the case of CWO model, the solid particle is surrounded by a water shell of uniform thickness, which is enclosed by the organic fluid. The electrical analogy is obtained by a corresponding network of "lossy capacitors". The parameters are selected in agreement with the tested materials and assumed geometry. Predicted κ' and κ'' values agreed with values measured for the COW mixtures, but did not agree well with the observed spectral response of CWO mixtures. In particular, the measured imaginary permittivity is significantly higher than predicted. Apparently, the organic fluid does not enclose wet particles (as assumed in the model) and the water phase remains forming continuous paths, which cause high conductivity in the mixture.

These results highlight the sensitivity of the electrical parameters of three-phase mixtures to the spatial distribution of the phases. From this point of view, the mechanical thorough mixing of the phases in the laboratory is a distinctive case which does not necessarily represent prevailing field situations.

Summary and Conclusions

Selected clays, electrolytes, and non-aqueous phase liquids were mixed and experimentally characterized with spectral permittivity measurements. Measurements clarified the interaction between soils, organic fluids and electrolytes, and the nature of the electrical properties.

- Multiple phenomena affect the permittivity of clayfluid mixtures; these are summarized in Table 6. Some processes prevail at kHz and MHz frequencies yet they may still manifest into the low GHz region; other processes govern the permittivity at high GHz frequencies.
- Ionic concentration and valance have no unique effect on the complex permittivity of electrolytes. Data must be interpreted taking into consideration frequency, valence and ion size. The real permittivity of organic fluids is small relative to water and the imaginary permittivity is almost zero.
- The back-calculated equivalent conductivity of wet bentonite particles decreases with the increase in the ion valence of the pore fluid, in agreement with the predicted thickness of double layers.
- The mixing order of electrolytes and organic fluids with clays influences the spectral response of the mixture, reflecting differences in double-layer formation, ion hydration, and the development of different soil

fabrics.

- Clay-water-NAPL systems are complex mixtures. The permittivity of three-phase mixtures is sensitive to the spatial distribution of the phases. Permittivity data and the volume fraction of each phase can be used to infer the spatial distribution of phases, and the formation of continuous percolation paths.
- Ground penetrating radar GPR and time domain reflectometry TDR can be used for one-time determination of field conditions, or to evaluate time-varying site conditions. Results presented in this study show that the resolvability of site parameters is limited with a one-time measurement. However, the effect of changes is more readily distinguishable.

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