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## A physical model of the low-frequency electrical polarization of clay rocks

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[1] Low-frequency (0.18 Hz to 1.5 kHz) effective dielectric spectra have been measured on a set of near-saturated samples of argillite. The measured spectra of the real part of the complex apparent permittivity did not show significant correlation with cation exchange capacity (CEC) per unit mass of rock values. They satisfied a power law relationship with the frequency, at least for samples with CEC values lower than 10 cmol/kg. The Maxwell-Wagner-Hanai-Bruggeman formulation used for a two-phase mixture has been modified to account for mutual polarization between the pockets of water located in the micropores and those located in the macropores. The results of the modeling calculations illustrate (1) the ability of this new formulation to reproduce the power law relationships of the measured spectra of the real and imaginary components of the complex permittivity and (2) the strong impact of the pore electrical conductivity.

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### 1. Introduction

[2] Low-frequency measurements (mHz to kHz) of complex resistivity were initially used to detect small concentrations of disseminated mineralization in the exploration of ore bodies [e.g., Marshall and Madden, 1959; Van Voorhis *et al.*, 1973]. Recently, attention has been focused on LF dielectric properties of rocks and soils as a mean of indirectly determining their cation exchange capacity (CEC) and specific surface area [Börner and Schön, 1991; Slater *et al.*, 2005], their grain size distribution [Lesmes and Morgan, 2001], and their hydraulic conductivity [Börner *et al.*, 1996; de Lima and Niwas, 2000; Comas and Slater, 2004; Binley *et al.*, 2005] and to monitor microcracking during the excavation and the desiccation of clay rocks [Kruschwitz and Yaramanci, 2004; Cosenza *et al.*, 2007]. Experimental investigations have shown that the pore throat diameters and the pore geometry of water-saturated geomaterials contribute significantly to both in-phase and out-of-phase conduction at low frequencies [Scott and Barker, 2003]. Scott [2006] conducted low-frequency measurements of saturated sandstones, suggesting that low-frequency polarization originates in the polarization of the electrical

double layer (EDL) coating the grains. A similar result was obtained for packs of rough or smooth glass beads by Leroy *et al.* [2008].

[3] Although these investigations have identified key parameters (pore throat diameters, pore geometry, grain size distribution, roughness of the grains, and EDL), the physical mechanisms that control the low-frequency properties of clean sediments, and, a fortiori, of clayey materials, are still a subject of considerable debate. In their seminal book, Dukhin and Shilov [1974] explained that the main theories on the cause of the polarization of clay materials can be divided into two schools of thought.

[4] Those of the first school take into account explicitly the electrical surface phenomena (EDL and surface conduction along the surface of the clay minerals). Among these approaches, the theoretical works of de Lima and Sharma [1992] are likely the most popular for clay rocks: the authors propose to mix a Maxwell-Wagner formulation and microscopic theories related to the polarization of the EDL around a single grain on the basis of Dukhin and Shilov's [1974] theory.

[5] In the opposite school of thought, some authors neglect the polarization mechanisms related to the EDL and believe that the observed low-frequency polarization in clayey material is due to their particular texture and especially to the self-similar organization of their pore space [e.g., Korosak *et al.*, 2007]. Lunev *et al.* [2001] and Lunev *et al.* [2002] proposed a model describing the low-frequency electrical properties of porous material characterized by a fractal geometry of their pore space. They used this model to interpret their low-frequency dielectric data obtained from kaolinite clay samples: the electrical behavior of clay and water in the porous space is modeled by a self-similar chain of resistance-capacitance or "recap" (resistance plus

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**Table 1.** Mineralogical Composition of the Selected Samples

	TM90-1260	TM90-1280	Super-Sauze	EST05-687 <sup>a</sup>	EST12-161
Calcite carbonates as percent of total mass <sup>b</sup>	17.0	17.2	26.4	20	43.7
Composition of the clay fraction <sup>c</sup>					
Interstratified IS	-	-	-	15.4	-
Interstratified IS with >80% of illite	36.7	37.4	-	-	-
Interstratified IS with 30–50% of illite	-	-	-	-	83.4
Kaolinite	29.1	30.9	-	16.9	-
Illite	18.1	19.6	88.7	-	13.1
Chlorite	16.0	12.1	11.3	35.4	3.5
Smectite	-	-	-	30.8	-
Water content <sup>d</sup> (wt %)	3.33	3.42	10.97	-	6.0
Fraction of porosity $\phi$	0.082	0.084	0.243	0.0787	0.142
CEC (cmol/kg)	9.62	9.53	6.36	18.3	15.4
$Q_v^e$ (C/m <sup>3</sup> )	$270 \times 10^6$	$295 \times 10^6$	$56 \times 10^6$	$608 \times 10^6$	$264 \times 10^6$

<sup>a</sup>From *Comparison* [2005].

<sup>b</sup>Mixed layer IS is mixed layer illite-smectite.

<sup>c</sup>Percent by weight finer than 2  $\mu\text{m}$ .

<sup>d</sup>Water content is not measured for EST05-687.

<sup>e</sup> $Q_v$  is the total excess of charge per unit pore volume (Stern and diffuse layers). It is given by  $Q_v = \rho_g \frac{1-\phi}{\phi} \text{CEC}$ , where  $\rho_g$  is the grain density (taken to be equal to 2.6 g/cm<sup>3</sup>) and  $\phi$  is the total porosity (taken to be equal to the average value measured in the site).

capacitance) electrical elements. In order to integrate the impact of the “bound water” filling the microporosity, these authors introduced a parallel circuit of two recap chains. However, it should be noted that *Lunev et al.* [2001] and *Lounev et al.* [2002] used a low CEC per unit mass of rock clay mineral (kaolinite) for which the influence of the EDL would be smaller in comparison with higher-CEC clay minerals like smectites. Consequently, the modeling approaches of both camps, which differ from the explicit introduction of EDL polarization, are likely not so contradictory.

[6] There is clearly a lack of experimental data for assessing the origin of the low-frequency polarization of clay rocks, especially on well-characterized rocks from the mineralogical point of view. In this paper, we provide (1) new measurements obtained with a variety of well-characterized clay rocks intensively studied for deep storage purposes and (2) a physical model explaining the data.

## 2. Phenomenological Aspects

### 2.1. Selected Clay Rocks and Experimental Investigations

[7] Five samples have been selected from three sites: the Tournemire site, the Super-Sauze site, and the Bure site, all located in France. The Tournemire site was chosen as a test site by the French Institute for Radioprotection and Nuclear Safety to study the confining properties of argillites for research purposes related to the long-term isolation of nuclear wastes. This site is located in southern France, at the western border of the Causses Basin, a Mesozoic sedimentary basin. Two samples were taken from well TM90, which was drilled in 2005 perpendicularly to the wall of a tunnel crossing a Toarcian argillite formation. Two cylindrical samples, labeled TM90-1260 and TM90-1280, each measuring 79.5 mm in diameter and 193–205 mm in length, were located 12 m from the gallery wall in a preserved zone outside the so-called excavation disturbed zone and outside the influence of the ambient air. Samples were immediately taken after the completion of drilling and

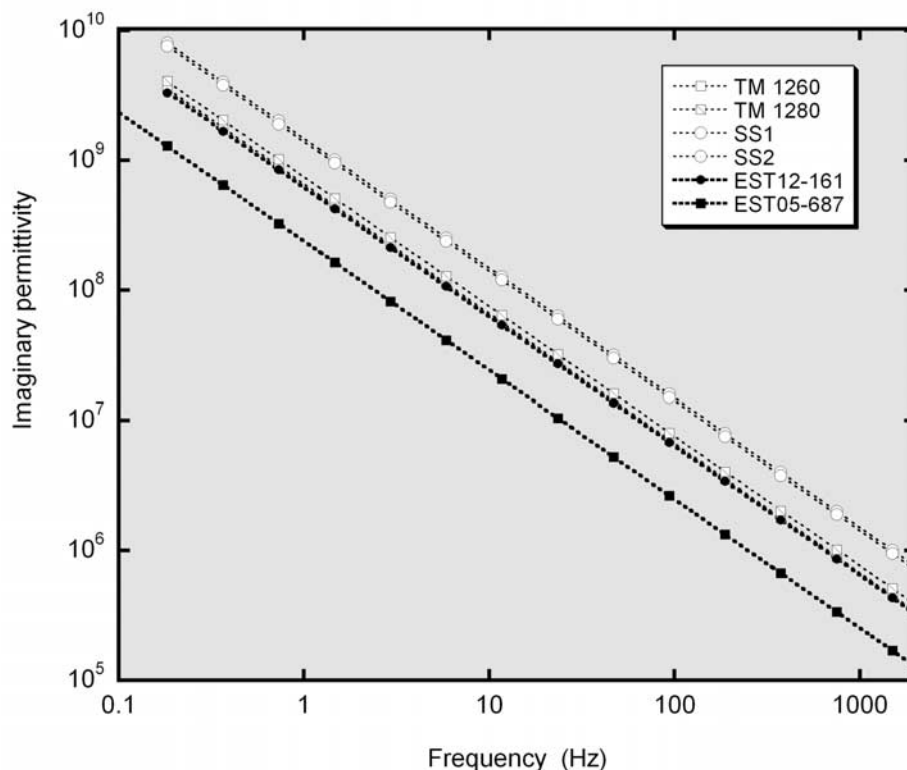
were put in Al-coated plastic bags under confined N<sub>2</sub> atmosphere.

[8] The mineralogical analyses of this Toarcian argillite have shown that clay minerals (kaolinite, illite, and interstratified illite-smectite) represent on average 40 wt % of the bulk rock composition [*De Windt et al.*, 1998]. The coarse fraction contains quartz (~20 wt %), K-feldspars, bioclasts, and pyrite (~2 wt %). Carbonates constitute about 15 wt % of the bulk rock composition. The porosity and the specific surface area of Tournemire argillites are in the ranges of 6–9% and 23–29 m<sup>2</sup>/g, respectively [*Bonin*, 1998]. The total CEC per unit pore volume ( $Q_v$ ) and the mineral composition of the clay fraction obtained by X-ray diffractometry of the two samples, TM90-1260 and TM90-1280, are given in Table 1. The CEC was determined by the cobalt-hexamine method, which is a destructive analytical technique.

[9] The second site corresponds to Super-Sauze. This site is an earthflow occurring in the Callovo-Oxfordian black marls located in the Barcelonnette Basin (Alpes-de-Haute-Provence, southern France) [e.g., *Schmutz*, 2000]. Percussion drillings in dry conditions have been carried out from the surface in order to take a representative sample measuring about 600 mm in length and 50 mm in diameter, which was carefully closed in a tight tube sampler. From this sample, two smaller and unfractured samples (SS1 and SS2), measuring 80 and 160 mm in length, respectively, have been made by cutting slowly and directly the tight tube sampler immediately prior to performing the low-frequency electrical measurements.

[10] The Callovo-Oxfordian black marl is a compact shale formation. Mineralogical analyses indicate that clay minerals (mostly illite and chlorite) constitute on average 37 wt % of the bulk composition (Table 1) [*Schmutz*, 2000]. The coarse fraction contains quartz (~30 wt %) and carbonates (~30 wt %). The porosity of Super-Sauze black marls is in the range of 17–26%. The CEC and the mineral composition of the clay fraction of a small sample taken from the same sampler as SS1 and SS2 are given in Table 1.

[11] The third site, the Bure Underground Research Laboratory, is a test site of the Agence Nationale pour le



**Figure 1.** The low-frequency spectra of the imaginary part of complex permittivity  $\varepsilon''$ . Open symbols, measurements on samples with CEC values lower than 10 cmol/kg. Solid symbols, measurements on samples with CEC values greater than 10 cmol/kg. Dotted lines, power law regressions for each sample.

Gestion des Déchets Radioactifs. This site has been created for the purpose of assessing the feasibility of a deep repository for isolation of radioactive wastes. This underground research laboratory is located in the eastern part of the Paris basin, at a depth of 490 m, in 130 m thick Callovo-Oxfordian argillites. Two samples were taken from two different boreholes, EST212 (sample 161 at a depth of 464.19 m) and EST205 (sample 687 at a depth of 489.51 m). The most abundant clay minerals include the R0-type interstratified illites-smectites (piles of unorderly flakes, 50–70% smectite) in the upper part of the formation (up to 490 m deep) [Yven *et al.*, 2007]. The samples EST12-161 and EST05-687 are 100–150 mm in length and 60–100 mm in diameter. In order to prevent damage and loss of water, after drilling, they were stored in confining and sealing cells named T1 cells. The CEC and the mineral composition of the clay fraction of samples are given in Table 1. The CEC and smectite content of this clay rock are significantly higher than those reported above.

[12] The low-frequency electrical measurements were obtained using the SIP FUCHS-II apparatus in the frequency range 0.18 Hz to 1.5 kHz. To minimize electrode polarization associated with electrochemical reactions occurring at the electrode sample contacts, measurements were performed with a four-electrode device using electrocardiogram Ag/AgCl electrodes as potential (or measuring) electrodes [Cosenza *et al.*, 2007]. The low-frequency measurements were performed immediately after removing the samples from their initial packaging (Al-coated plastic bags, tight tube samplers, and T1 cells), in a near-saturated state.

## 2.2. Results and Discussion

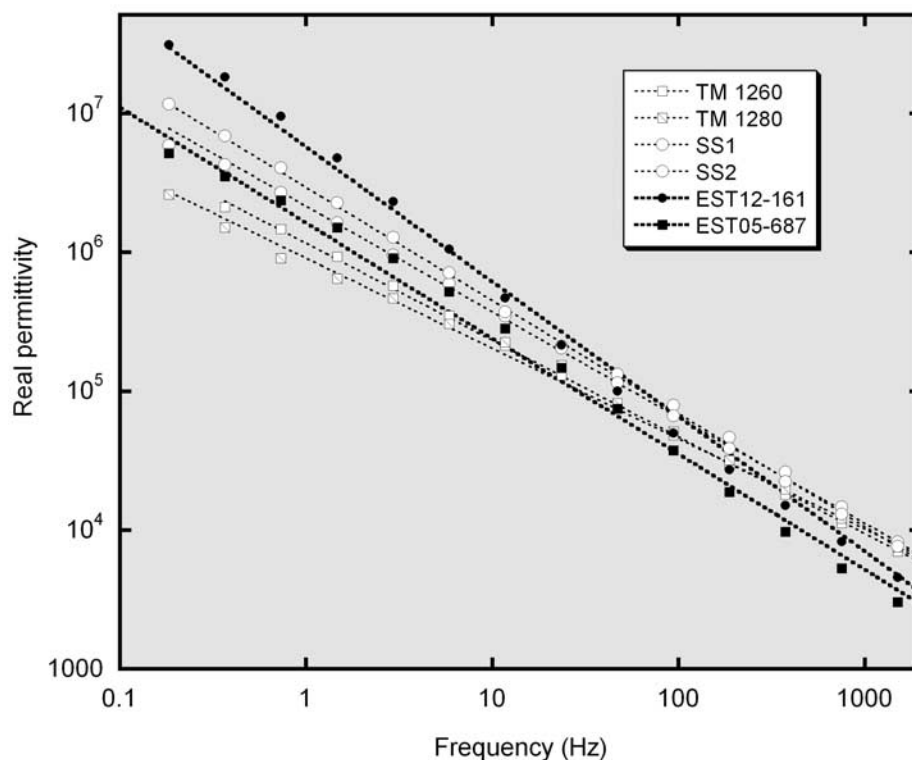
[13] The low-frequency spectra of the relative complex permittivity (imaginary part and real part) measured on the clay rock samples are given in Figures 1 and 2. The spectra of the effective complex permittivity have been found to deviate from the classical Debye relationship in two ways. First, the relative imaginary permittivity  $\varepsilon''$  is inversely proportional to the frequency  $f$  (i.e.,  $\varepsilon'' \propto f^{-1}$ ). This clearly indicates that the dielectric losses in these clayey materials are purely ohmic (no influence of losses related to dipolar polarization phenomena). Indeed, the relative imaginary permittivity or the total dielectric losses  $\varepsilon''$  is usually divided into two parts: a pure dielectric part  $\varepsilon''_d$  and an ohmic part  $\sigma_{dc}/(2\pi f\varepsilon_0)$ , where  $\sigma_{dc}$  is the direct current (DC) conductivity and  $\varepsilon_0$  is the permittivity of vacuum [e.g., Guéguen and Palciauskas, 1994]. The second contribution, the ohmic contribution, is inversely proportional to the frequency.

[14] Second, the relative real permittivity  $\varepsilon'$  measurements given in Figure 2 show two remarkable features.

[15] 1. The relative real permittivity exhibits enormously high values (up to  $3 \times 10^{10}$ ) in comparison with that of water ( $\sim 80$ ) and minerals ( $\sim 5$ – $10$ ).

[16] 2. The spectra of  $\varepsilon'$  exhibit a strong nonlinear dependence with frequency. When clay rocks with low CEC values are considered (Figure 2), we observe that  $\varepsilon' = Af^{-\alpha}$ , where  $A$  is a constant in the range  $(0.91$ – $2.90) \times 10^6$  and  $\alpha$  is an exponent in the range 0.65–0.81 (regression coefficient  $R$  in the range 0.991–0.999). For clayey samples





**Figure 2.** The low-frequency spectra of the real part of complex permittivity  $\epsilon'$ . Open symbols, measurements on samples with CEC values lower than 10 cmol/kg. Solid symbols, measurements on samples with CEC values greater than 10 cmol/kg. Dotted lines, power law regressions for each sample.

with higher CEC values, the agreement with a power law is slightly poorer ( $R$  in the range 0.972–0.997).

[17] Considering the first point, the gigantic values of  $\epsilon'$  have been extensively discussed in the literature, and two effects have often been proposed: (1) the Maxwell-Wagner effect due to the presence of thin platy particles perpendicular to the direction of the electric field [e.g., Sen, 1981] and (2) electrolyte-grain interface polarization associated with electrochemical phenomena [de Lima and Sharma, 1992].

[18] Considering the second point, the measured spectra shown in Figure 1 also exhibit an unexpected result: no clear relationship can be detected between the measured spectra of the real component  $\epsilon'(f)$  and the CEC (or  $Q_v$ ) values of each sample. The amplitude of  $\epsilon'$  of the SS samples with the lowest CEC values and that of sample EST05-687 with the highest CEC value are very close. Moreover, the samples from the Bure site with similar petrophysical properties (CEC and water content) showed very different responses in the low-frequency range (0.18–10 Hz).

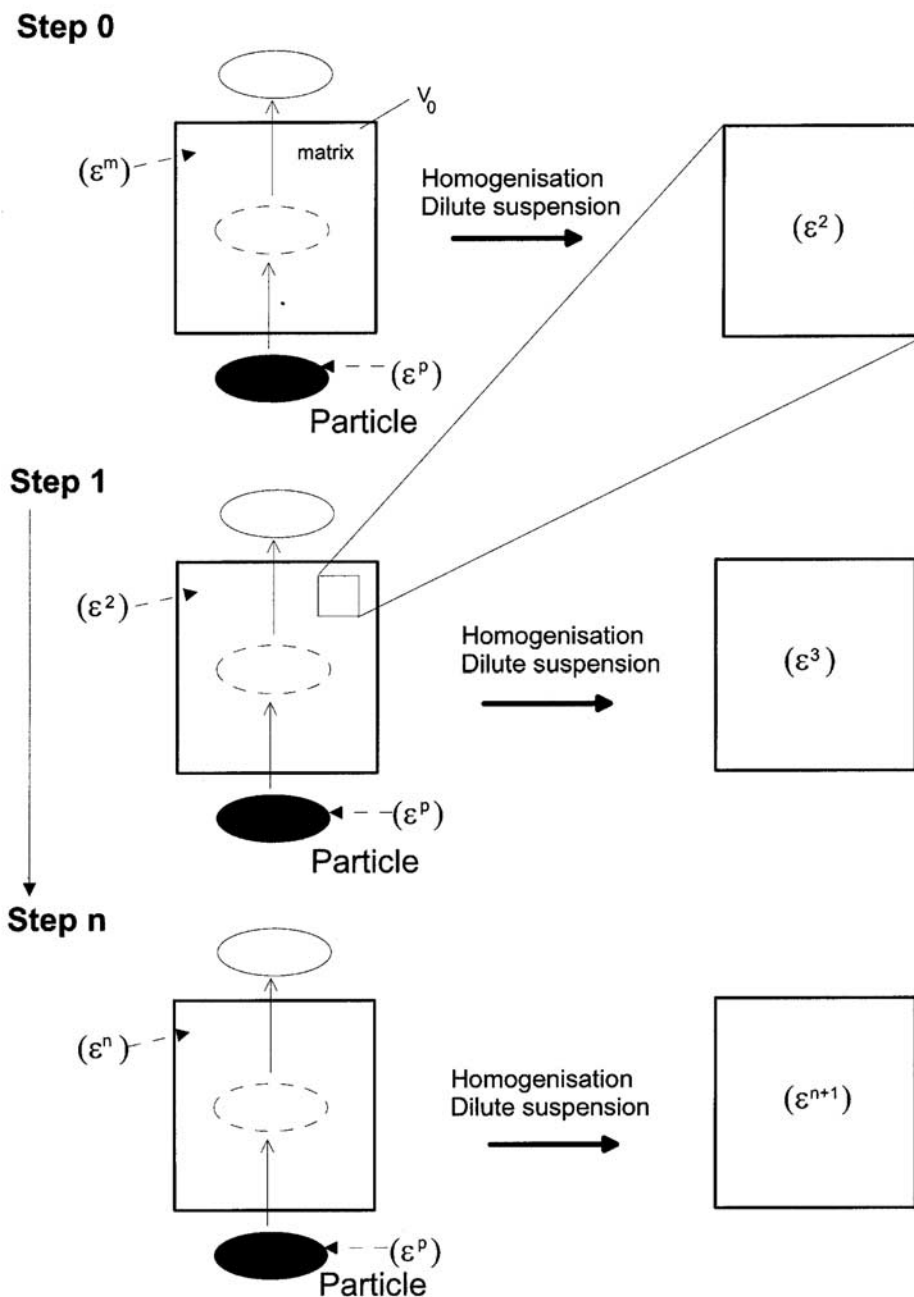
[19] Since most theoretical studies show that the dielectric responses associated with electrochemical phenomena [de Lima and Sharma, 1992] are strongly related to the surface conductivity that is proportional to CEC or  $Q_v$ , these comparisons suggest that the impact of the electrochemical phenomena is not, at least for the studied samples, of the first order. Consequently, these results confirm that the power law relationship that fits the measurements obtained with the samples with the lowest CEC values is related mainly to the texture of the clay rocks (particle size

distribution, pore size distribution, shape and location of clay aggregates, geometrical relationship between the clay aggregates and the nonclay minerals, microscale particle-to-particle contacts, etc.), as it is often mentioned in other studies with clay materials.

[20] Indeed, a power law has been evidenced by Thevanayagam [1997] and Lounev *et al.* [2002], who used unconsolidated and pure clay-water systems. Their results were interpreted as a pure textural effect associated with self-similar patterns at the microlevel structure. The first theoretical study [Thevanayagam, 1997] dealt with saturated kaolinite and montmorillonite in the kilohertz range to the high megahertz range. Lounev *et al.* [2002] studied dielectric spectra of artificial kaolinite-electrolyte systems in the range  $10^{-2}$ – $10^6$  Hz. Both approaches used electrical fractal networks assuming a self-similarity of the underlying physical processes and consequently invoked the concept of fractals (fractal solid skeleton and fractal pore surface) to explain the observed dielectric responses since experimental evidences for scale invariance in argillaceous soils and sediments exist [e.g., Krohn, 1988; Van Damme, 1995].

[21] However, at this stage, we feel that the application of an electrical fractal network model may be irrelevant in our context for two reasons.

[22] 1. Contrary to the materials used by Thevanayagam [1997] and Lounev *et al.* [2002], an argillaceous rock is not a pure clay material. It is composed of silica quartz and carbonates, often for the most part, with grains covering a large range of sizes and shapes. Consequently, it is difficult



**Figure 3.** The iterative process of a DEM scheme for a two-phase mixture.

to appreciate how the fractal regime reflects the reality of the texture.

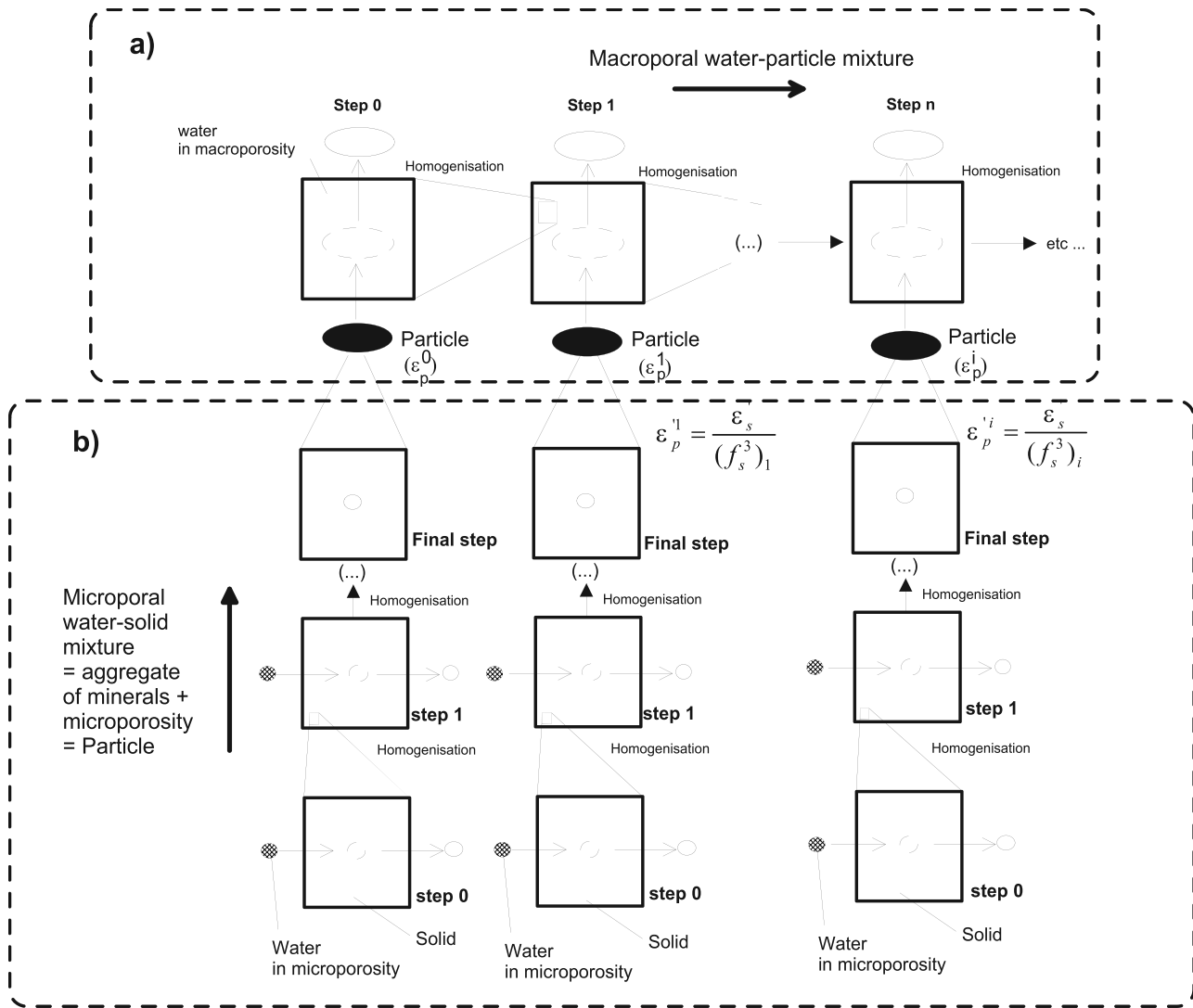
[23] 2. Electrical (fractal or not) network models suffer from at least two drawbacks. On the one hand, these models introduced empirical parameters for which the physical meaning is not clear. On the other hand, it is known that a measured spectrum can be represented by different electrical circuits with different physical meanings (uniqueness problem).

[24] In section 3, a new theoretical and simpler approach is proposed in order (1) to avoid the drawbacks of the electrical network models and (2) to model the low-frequency electrical responses of the clay rock samples with low CEC

values (i.e., the power law relationship), for which the impact of the EDL is assumed to be negligible.

### 3. Theoretical Aspects

[25] A simple and physically based approach for modeling the electrical properties of a mixture of different components is the Maxwell-Wagner-Hanai-Bruggeman (MWHB) equation, derived from the differential effective medium (DEM) theory [e.g., *Dukhin and Shilov, 1974; de Lima and Sharma, 1992*]. The DEM schemes offer four advantages: (1) all the parameters of this model have an explicit physical definition (i.e., no fitting parameters), (2) this model is easy to implement numerically, (3) the



**Figure 4.** The imbricated DEM schemes. (a) Iterative process of the DEM scheme used for modeling the effective complex permittivity of macroporal water-particle mixture. A particle is an aggregate of clay minerals and nonclay minerals (quartz and carbonate grains) with water in the micropores. (b) Iterative process of the DEM scheme used for modeling the effective complex permittivity of particles (aggregates of clay and nonclay minerals with water in micropores). In the homogenization scheme (Figure 4b), water is in the micropores.

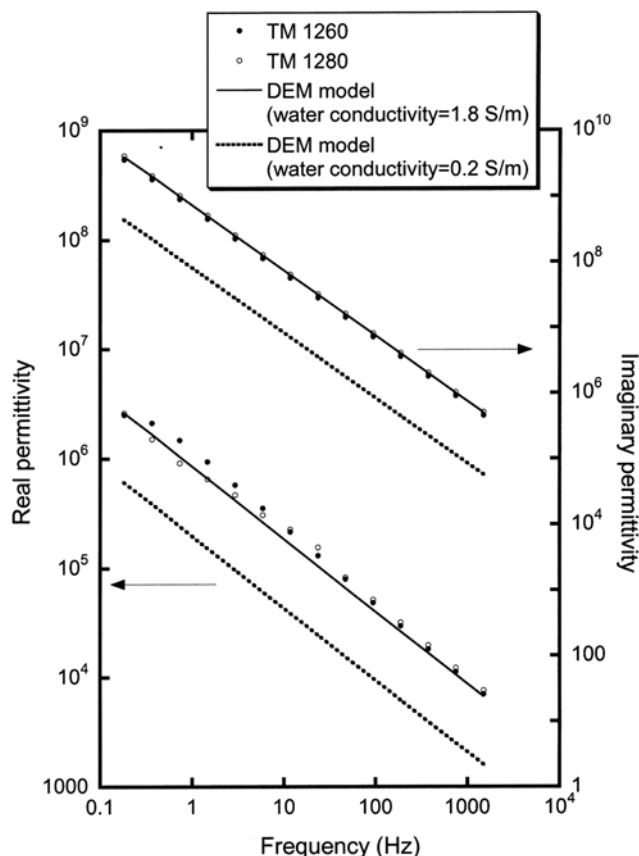
influence of the particle shape can be explicitly accounted for [e.g., Jones and Friedman, 2000], and (4) the model integrates the electromagnetic interactions between the different heterogeneities by an iterative process, leading to good agreements with dielectric data [e.g., Cosenza et al., 2003].

[26] Following an iterative process, the effective property of the mixture is explicitly calculated from an initial material through a series of incremental additions of elementary units. The mixture is built up by starting with a homogeneous medium and then replacing a small amount of the starting medium with another component with an ideal geometry (sphere or ellipsoid). For instance, consider a mixture of two components: spheroidal particles with an effective complex permittivity ε<sub>p</sub> are embedded in a matrix characterized by an effective complex permittivity ε<sub>m</sub>. The procedure begins with the initial material m corresponding to a relative permittivity ε<sub>m</sub> in a volume V<sub>0</sub>. A small volume

of phase p, δV<sub>p</sub>, is imbedded in phase m in such a way that the volume remains fixed at V<sub>0</sub>. The effective relative permittivity of the mixture is calculated considering a dilute suspension of particles p in a medium m. Now in the volume V<sub>0</sub>, the mixture has a homogenized effective complex permittivity ε<sub>2</sub> and constitutes the initial medium of the next step. A schematic of the iterative process is shown in Figure 3. The construction process continues such that (1) at each stage, the embedded particles are in dilute concentration and (2) the required volume fraction φ<sub>p</sub> is satisfied. Finally, the effective complex permittivity of the mixture ε<sub>mix</sub> is given by the MWHB equation [e.g., Chen and Or, 2006]:

$$\frac{\epsilon_p - \epsilon_{\text{mix}}}{\epsilon_p - \epsilon_m} \left( \frac{\epsilon_m}{\epsilon_{\text{mix}}} \right)^{1/m^*} = 1 - \phi_p, \quad (1)$$

where φ<sub>p</sub> is the volume fraction of spheroidal inclusions and m\* is a particle shape factor related to the eccentricity of the



**Figure 5.** Simulated and experimental spectra of the complex permittivity of Tournemire samples. The dotted lines and the solid lines show the imbricated DEM model with a water conductivity equal to 0.2 and 1.8 S/m, respectively.

spheroidal particles. This exponent is related to the “cementation exponent” because this is the same exponent that enters into Archie’s first law. For spherical particles and in the DC limit,  $m^* = 1.5$  [e.g., Sen, 1984].

[27] The iterative process associated with the DEM approach is not primarily used to model fractal or self-similar media. It is a better and intuitive way to account for the electromagnetic interactions (i.e., mutual polarizations) between heterogeneities in comparison with other effective medium approximations (i.e., the dilute approximation which neglects these interactions and the self-similar approximation which overestimates them) [Dukhin and Shilov, 1974].

[28] We propose to combine DEM schemes and the intuition of Lunev et al. [2001] and Lounev et al. [2002]. The low-frequency electrical properties of the low-CEC clay rocks result in the electromagnetic interaction between two states of water: the free water in the macroporosity and the water in the microporosity. Following the textural model proposed by Yven et al. [2007] for argillite, the macroporosity is mostly located at the interface between the clay matrix and the other minerals (carbonates and tectosilicates). It is characterized by micrometric to submicrometric pore sizes. The microporosity is the internal porosity of the

clay matrix (around clay aggregates and particles) characterized by inframetric to nanometric pore sizes.

[29] Classical DEM schemes (1) cannot reproduce power law spectra [Comparison, 2005] and (2) cannot account for heterogeneities with very different spatial scales. For this reason, in order to account for the mutual interaction between these states of water, two imbricated DEM schemes are considered: a first DEM scheme is introduced for modeling the mixture of “free” water and particles (aggregates of clayey units and nonclay minerals) in which a second DEM is imbricated to account for the microporal water in the particles (Figure 4).

[30] Regarding the latter scheme, the microporal water-solid mixture, two additional assumptions are considered.

[31] 1. The water electrical conductivity in the microporosity is much greater than the electrical conductivity of either the mixture or of the solid alone: the effects of the EDL and of surface conduction are supposed to be negligible for the lowest-CEC materials. As a matter of fact, microvolumes of water in the micropores are considered as conducting particles: the electrical field in these closed microvolumes tends to zero, and hence their permittivity tends to infinity. This assumption means that in agreement with experimental and thermodynamical arguments [Blackmore, 1978; Leroy et al., 2007], the microporal water has to be very concentrated in comparison with that of macropores.

[32] 2. For the sake of simplicity, the microvolumes of water in the microporosity are spherical. Following these assumptions and the DEM scheme given in Figure 4b (conducting water microspheres in an insulating solid matrix), the real part of the complex dielectric constant of the microporal water-solid mixture (i.e., particle)  $\epsilon'_p$  is given by [e.g., Dukhin and Shilov, 1974]

$$\epsilon'_p = \frac{\epsilon'_s}{(f_s)^3}, \quad (2)$$

where  $\epsilon'_s$  is the real part of the complex dielectric constant of the solid and  $f_s$  is the volumetric fraction of the solid. It should be noted that equation (2) has been successfully used to model the permittivity of a mixture of water droplets in oil emulsions [Dukhin and Shilov, 1974].

[33] Moreover, since the electrical conductivity of the solid is considered negligible, the electrical conductivity of the microporal water-solid mixture is equal to zero, following the DEM scheme (Figure 4b). This assumption means that for these low-CEC argillites, the bulk rock electrical conductivity is mainly controlled by that of the macropores and hence obeys Archie’s first law. This assumption is usually checked by measuring rock conductivity as a function of water conductivity, i.e., with different brine salinities [e.g., Waxman and Smits, 1968]. However, considering argillites, this classical procedure is difficult to apply for at least two reasons. First, in order to control the brine conductivity in the clay rock sample, the sample has to be leached continuously: a chemical equilibrium should be reached when the brine conductivity extracted at the output of the sample is equal to that subjected at the input. From our own experience, in the case of a clay rock sample with a very low intrinsic permeability and diffusion coefficient



(typically equal to  $10^{-20}$  m<sup>2</sup> and  $10^{-11}$  m<sup>2</sup>/s, respectively [e.g., Boisson et al., 2001]), this chemical equilibrium for a given brine salinity can take very long to reach, typically a few weeks for a decimetric sample. Second, when the macropore water chemistry is modified in a clay sample during a leaching experiment, this may also lead to a change in the micropore composition [Leroy et al., 2007]. This may induce textural changes by shrinkage or swelling of the clay aggregates and changes in the surface conductivity, which are both difficult to control. To our knowledge, no study on the electrical properties of natural clay rock samples used this time-consuming and complex procedure. Moreover, experiments performed on artificial compacted clay samples wetted by means of a flow of a low-concentration ( $10^{-2}$  mol/L) NaCl solution [Mammari et al., 2001] suggest that Archie's law can be used as a good first approximation, except for pure montmorillonite. This conclusion is also confirmed when Archie's law is expressed in terms of diffusion coefficients: a good fit with Archie's law is obtained using the transport through or effective porosity [Van Loon et al., 2003; Rosanne et al., 2003; Blum et al., 2007].

[34] This approach was applied to Tournemire samples for which the electrical conductivity of interstitial water has been estimated to be equal to 0.2 S/m on average from total dissolved salts measurements obtained from the water of the site [Bonin, 1998]. We used  $\epsilon'_w = 80$  (relative permittivity of water in macropores) and  $\epsilon'_s = 5$  (typical value for silica). For the sake of simplicity, all particles (microporal water-solid mixtures) are assumed to be spherical (i.e.,  $m^* = 1.5$  or  $1/m^* = 0.66$  in equation (1)). The total porosity was taken to be equal to 8% [Bonin, 1998]. The results of DEM calculations for different values of water conductivity (0.2 and 1.8 S/m) are shown in Figure 5. A satisfactory agreement with the experimental data can be observed with a water conductivity value much greater than the measured average from the water of the site. This discrepancy is not surprising since the water collected from the site is not necessarily in chemical equilibrium with that in the clay rock. However, despite the uncertainties of the used parameters, the imbricated DEM schemes can reproduce the observed order of magnitudes and the power law relationship of the measured spectra of both components of the complex permittivity. The theoretical exponent associated with the real permittivity (i.e.,  $1/m^* = 0.66$ ) is close to the observed power law exponents  $\alpha$  obtained in both samples TM90-1260 and TM90-1280 (0.70 and 0.65, respectively).

#### 4. Implications and Concluding Statements

[35] The experimental results of this study do not show a strong dependence on the measured CEC values and consequently on the physicochemical phenomena occurring at the surface of clay minerals. Consequently, in order to capture the main physical process involved in these measurements, we suggest that the existence of numerous conducting micropores is responsible for the observed power law relationships. This assumption is supported by a DEM approach accounting for the mutual electrical polarization between the water pockets of the micropores and those of the macropores. This new and general approach could be

extended to the low-frequency spectra of materials with dual porosity like zeolites, zeoponic, and pumice.

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