WETTABILITY AND DIELECTRIC CONSTANT

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ABSTRACT
The wettability of 47 samples (both partially and 100% water saturated) has been studied using dielectric constant measurements in the 100 Hz - 10 GHz frequency interval. It is shown that the underlying mechanisms behind dielectric dispersion can be divided into three groups: low-frequency (< 10 kHz) effects dependent on the connectivity of the water phase, Maxwell-Wagner polarisation effects (10 kHz to 1 GHz) that are essentially controlled by the shape of the water inclusions, and high-frequency effects (> 1 GHz) related to specific surface. Systematic differences have been observed on varying wettability throughout the frequency range investigated. Parameters such as the relaxation time and the ratio of high-frequency to low-frequency conductivity are shown to be good indicators of rock wettability. Based on the results obtained, a new laboratory technique is presented, for the rapid measurement of core wettability and the characterisation of wettability heterogeneity at the plug scale. Also, the possibility of measuring in-situ wettability using electric logs operating at different frequencies is discussed.

INTRODUCTION
Electrical measurements represent a major source of information for estimation of oil content in a reservoir. Thus, it is important that they are accurate and correctly interpreted. Since wettability strongly affects the electrical response of rocks, correct interpretation of logs requires that wettability be properly accounted for. This raises two questions: What is the effect of wettability on electrical conductivity? Can we determine in-situ wettability from electric measurements?

The objective of this paper is to answer these two questions. The most studied effect of wettability on conductivity is concentrated in the saturation exponent (n) of the second Archie law. If the rock is water-wet, the saturation exponent assumes values of the order of 2, while values of up to 10 may be reached in oil-wet contexts. This effect dominates at low frequencies (< 10 kHz) and is related to the *connectivity* of water in the pore space, which is good when the rock is water-wet and poor when the rock is oil-wet (provided that the water saturation is low enough). At intermediate frequencies (10 kHz to 1 GHz) connectivity effects become negligible. In this frequency interval the *shape* of the water inclusions is the most critical parameter and the electrical response of the rock is no longer affected by the degree of continuity of the water. Interfacial polarisation or Maxwell-Wagner mechanisms are prevalent at these frequencies, and wettability still plays a fundamental role. At higher frequencies (> 1 GHz) *surface roughness* effects appear. These cause a characteristic dispersion (i.e. variation with frequency) of the electrical properties of the rock, essentially related to the specific surface of the water inclusions. Again, wettability is an important factor, as water surface to volume ratios depend on whether water is in contact with the rock or not.

This paper mainly investigates shape and surface roughness effects.

BACKGROUND
The macroscopic electrical behaviour of rock or any other material is described by Maxwell's equations and certain constitutive relationships. When a rock is subjected to a sinusoidal electric field (with a time dependence e^{iwt}), the constitutive dielectric equation $\mathbf{D} = \boldsymbol{e}_0 \boldsymbol{e}_d \mathbf{E}$, Ohm's law $\mathbf{J} = \boldsymbol{s}_c \mathbf{E}$ and Maxwell's equation for the total current can be combined to obtain,

$$\mathbf{J}_t = (\boldsymbol{s}_c + iw\boldsymbol{e}_0\boldsymbol{e}_d)\mathbf{E} \tag{1}$$

where $i = \sqrt{-1}$ is the imaginary unity, $\boldsymbol{e}_0 = 8.854 \times 10^{-12}$ Farad/m is the vacuum permittivity, and $\boldsymbol{s}_c$ (conductivity) and $\boldsymbol{e}_d$ (dielectric constant) are complex quantities dependent on the angular frequency w. $\mathbf{J}_t$ represents the sum of two current densities: one is due to the drift of free charges under the action of the applied electric field $\mathbf{E}$, and the other is related to the oscillations in the distribution of bound charges. Practically, measurements give only access to the total current density $\mathbf{J}_t$, so it is usual to work with a

synthetic conductivity $\boldsymbol{s}$ or a synthetic dielectric constant $\boldsymbol{e}$, which include both free ($\boldsymbol{s}_c$) and bound charge related mechanisms ($\boldsymbol{e}_d$). In so doing, one uses a generalised Ohm's law of the form $\mathbf{J}_t = \boldsymbol{s}\mathbf{E}$, or, indifferently, a generalised constitutive dielectric equation of the form $\mathbf{D}_t = \boldsymbol{e}_0\boldsymbol{e}\mathbf{E}$, where $\mathbf{D}_t$ is the total electric displacement. The various quantities are related to each other as follows:

$$\boldsymbol{s} = \boldsymbol{s}_c + i\boldsymbol{w}\boldsymbol{e}_0\boldsymbol{e}_d \tag{2a}$$

$$\boldsymbol{s} = i\boldsymbol{w}\boldsymbol{e}_0\boldsymbol{e} \tag{2b}$$

In this light, synthetic conductivity and dielectric constant are perfectly equivalent, and it is possible to derive the dielectric properties of a rock from conductivity measurements, or vice-versa. For a standard reference see [1]. In the following, terms "conductivity" and "dielectric constant" will be used instead of "synthetic conductivity" and "synthetic dielectric constant".

Dielectric constant model (100 Hz to 10 GHz). The dielectric constant of rocks containing various amounts of water is dependent on frequency. This behaviour is generally referred to as dispersive. At low frequencies, values of $\boldsymbol{e}$ exceeding 10^3 are often observed, which is more than an order of magnitude greater than the dielectric constant of any constituent material. At the other extreme, at high frequencies, $\boldsymbol{e}$ attains a limiting value of the order of 10. The dielectric constant is a complex quantity:

$$\boldsymbol{e}(\boldsymbol{w}) = \boldsymbol{e}'(\boldsymbol{w}) - i\,\boldsymbol{e}''(\boldsymbol{w}) \tag{3}$$

where $\boldsymbol{e}(\boldsymbol{w})$ is split into a real (single prime) and an imaginary (double prime) part. In the 100 Hz - 10 GHz frequency range, $\boldsymbol{e}(\boldsymbol{w})$ can be described by overlapping the contributions of four terms: a real constant ($\boldsymbol{e}_\mathtext{¥}$), a complex function of frequency ($\boldsymbol{e}_{MW}(\boldsymbol{w})$) which models Maxwell-Wagner (MW) polarisation, and two complex power law functions ($\boldsymbol{e}_{LFP}(\boldsymbol{w})$ and $\boldsymbol{e}_{HFP}(\boldsymbol{w})$) associated with charge transport [2-6]. Thus:

$$\boldsymbol{e}(\boldsymbol{w}) = \boldsymbol{e}_\mathtext{¥} + \boldsymbol{e}_{LFP}(\boldsymbol{w}) + \boldsymbol{e}_{MW}(\boldsymbol{w}) + \boldsymbol{e}_{HFP}(\boldsymbol{w}) \tag{4}$$

where:

$$\varepsilon_{LFP}(\omega) = \frac{D}{\varepsilon_0 (i\omega)^Q} \tag{4a}$$

$$\boldsymbol{e}_{MW}(\boldsymbol{w}) = \frac{\Delta\boldsymbol{e}}{1 + (i\boldsymbol{w}\boldsymbol{t})^{1-a}} \tag{4b}$$

$$\varepsilon_{HFP}(\omega) = \frac{A}{\varepsilon_0 (i\omega)^N} \tag{4c}$$

and $\boldsymbol{De}$, $\boldsymbol{t}$, $\boldsymbol{a}$ ($0<\boldsymbol{a}<1$), D, A, Q and N ($0<N<Q\le1$) are real parameters.

Each of the frequency-dependent terms that appear in Eq. 4 dominates the dielectric constant in a given frequency interval. At low frequencies $\boldsymbol{e}_{LFP}$ (LFP = Low Frequency Power law) is the most prevalent one. In the intermediate range $\boldsymbol{e}_{MW}$ is the main cause of the dispersive behaviour of the rock, while at high frequencies the dielectric constant is essentially controlled by $\boldsymbol{e}_{HFP}$ (HFP = High Frequency Power law).

Using Eq. 2b, it is possible to express $\boldsymbol{e}(\boldsymbol{w})$ in terms of conductivity, as:

$$\boldsymbol{s}(\boldsymbol{w}) = i\boldsymbol{w}\boldsymbol{e}_0\boldsymbol{e}_\infty + D(i\boldsymbol{w})^{n_1} + \frac{i\boldsymbol{w}\boldsymbol{e}_0\Delta\boldsymbol{e}}{1 + (i\boldsymbol{w}\boldsymbol{t})^{1-a}} + A(i\boldsymbol{w})^{n_2} \tag{5}$$

where $n_1 = 1-Q$ and $n_2 = 1-N$. Exponents n_1 and n_2 are characteristic of two regimes: a low frequency regime ($0<n_1<0.5$) associated with long range charge diffusion and a high frequency regime associated with short range conduction [7]. In the limit $n_1=0$, conductivity tends to D at low frequencies. Since D is real, low-frequency transport is not dispersive. When $0<n_1<n_2$, on the other hand, conductivity has an imaginary part and transport is dispersive also at low frequencies.

The effect of wettability on each of the above mechanisms is discussed in the following three subchapters.

Low frequency transport (100 Hz to 10 kHz). The low frequency behaviour of rocks is essentially related to the degree of connectivity of the water inclusions. The effect of wettability in this frequency range has been extensively studied (see, for instance, [8, 9]). The main point is that the wetting fluid forms a continuous phase down to very low saturations, while the non-wetting fluid is isolated in pockets even at rather large saturations. As a result, a water-wet system will generally exhibit larger conductivities.

Differences are also observed in the saturation exponent (n) that appears in the second Archie law. If water is the wetting fluid, the conductivity of the rock will decrease slowly with decreasing water saturation, because the water phase remains continuous even at low water saturations, and the saturation exponent will consequently be low. On the other hand, if water is the non-wetting phase, the low-frequency conductivity of the rock will decrease at a much faster rate, since some of the water will become isolated and not contribute to the conductivity, as the water saturation is lowered. As a result, the saturation exponent will be high.

Maxwell-Wagner polarisation (10 kHz to 1 GHz). The behaviour of the rock in the 10 kHz - 1 GHz frequency range is mainly related to the shape of the water inclusions. Maxwell-Wagner polarisation is the dominant mechanism at these frequencies. MW polarisation is an interfacial phenomenon, consisting in the trapping of initially free charge carriers at boundaries (water/oil or water/rock interfaces) after they have migrated some distance. The field distortion caused by the accumulation of these charges increases the overall capacitance of the system which results in high values of e'_{MW}, the real part of expression (4b). This effect is observed at frequencies $< 1/t$, i.e. when the ions have time to concentrate at the borders of the conducting regions (parameter t is called the relaxation time). At frequencies of the order of $1/2pt$, the imaginary part e''_{MW} peaks, showing maximum dissipation, while e'_{MW} begins to decrease. At higher frequencies ($>>1/t$) the ions do not have time to accumulate and MW polarisation does not occur, causing both e'_{MW} and e''_{MW} to drop off.

A fundamental contribution in studying the effect of wettability on MW polarisation was made by Sillars [10] and developed later by Lysne [11], who calculated the dielectric response for a simple two-phase system, consisting of an insulating phase (matrix and oil) containing a disperse conducting phase (brine). Sillars considered small, electrically non-interacting spheroidal inclusions of water, all with the same aspect ratio, and obtained a response similar to e_{MW} (Eq. 4b), with $a = 0$. By indicating the dielectric constant of the insulating phase with e_i, and the dielectric constant and dc conductivity of water with e_w and s_w respectively, he obtained the following relationships for the other parameters t and De :

$$t = e_0 \frac{e_i(b-1) + e_w}{s_w}$$ (6a)

$$\Delta e = \frac{e_i f S_w g b^2}{e_i(b-1) + e_w}$$ (6b)

where F is the rock porosity, S_w the water saturation, g a factor that takes into account the isotropic orientation of the water inclusions ($1/3 < g < 1$) and b a shape parameter. About real systems, where water inclusions have different shapes, Lysne showed that the MW polarisation could be obtained by summing the different contributions at time $t(b)$ related to different b parameters, each one with its own weight $De(b)$. For a symmetric b distribution e_{MW} can be expressed by Eq.(4b), where a is a parameter controlling the width of the relaxation time distribution: the wider the distribution of inclusion aspect ratios, the higher the a parameter. When the water inclusions can be described as oblate or spherical spheroids (as in the case of an oil-wet rock at irreducible water saturation) $b \leq 3$; when the water inclusions are described as very elongated spheroids (as in the case of a water-wet rock, with a water film covering most of the surfaces) $b >> 3$. By introducing these values in Eq. (6a) and (6b), it is found that for an equal water conductivity and saturation, both the relaxation time t and the relaxation strength De are several orders of magnitude greater in a water-wet rock than in an oil-wet rock at irreducible water saturation. Thus, MW polarisation fades out at lower frequencies in a water-wet system, while in an oil-wet system a MW contribution (although of lower strength) is still active at high frequency. From Eqs.(6) it follows that, for low water saturation, the shape (and not the size) of water inclusions plays the most important role, determining the features of electric response: more elongated polarised charge distributions yield higher polarisation strengths and slower charge relaxation times. A previous study [12], carried out on model systems, showed differences of up to three orders of magnitude in the relaxation times of water-wet and oil-wet samples.

High frequency transport (> 1 GHz). The effect of wettability on high-frequency transport processes has been investigated to a lesser extent. The high-frequency behaviour of the rock is probably related to the

roughness of the water interfaces. Although there are no conclusive results in the literature, various authors have recognised the fractal geometry of the medium as a key parameter [5,6,13].

It has been noted [14] that rocks with higher surface area show greater dispersion in the intermediate/high frequency range (MHz to a few GHz). This would imply that exponent N in Eq. (4c) is an increasing function of the surface area of the water inclusions. In a water-wet system, the water is in contact with the rock, so the water interfaces have the same roughness as the mineral surfaces. Consequently, high values of N can be expected, especially in the presence of clay minerals. When the rock is oil-wet, two cases can be considered: a) the water is mainly in contact with the oil and the water interfaces are smoother; b) even when oil is not present, hydrophobic surfaces can hinder water from wetting some very rough surfaces (both situations have been investigated in this study). In both cases the interfacial area is less than for a water-wet system and thus N is lower.

MATERIALS AND EXPERIMENTAL PROCEDURE

Four Berea sandstone plugs and 43 samples (both sandstone and carbonate) taken from 9 reservoirs were analysed in two different wetting conditions: a strongly water-wet condition obtained by cleaning the sample and an oil-wet condition obtained by silanisation treatment [15]. Following preparation, the samples, 1" or 2" in diameter and 0.6 to 1 cm thick, were saturated with brine: a part of them was analysed in this state of saturation; another part was analysed after centrifuging in an oil environment at capillary pressures ranging from 0.5 to 1 bar. Brine (78.8 g/l) and a refined mineral oil (Soltrol 130) were used as the saturating fluids.

Sample silanisation was performed as follows: on completion of the cleaning and drying, each of the selected samples was evacuated to 0.1 mbar and heated to 290°C in a vacuum oven. The inlet port of the oven was connected to a glass container, filled with 100 ml bis(dimethylamino)dimethylsilane and heated to 50°C for vaporisation of the silane. After maximum vacuum was reached, the oven was closed to the pump and vapour from liquid silane slowly admitted. The inlet port of the oven was then closed, and the samples remained in the silane atmosphere for 3 hours.

Dielectric constant measurements were carried out in the 100 Hz - 10 GHz frequency range, using two techniques: *impedance measurements* in the range 100 Hz - 40 MHz, and *Time Domain Reflectometry (TDR) measurements* in the range 25 MHz - 10 GHz.

A HP 4194A Impedance Analyzer was used for the impedance measurements. The samples were placed in a parallel plate capacitor specifically designed for the experiment, and a standard two-contact technique was used. The temperature was kept constant at 25.0 °C and controlled within 0.1 °C during the measurements. The Impedance Analyzer measured the total impedance, Z_T, of the equivalent circuit illustrated in **Fig. 1a**. Z_L was measured by short-circuiting the capacitor. The impedance Z_C associated with the parallel combination of the elements C_x and eC_0 was obtained by subtracting the value Z_L from the total impedance Z_T (errors can be effectively minimised if $Z_L << Z_T$). Z_C can be expressed as:

$$Z_C(w) = \frac{1}{iwC_0\,e(w) + iwC_x} \qquad (7)$$

By introducing standard samples of known permittivity into the capacitor, both C_x and C_0 ($C_x = 0.17$ pF, $C_0 = 3.55$ pF) were determined. The dielectric constant of the tested sample was then obtained by measuring the open-circuit impedance of the system without the sample (Z_0), and the total impedance with the sample placed in the capacitor (Z_T). The following equation was used:

$$e(w) = 1 + \frac{\left[Z_T(w) - Z_L(w)\right]^{-1} - \left[Z_0(w)\right]^{-1}}{iwC_0} \qquad (8)$$

To improve electrical contact on measuring totally water saturated samples, a thin paper filter, saturated with the sample water, was placed between the capacitor plates and the sample. By short-circuiting the capacitor with the filter, a resistance $R=67$ mΩ, independent of the frequency within 2% for the entire range investigated, was measured. This slightly increased the Z_L value, which remained, however, within reasonable limits. The measurements carried out on partially water-saturated samples were performed

without filters, to prevent the water-wet samples imbibing brine from the paper filters during the determination.
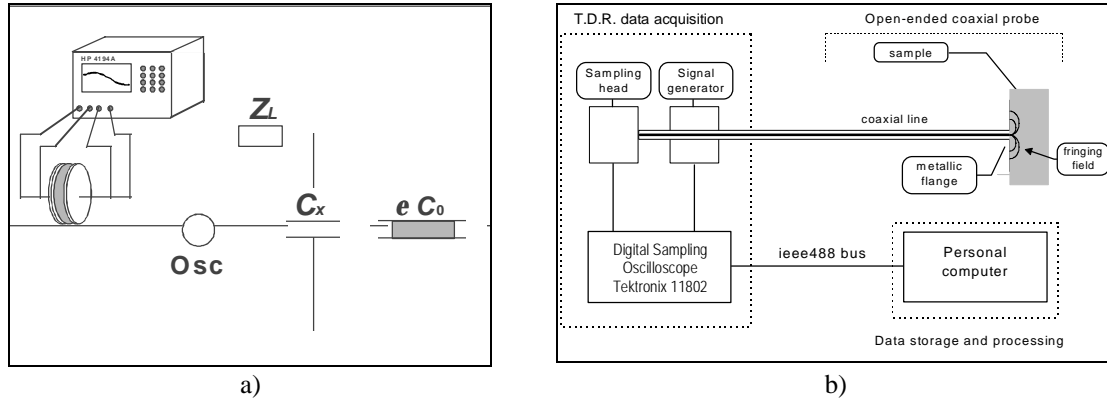

Fig. 1 - Experimental apparatus. **a)** The various circuit elements have the following physical meaning: the product eC_0 represents the complex impedance of the capacitor/sample system (C_0 = capacitance of the empty capacitor; $e(w)$ = dielectric constant of the sample); the capacitance C_x takes into account the parasitic capacitance parallel to the capacitor; the series impedance Z_L describes the effect of the interconnecting cables (Z_L is represented by a series combination of a resistance $R = 1.2$ mΩ and an inductance $L = 60$ nH). **b)** A digital sampling oscilloscope (Tektronix 11802) generates a step-like signal that propagates along the coaxial line and is reflected by the open probe. The dielectric constant of the sample is a function of the reflection coefficient, which is determined by the magnitude and the phase of the fringing field inside the sample. The incident and reflected signals are sampled, digitised and transferred to a computer for processing.

Dielectric measurements in the 25 MHz - 10 GHz range were carried out by the TDR technique, which uses a coaxial transmission line with an open-circuit configuration [16]. This technique is based on the general principle that a signal, which propagates from a coaxial line into a rock, is partially reflected at the boundary. Since the dielectric properties of the sample affect the reflected signal, dielectric constant of the sample can be calculated. The experimental apparatus is shown in **Fig. 1b**. The apparatus was calibrated with measurements carried out on fluids of known permittivity. Quick (the probe is simply placed against the sample) and reliable measurements up to 10 GHz were taken. The investigation depth was lower than 5 mm. The signal/noise ratio was good and the measurements, repeated at different points in the sample surface, were reproducible.

RESULTS AND DISCUSSION
Measurements on partially water saturated samples. We analysed 31 partially water saturated samples (4 Berea sandstone and 27 reservoir samples from 9 fields), whose main petrophysical characteristics are listed in **Tab. 1**. For more details, reference should be made to Ref. [12] and [17]. In this section, we discuss measurements carried out on a water-wet sample and a silanized sample taken from a sandstone reservoir (reservoir K). The remaining samples gave analogous results. **Fig. 2** shows a plot of loss angle tangent vs. frequency measured for the two samples. The loss angle tangent is defined as the ratio between the imaginary part and the real part of the dielectric constant $e(w)$.

While the water-wet sample (solid triangles) exhibits one single peak at a frequency of around 3 MHz, the silanized sample (open circles) shows two peaks, at frequencies of 200 kHz and 300 MHz respectively. Each of these peaks reveals a MW mechanism, with a relaxation time t that is inversely proportional to the frequency of the peak. Fitting Eq.(4) to the data, the high frequency power law term (Eq. 4c) was found to be negligible; t values of 0.13 μs for the water-wet sample, and of 10 μs and 0.3 ns for the silanized sample were obtained. Following Eq.(6a), long relaxation times t indicate water-wet situations, while shorter t are associated with oil-wet states. The curves in **Fig. 2** indicate a uniform water wettability for the water-wet sample, which exhibits one single, fairly long relaxation time, and heterogeneous wettability for the silanized sample, which shows two different relaxation times, due to the coexistence of

oil-wet and water-wet surfaces. MW dielectric strengths are lower for the silanized sample, yielding lower values of tan(d) at low frequency. MW peaks appear wider for the silanized sample, as should occur for a wide distribution of relaxation times related to a heterogeneous state of wettability. This result was confirmed also by the value of the a parameter that is higher (corresponding to wider distributions) for silanized samples than for cleaned water-wet samples (see ref. [17]).

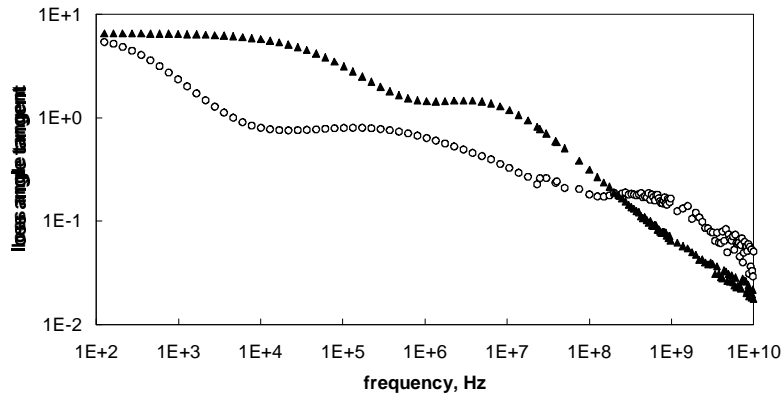**Fig. 2** - Log-Log plot of the loss angle tangent (tanδ) vs. frequency for two partially water saturated sandstone samples. Silanized sample (K3): open circles; water-wet sample (K13): solid triangles

On the basis of these results, a lab procedure has been defined to measure wettability, which involves electric measurements on a preserved (or aged) sample and repetition of the measurements after having cleaned the sample. Wettability can be discriminated using this technique if the sample has a water saturation of less than 40%. This can be achieved by centrifuging the sample in an oil environment at high capillary pressure. The test procedure is as follows: 1) Flood a preserved (or aged) sample with Soltrol oil to remove reservoir oil; 2) Centrifuge under Soltrol to reach Sw values < 40%; 3) Measure the dielectric constant of the sample in the 100 Hz - 10 GHz frequency range, combining low frequency impedance measurements with high frequency TDR measurements; 4) Clean the sample using Soxhlet extraction; 5) Saturate with brine; 6) Centrifuge the sample under Soltrol, applying the same capillary pressure as in 2); 7) Measure the dielectric constant in the 100 Hz - 10 GHz frequency range; 8) Analyse changes in the parameters controlled by the wettability, i.e. relaxation time t, relaxation strength De and loss tangent $tan(d)$.

Compared to traditional methods (Amott and USBM), the dielectric technique involves very short measuring times. Carrying out the procedure described above takes approximately 2 days instead of several weeks. The advantage is that more samples can be analysed for a reservoir study. Also, in the case of mixed-wetted systems, the dielectric technique gives indications that an Amott or USBM test cannot provide. The dielectric spectra are sensitive to water-wet and oil-wet mineral surfaces, and it is possible to separate the contributions.
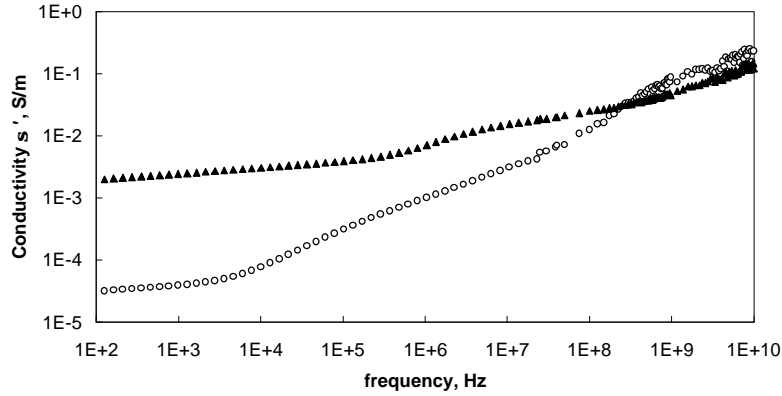
Fig. 3 - Log-Log plot of conductivity versus frequency for two sandstone samples. Silanized sample (K3): open circles; water-wet sample (K13): solid triangles

In-situ wettability can be evaluated, in theory, by comparing the responses of electric logs operating at different frequencies. Let us consider **Fig. 3**, which illustrates a conductivity vs. frequency plot obtained for the same samples shown in **Fig. 2**. What we mean here by conductivity is, in fact, the real part of conductivity, as defined in Eq.(2b), i.e. the expression $\omega\varepsilon_0\varepsilon''(\omega)$, which is usually indicated as $\sigma'(\omega)$. A σ' vs. frequency plot such as that of **Fig. 3** contains essentially the same information as a ε'' vs. frequency plot, just presented in another form. Both curves in **Fig. 3** increase with frequency, although with different slopes. The conductivity of the water-wet sample (solid triangles) increases by a factor 10, from 1 kHz to 2 MHz, whereas the conductivity of the silanized sample (open circles) increases by a factor 100 in the same frequency interval. Similar results were obtained for the other samples. **Tab. 1** reports the conductivity values measured at 1 kHz and 2 MHz on each of the analysed samples, as well as their ratio. Apart from the 4 samples taken from reservoir PL, which exhibit no significant difference between "cleaned" and "silanized", the ratio between the conductivity at 2 MHz and the conductivity at 1 kHz is systematically higher for the silanized samples. A difference of one order of magnitude is observed, on average, for the reservoir samples, with the Berea samples showing a difference of as much as three orders of magnitude. The anomalous behaviour of poorly consolidated PL sandstone is probably due to the presence of elongated, not interrupted, water inclusions both in cleaned and silanised samples (PL silanised samples have a very high conductivity).

Reservoir Code	Sample Code	Treatment	Lithology	Porosity (%)	Sw (%)	Conductivity (S/m) 1 kHz	Conductivity (S/m) 2 MHz	Cond. Ratio
Berea	C	Silanized	Berea sand.	19.1	44.6	1.70×10^{-7}	6.41×10^{-4}	3800
	D	Silanized		19.4	36.1	2.83×10^{-7}	6.22×10^{-4}	2200
	G	Cleaned		21.7	18.4	5.19×10^{-3}	1.65×10^{-2}	3.18
	H	Cleaned		21.4	21.9	4.40×10^{-3}	1.12×10^{-2}	2.55
A	2	Silanized	carbonate	16.3	60.4	6.82×10^{-5}	5.93×10^{-3}	86.9
	9	Cleaned		13.4	68.2	3.20×10^{-2}	3.87×10^{-2}	1.21
D	6	Silanized	sandstone	12.2	18.6	6.52×10^{-5}	3.01×10^{-3}	46.2
	8	Cleaned		12.8	13.7	1.14×10^{-3}	7.25×10^{-3}	6.34
P	10	Silanized	carbonate	18.3	20.6	8.99×10^{-5}	3.36×10^{-3}	37.4
	16	Cleaned		17.0	36.1	4.98×10^{-3}	1.84×10^{-2}	3.70
V	8	Silanized	carbonate	23.9	22.3	2.79×10^{-4}	3.84×10^{-3}	13.7
	16	Cleaned		26.3	46.5	2.28×10^{-2}	5.81×10^{-2}	2.55
K	3	Silanized	sandstone	23.2	17.8	3.97×10^{-5}	2.35×10^{-3}	59.3
	98	Silanized		22.2	16.9	1.17×10^{-4}	2.46×10^{-3}	21.1
	13	Cleaned		22.7	8.2	2.47×10^{-3}	1.06×10^{-2}	4.30
	99	Cleaned		21.8	9.0	7.16×10^{-4}	7.46×10^{-3}	10.4
L	10	Silanized	sandstone	13.5 (?)	11-13	1.86×10^{-3}	8.08×10^{-3}	4.34
	98	Silanized		22.0	8.4	2.64×10^{-4}	3.44×10^{-3}	13.0
	17	Cleaned		22.7	31.0	5.95×10^{-2}	6.96×10^{-2}	1.17
	99	Cleaned		23.8	3.7	1.99×10^{-3}	8.10×10^{-3}	4.07
B	7	Silanized	sandstone	13.0	33.2	4.73×10^{-5}	3.09×10^{-3}	65.2
	11	Cleaned		13.8	63.2	3.72×10^{-3}	1.13×10^{-2}	3.04
	23	Cleaned		13.3	47.4	2.31×10^{-2}	3.19×10^{-2}	1.38
PL	9	Silanized	sandstone	≈ 25	≈ 20	5.76×10^{-2}	6.68×10^{-2}	1.16
	11	Silanized		≈ 25	≈ 20	2.14×10^{-2}	2.38×10^{-2}	1.11
	6	Cleaned		≈ 25	≈ 20	4.00×10^{-1}	4.04×10^{-1}	1.01
	16	Cleaned		≈ 25	≈ 20	2.40×10^{-1}	2.45×10^{-1}	1.02
R	7	Silanized	sandstone	13.8	12.7	1.84×10^{-5}	1.61×10^{-3}	87.5
	98	Silanized		13.8	11.0	1.11×10^{-5}	2.13×10^{-3}	193
	11	Cleaned		13.5	30.1	5.47×10^{-4}	4.20×10^{-3}	7.69
	99	Cleaned		13.9	7.0	1.05×10^{-4}	1.98×10^{-3}	18.8

Tab. 1: Petrophysical characteristics and electrical conductivities (at 1 kHz and 2 MHz) of the samples analysed

These results suggest a new method for measuring in-situ wettability. If the formation conductivity measured with a tool operating at intermediate/high frequency (e.g. a 2 MHz Compensated Dual Resistivity tool) is far greater (orders of magnitude) than the conductivity measured with a tool operating at low frequency (a 1 kHz Spherically Focussed Resistivity tool), the formation is probably oil-wet; if the conductivity measured with a intermediate/high frequency tool is the same or slightly higher than the conductivity recorded with a low frequency tool, the formation is water-wet. We are currently assessing the feasibility of this new measurement technique. The main limitations probably include:

a) Interpretation problems due to crude oil. The laboratory tests described in this paper were carried out with a mineral oil (Soltrol 130) whose dielectric response is flat over the entire frequency range investigated. Matters are certainly more complex in the reservoir. If the oil is polar, a dipolar polarisation mechanism, independent of the wettability, could occur along with the MW polarisation. In this case, the effect of wettability on the electric properties of the rock could be masked.

b) Problems linked to the different investigation depths and direction of tools operating at different frequencies. Homogeneous and isotropic formations are preferable. The greater the difference between the operating frequencies of the selected tools, the greater the difference between the investigated volumes. On the other hand, if tools are used which operate at similar frequencies (e.g. a 20 kHz AIT -Array Induction Imager Tool and a 100 kHz AIT), the variation in the responses of the tools decreases significantly and so does the possibility of identifying the formation wettability.

c) The water saturation of the formation must be less than 40%. With water saturations above this value, the effect of wettability on conductivity is masked and difficult to identify. An oil-base mud is therefore

required (if a water-base mud is used, the invaded zone, investigated by the logs, will have a water saturation which is too high). However, the risks of altering the wettability of the invaded zone are extremely high when using oil-base mud. The mud must therefore be inert (Does inert oil-base mud exist?).

Measurements on totally water saturated samples. These measurements were carried out on 16 reservoir samples; some of their petrophysical characteristics are given in **Tab. 2**. The samples were collected from 8 reservoirs (two samples for each reservoir). Half were silanized and the other half analysed in a strong water-wet condition. All measurements were affected by the electrode polarisation effect up to a critical frequency f_c of the order of 10^5 Hz. Because of the electrode polarisation, the real part of the dielectric constant e' assumed extremely high values, strongly dependent on the applied voltage. Since it was not possible to correct the measured data, reliable results are only available at frequencies higher than f_c. **Fig. 4** shows the dielectric spectra measured on two samples taken from sandstone reservoir B.
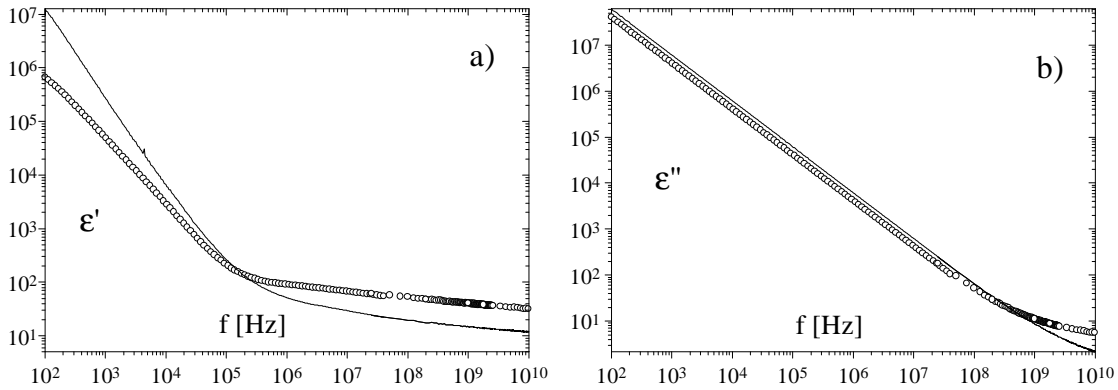

Fig. 4 - Log-Log plot of permittivity versus frequency for two 100% water saturated sandstone samples: a) real part e'; b) imaginary part e''. Silanized sample (B6): open circles; water-wet sample (B12): solid line.

Let us first consider **Fig. 4a**. Both samples clearly exhibit two trends: up to 10^5 Hz, both e' curves are affected by electrode polarisation. This effect is described by a power law, $e' = Bw^{-M}$ with $M > 1$ for both samples. Exponents ranging from 1 to 2 are characteristic of phenomena associated with electrode polarisation. Above 10^6 Hz, the e' curves are no longer influenced by spurious effects and it is possible to obtain information on the properties of the sample. In this range, e' can still be modelled with a power law, of the form $e' = Cw^{-N}$, according to Eq.(4c). The silanized sample (open circles) has greater e' values than the water-wet sample (solid line). The C factor is 6.6×10^2 for the silanized sample and 1.24×10^3 for the water-wet sample; the exponent N is 0.133 for the silanized sample and 0.229 for the water-wet sample.

The e'' curves are not affected by the polarisation of the electrodes (**Fig. 4b**), being of the form $e'' = Fw^{-Q}$ from 10^2 Hz up to frequencies of the order of 10^9 Hz, with $Q = 0.999$ for both samples. As $Q \cong 1$, e'' is inversely proportional to the frequency. This means that the response of the samples is dominated by the contribution of non-dispersive charge transport (i.e. in Eq. 5, $n_1 \cong 0$). At higher frequencies, e'' deviates from inverse proportionality, first for the silanized sample then for the water-wet sample, and switches to a power law with a smaller exponent, similar to the one observed for e'. The dc conductivity, calculated by averaging the low frequency values of $we_0e''(w)$, is 0.232 S/m for the silanized sample and 0.344 S/m for the water-wet sample. From these values, a cementation exponent m of 1.85 for the silanized sample and 1.65 for the water-wet sample were calculated.

The other samples gave similar results. The significant parameters which can be extracted from the measurements are: the high frequency exponent N (which can be derived from the law $e' = Cw^{-N}$), the dc conductivity and the cementation exponent m (obtainable from the trend of e''). The overall results are summarised in **Tab. 2**.

Reservoir Code	Sample Code	Treatment	Lithology	Porosity (%)	Sw (%)	dc Conductivity (S/m)	m	N
A	4	silanized	Carbonate	15	100	0.164	2.14	0.129
	8	cleaned		15	100	0.232	1.96	0.171
D	2	silanized	Sandstone	12.5	100	0.281	1.69	0.174
	9	cleaned		12.5	100	0.262	1.73	0.182
P	13	silanized	Carbonate	17.6	100	0.228	2.15	0.200
	17	cleaned		17.6	100	0.290	2.01	0.242
V	6	silanized	Carbonate	25	100	0.514	2.10	0.218
	17	cleaned		25	100	0.747	1.83	0.272
K	6	silanized	Sandstone	22.5	100	0.712	1.74	0.154
	14	cleaned		22.5	100	0.743	1.71	0.274
L	5	silanized	Sandstone	23	100	0.451	2.07	0.239
	18	cleaned		23	100	0.627	1.85	0.247
B	6	silanized	Sandstone	13.4	100	0.232	1.85	0.133
	12	cleaned		13.4	100	0.344	1.65	0.229
R	9	silanized	Sandstone	13.7	100	0.343	1.67	0.050
	14	cleaned		13.7	100	0.509	1.47	0.107

Tab. 2: Totally water saturated samples: petrophysical characteristics, dc conductivity, cementation exponent *m* and exponent *N* of the power law that models the high-frequency response of the samples

The response of the 100% water saturated samples is very different from that of the partially water saturated samples. In the 100% water saturated samples, the MW effect cannot be observed and the global response appears to be dominated by the contributions of the transport terms (Eqs. 4a and 4c). More precisely, the MW term (Eq. 4b) is negligible at the intermediate/high frequencies, due to the elongated shape of the water phase, which results in long MW relaxation times, shifting the MW effect to low frequencies. In the low frequency range, on the other hand, electrode polarisation effects dominate.

The data of **Tab. 2** show that both the dc conductivity and exponent *N* are lower in the silanized samples. This difference is probably related to the efficiency of the silanization treatment and to the mineral and geometric characteristics of the pore space. Some of the analysed samples had a high content of clay minerals, especially kaolinite, chlorite and illite, and LTSEM (Low Temperature Scanning Electron Microscopy) and EDX analyses showed that the silanisation treatment made kaolinite and chlorite oil-wet, while illite remained water wet (**Fig. 5**). The presence of oil-wet clays probably reduced the surface conductivity of the rock, and consequently lowered the overall dc conductivity of the silanized samples.

At high frequencies, the dielectric constant is proportional to $(i w)^{-N}$. Various authors have observed this behaviour [5, 6, 18, 19], and published values of the exponent *N* are comparable to those in **Tab. 2**. Some have hypothesised that *N* increases with the surface to volume ratio (*S/V*) of the rock: *N* should be linked to the fractal dimension of surfaces. According to Ruffet and co-workers [5] the general relationship is: $N = a \ln(S/V) + b$, where *a* and *b* are parameters dependent on the rock and the water salinity. The fact that *N* is greater in the water-wet samples should therefore imply that the water-wet samples have a greater surface to volume ratio. We tested this assumption on twin samples of Berea sandstone, one water-wet and the other silanized, using the B.E.T Krypton adsorption method, which in fact did yield a surface area of 0.75 m^2/g in the water-wet case and 0.16 m^2/g in the silanized case.

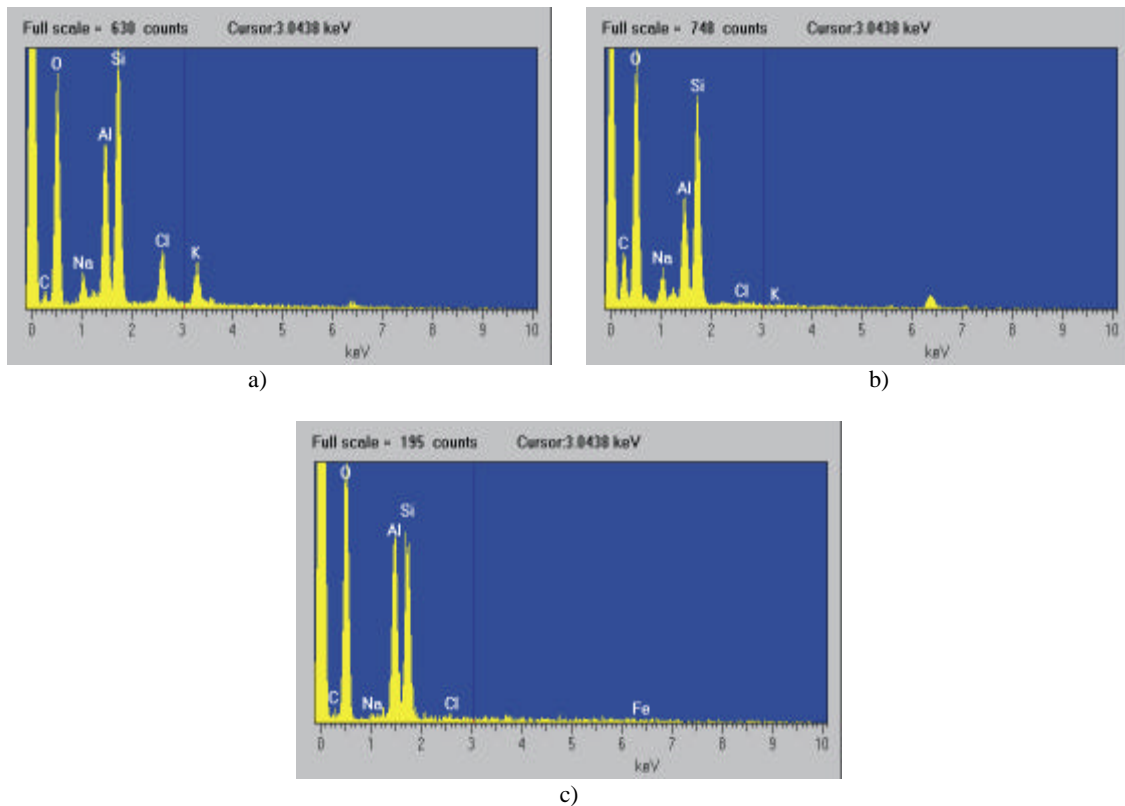a)   b)

c)

Fig. 5 - EDX (Energy Dispersive X-ray analysis) spectra measured on a silanized sample, saturated with brine and pentadecane (reservoir R). a) Illite aggregate: elements O, Al, Si and K are associated with illite, while Na and Cl indicate the presence of water. b) Chlorite aggregate: elements O, Al, Na and Si are associated with chlorite, while considerable C content indicates the presence of oil. Since no Cl is detected, water is absent. c) Kaolinite aggregate: elements O, Al and Si are associated with kaolinite. Elements Na and Cl are absent.

CONCLUSIONS

The electric response of partially and 100% water saturated rock samples was measured in the frequency range 100 Hz - 10 GHz. The following parameters were identified, which seem to depend primarily on rock wettability:

- *Loss angle tangent*. A plot of loss angle vs. frequency makes it possible to identify the presence of MW polarisation mechanisms and to evaluate the associated relaxation time *t*. The relaxation time is identified by an adsorption peak in the *e"/e'* vs. frequency curve. The longer the relaxation time, the more water-wet the sample. When two separate MW mechanisms occur, heterogeneous wetting situations may be identified. Based on the results a laboratory technique has been defined which involves making dielectric measurements in the 100 Hz - 10 GHz range on a preserved sample, and repetition of the measurements after the cleaning of the sample. Analysis of the variation of the relaxation time and strength gives information about the initial wettability of the sample. The test takes approximately 2 days.

- *Conductivity ratio*. The "high frequency conductivity to low frequency conductivity" ratio is another good estimator of rock wettability. The higher this ratio, the more oil-wet the sample. This concept can be applied, in theory, to electric logs interpretation for in-situ wettability determination. The idea is to compare the response of tools operating at different frequencies (for instance a 2 MHz tool with a 1 kHz tool). If the ratio of the conductivities is less than 10 the reservoir is probably water-wet, whereas values greater than 50 should indicate intermediate/oil-wet conditions.

- *Exponent N*. Exponent *N* of the power law which describes *e'* data measured at high frequencies on

100% water saturated samples is greater in the water-wet samples than in the oil-wet ones. N is linked to the surface/volume ratio, which, in turn, is a function of the fractal dimension of the surfaces. All silanized samples exhibited low N values, indicating smoother surfaces than the corresponding untreated samples.

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NOMENCLATURE

a = real parameter ($0 < a < 1$)
b = shape parameter of the water inclusions
De = Maxwell-Wagner relaxation strength
$e(w) = e'(w) - ie''(w) =$ total dielectric constant
$e_{LFP}(w) = e_{LFP}'(w) - i\,e_{LFP}''(w) =$ contribution of low-frequency transport to dielectric constant
$e_{MW}(w) = e_{MW}'(w) - i\,e_{MW}''(w) =$ contribution of Maxwell-Wagner polarisation to dielectric constant
$e_{HFP}(w) = e_{HFP}'(w) - i\,e_{HFP}''(w) =$ contribution of high-frequency transport to dielectric constant
e_0 = permittivity of the empty space (= 8.854×10^{-12} Farad/m)
e_{∞} = unrelaxed dielectric constant
e_d = dielectric constant
e_i = dielectric constant of matrix + oil
e_w = dielectric constant of water
f = rock porosity
$w = 2\pi f$ = angular frequency (Hz)
$s(w) = s'(w) + is''(w) =$ total conductivity (S/m)
s_c = conductivity (S/m)
s_{dc} = sample dc conductivity (= average of the low-frequency values of $we_0e''(w)$)
s_w = dc conductivity of water
t = Maxwell-Wagner relaxation time (s)
A = high-frequency transport strength (F·s^{-N}/m)
C_0 = capacitance of the empty cell (Farad)
D = low-frequency transport strength (F·s^{-Q}/m)
$\mathbf{D}$ = dielectric displacement (bound charges)
$\mathbf{D_t}$ = total dielectric displacement
$\mathbf{E}$ = electric field
f_c = critical frequency for electrode polarisation (Hz)
g = inclusion orientation factor
i = imaginary unit
$\mathbf{J}$ = current density (free charges)
$\mathbf{J_t}$ = total current density
m = cementation exponent
$n_1 = 1 - Q$
$n_2 = 1 - N$
N = high-frequency exponent
Q = low-frequency exponent ($0 < N < Q < 1$)
S_w = water saturation
$\tan(\delta) = e''/e' =$ loss tangent
Z_T = total impedance of the equivalent circuit (Ω)
Z_L = short-circuit impedance (Ω)

Z_0 = open-circuit impedance (Ω)

REFERENCES
1. von Hippell, A.: "Dielectrics and Waves", (1954) Wiley, N.Y.
2. Da Rocha, B.R.P and Habashy, T.: "Fractal geometry, porosity and complex resistivity: from rough pore interfaces to hand specimens", from Lovell & Harvey (eds), 1997, Developments in Petrophysics, Geological Society Special Publication No. 122, pp. 277-286.
3. Borner, F.D.: "Combined complex conductivity and dielectric measurements on core samples", SCA paper No. 9736 presented at the 1997 SCA International Symposium.
4. Lockner, A.A. and Byerlee, J.D.: "Complex Resistivity Measurements of Confined Rock", (1985) Journal of Geophysical Research, 90, 7837-7847.
5. Ruffet, C., Gueguen, Y. and Darot, M.: "Complex conductivity measurements and fractal nature of porosity", (1991) Geophysics, 56, 758-768.
6. Wong, P.: "Fractal surfaces in porous media", Physics and Chemistry of Porous Media, AIP, New York, (1987), 304-318.
7. Dissado, L.A. and Hill, R.M.: "Anomalous Low-frequency Dispersion", (1984), J.Chem.Soc.Faraday Trans., 80, 291-319.
8. Archie, G.E.: "The electrical resistivity log as an aid in determining some reservoir characteristics", (1946) Trans. AIME, Vol. 146.
9. Donaldson, E.C. and Siddaqui, T.K.: "Relationship between the Archie saturation exponent and wettability", (1987) paper SPE 16970.
10. Sillars, R.W.: "The properties of a dielectric containing semiconducting particles of various shapes" (1937), J. Inst. Elec. Eng., 80, 378-394.
11. Lysne P.C.: "A model for the hf electrical response of wet rocks", (1983), Geophysics, 48, 775-786.
12. Bona, N., Rossi, E., Venturini, C., Capaccioli, S., Lucchesi, M. and Rolla, P.A.: "Characterization of rock wettability through dielectric measurements", (1998) Revue de l'Institut Francais du Pétrole, 53, 771-783.
13. Wong, P., Howard, J. and Lin, J.S.: "Surface roughening and the fractal nature of rocks", (1986), Physical Review Letters, 57, 637-640.
14. Thevanayagam, S.: "Dielectric dispersion of porous media as a fractal phenomenon", (1997) J. Appl. Phys., 82, (5), 2358-2547.
15. Takach, N.E., Bennett, L.B. and Douglas, C.B.: "Generation of oil-wet model sandstone surfaces", (1989) paper SPE 18465 presented at the 1989 International Symposium on Oilfield Chemistry.
16. Casalini, R., Livi, A. and Rolla, P.A.: "The transfer function in T.D.R. Dielectric measurements ", (1994) Jpn. J. Appl. Phys., 33, L1271-L1273.
17. Bona, N., Rossi, E. and Capaccioli, S.: "Electrical measurements in the 100 Hz-10 GHz frequency range for efficient rock wettability evaluation", (1999) paper SPE 50720 presented at the 1999 International Symposium on Oilfield Chemistry.
18. Knight, R. and Nur, A.: "The dielectric constant of sandstones,60 kHz to 4 MHz", (1987) Geophysics, 52, 5, 644-654.
19. Glover, P.W.J., Meredith, P.G., Sammonds, P.R. and Murrell, S.A.F.: "Ionic surface electrical conductivity in sandstone", (1994) Journal of Geophysical Research, 99, 21635-21650.