DETERMINATION OF POROSITY BY DIELECTRIC PERMITTIVITY MEASUREMENTS IN POROUS CERAMICS.

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Abstract

Porosity of reservoir rocks is of special interest for the oil industry. Sintered ceramics can simulate this rocks, and thereby, are a common tool to study physical properties of reservoir rocks. Resistivity and permittivity measurements have been used to detect fluids (water or oil) in porous rocks, however the porosity still hasn’t been determined by electrical means. The effects of porosity on conductivity and on complex dielectric permittivity of porous ceramics have been reported. The permittivity of a system composed of several components (labeled “mixture”) can be estimated from the permittivities and concentrations of each one of the components. Using as precursor materials silica, kaolin, shale and feldspar, ceramics to simulate reservoir rocks were sintered: dense ones with porosities less than 5% and light ones, with 20-30% of porosity. These ceramics were characterized by XRD, SEM and porosity measurements. Then, conductivity and capacitance measurements were performed in order to determine the ceramic dielectric properties. The measurements were made from 10 Hz to 1 MHz at room temperature. The porosity could not be estimated from conventional “mixture laws” but, using a fractal description of the medium, it was possible to calculate the porosity of the system using a fractal description of the medium. The method was compared to Archimedes method measurements.

Key words: mixture laws, dielectric permittivity, fractal dimension, ceramic, reservoir rock.

1. Introduction

The oil industry has a special interest in studying the porosity of reservoir rocks. The sintering of ceramics to simulate these rocks is a common methodology employed to study their physical properties. Previous authors have applied resistivity and dielectric permittivity measurements to detect fluids in porous rocks [1, 2, 3], however the porosity determined by other methods [1] still hasn’t been calculated by electrical methods [4].

The effect of porosity on the conductivity permittivity of porous ceramics is a subject of current interest [5 to 11]. With a relevant mathematical model...
for a mixture, it is possible to estimate the physical properties of the mixture knowing the physical properties and concentrations of each one of the components. Usually, this property (i.e., permittivity) is estimated from the “mixture laws” [12 to 16], knowing the permittivities and concentrations of the components. However, these formulas cannot always be extrapolated as they were obtained empirically, based on a simple description of the geometry of the porous system (spheres, circles, needles, etc.) and on their distribution in the volume (series or parallel layers).

In the present work we evaluate the porosity from dielectric permittivity (real part) measurements, in a two component system (matrix + pores). Porous ceramics were used to perform the conductivity and capacitance measurements in the frequency range from 10 Hz to 1 MHz at room temperature and allowed the study of some of the “mixture laws” commonly found in the literature in order to calculate the porosity, knowing the dielectric permittivities of the components and determining experimentally the permittivity of the mixtures.

Some authors using computerized analysis of sedimentary rocks micrographs taken with scanning electron microscope (SEM) have shown that the porous medium [17 to 20] can be described using fractal geometry. Based on these results, a “mixture law” is proposed considering the fractal geometry of the system. This is achieved taking into account that the dielectric relaxation process develops over a fractal structure, i.e., performing a fractal description of the ceramic structure (including the pores). The fractal dimension is then linked to the dielectric relaxation process [21], and the porosity can be calculated from the fractal dimension [22,23].

In order to establish comparisons, the porosity of the system is calculated by Archimedes method.

NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>Df</td>
<td>Fractal dimension</td>
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<tr>
<td>D_E</td>
<td>Euclidean or topological dimension</td>
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<tr>
<td>D_W</td>
<td>Fractal dimension of random movement</td>
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<td>(\phi)</td>
<td>Porosity</td>
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<tr>
<td>h</td>
<td>Lower limit of similarity</td>
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<td>H</td>
<td>Upper limit of similarity</td>
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<td>E</td>
<td>Applied electric field</td>
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<td>P</td>
<td>Polarization of a material</td>
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<tr>
<td>(\sigma_f)</td>
<td>Conductivity due to free charges</td>
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<td>(\sigma_d)</td>
<td>Conductivity due to bound charges</td>
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<tr>
<td>(\tau)</td>
<td>Relaxation time</td>
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<td>(\varepsilon_0)</td>
<td>Free space dielectric permittivity</td>
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<td>(\varepsilon)</td>
<td>Dielectric Permittivity (complex) of a material ((\varepsilon = \varepsilon' - \varepsilon''))</td>
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<td>(\varepsilon')</td>
<td>Dielectric Permittivity (real part) of a material</td>
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<td>(\varepsilon'')</td>
<td>Dielectric Permittivity (imaginary part) of a material</td>
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<td>(\kappa)</td>
<td>Relative dielectric permittivity (complex) of a material ((\kappa = \kappa' - \varepsilon''))</td>
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<td>Relative dielectric permittivity (real part) of a material</td>
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<td>(\kappa'')</td>
<td>Relative dielectric permittivity (imaginary part) of a material</td>
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<td>(\kappa_{air})</td>
<td>Relative dielectric permittivity (real part) of air</td>
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<tr>
<td>(\kappa_{cer})</td>
<td>Relative dielectric permittivity (real part) of the ceramic</td>
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<td>(\kappa_{rel})</td>
<td>Relative dielectric permittivity (real part) of the ceramic, calculated from the mixture law formulas</td>
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<tr>
<td>(\Psi(t))</td>
<td>KWW function</td>
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<tr>
<td>(\omega)</td>
<td>Electric field frequency</td>
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<td>(\omega_c)</td>
<td>Crossover frequency or correlation length</td>
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<tr>
<td>(M(\omega))</td>
<td>Diffusion coefficient in frequency domain</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
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<td>XRD</td>
<td>X ray diffraction</td>
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2. Fractal Geometry and Porosity

A fractal is a mathematical object with a fractional or fractal dimension \(D_f\) [24]. \(D_f\) supplies a way to measure the irregularity of systems or processes. Normally lines have Euclidean dimension \(D_f=1\), surfaces have \(D_f=2\) and solids, \(D_f=3\). However, a rough curved surface is an object with dimension between 2 and 3. The dimension of a fractal object is any real number between 1 and 3 and characterizes the way in which the measured length grows, while the scale diminishes. The fractal dimension is defined as:

\[
D_f = \frac{\log(L_2/L_1)}{\log(s_1/s_2)} = \frac{\ln(L_2/L_1)}{\ln(s_1/s_2)}
\]

where:

- \(L_1\) and \(L_2\) are two measured lengths of the same curve
- \(s_1\), \(s_2\) are the sizes of the yardsticks used in the measurements.

As an example, if the longitudinal of a coast line is measured, due to the scale invariance this longitudinal grows as the yardstick diminishes, in agreement to equation (1). This equation is also called a power law relationship. Many other phenomena are scale invariant such as the frequency-size distributions of rock fragments [25], earthquakes [26,27], topographical characterization of rough surfaces [28,29], fractured surfaces of materials [30], pores and poral space of sedimentary rocks [17, 18, 20, 22], the Brownian movement of particles [24] and the conductivity-dielectric permittivity of disordered materials [21, 31].

It is important to emphasize that fractals are an idealization. No curve or surface in the real world is a fractal. A fractal is a mathematical object. Real objects are produced by processes that act over a finite range of scales. Therefore estimates of \(D_f\) can vary with scale.
The variation may serve to characterize the relative importance of different processes at different scales.

Real porous materials show fractal structures over some scales. The interface solid-pore may also be a fractal. Assuming that the porous space volume can be determined by the fractal structure, it is possible to find a relationship between porosity and fractal dimension [32]. Therefore for a volume element with macroscopic linear size $H$, the porous space volume $V_p$ is given in units of characteristic pore size $h$ as:

$$V_p = G \left( \frac{H}{h} \right)^{D_f}$$

where $D_f$ is the fractal dimension, $H$ and $h$ agree with the upper and lower limits of similarity respectively. The constant $G$ is a geometrical factor. The volume of the whole sample scales can be expressed in $h$ units as:

$$V = G \left( \frac{H}{h} \right)^{D_E}$$

where $D_E = 3$ is the Euclidean dimension. Therefore, porosity volumetric fraction $\phi = V_p/V$ can be written [32] as:

$$\phi = \left( \frac{h}{H} \right)^{3-D_f}$$

where $h$ and $H$ are the lower and upper limits of similarity and $D_f$ is the fractal dimension of the object.

The similarity interval of the porous medium must be known in order to apply this model, and the measurement technique must coincide with this interval. Moreover, the fractal dimension must be constant during this interval. In this case the parameter $\phi$ in equation (4) is the macroscopic porosity of the material. Equation (4) has been used to obtain the porosity in sedimentary rocks from TEM measurements [20]. Using the technique for the determination of length with different yardsticks [17] or with the counting box method [18], the fractal dimension of the rocks was assessed.

Hereafter, the volumetric fraction of porosity $\phi$ is calculated from equation (4) and dielectric permittivity measurements, when demonstrated the relationship between the fractal dimension of the ceramic and dielectric permittivity measurements. We assume that the porous medium of a ceramic material can be described as a self-affine fractal [33] due to the fact that in different directions the irregularities can scale in different ways, i.e., we can take into account the irregularities present in the structure and the irregularities present at the solid-pore interface.

3. Polarization and Dielectric Permittivity

The therm dielectric is used for any system capable of polarizing itself under the effect of an electric field [34]. When an electric field is applied to a material, in addition to a current of free charges, there is a local redistribution of bound charges to new equilibrium positions: this phenomenon is called polarization. When a low-frequency electric field is applied, bound charges can keep up with the changing field and be in equilibrium with the instantaneous value of the field. But if the field oscillates too rapidly, some charge-redistribution processes will not keep up with the field and fully contribute to the polarization. The relationship between applied electric field (E) and polarization (P) is given by:

$$P = (\varepsilon - \varepsilon_o)E$$

where $\varepsilon_o$ is the dielectric permittivity of free space ($\varepsilon_o = 8.85 \times 10^{-12}$ F/m) and $\varepsilon$ is the dielectric permittivity of the material. In ceramic materials, the following polarization processes can take place [35]:

- electronic polarization
- ionic polarization
- dipolar orientation polarization
- Maxwell-Wagner-Sillars (MWS) polarization

The last one occurs in heterogeneous materials where the polarization is the consequence of solid interface effects which strongly depend on microstructure and constituent materials. They are usually important at frequencies of 100 Hz and lower. Possible polarization processes for ceramic samples used in this study, by no presenting permanent dipoles, are the ionic, electronic and MWS ones. However, due to the frequency and temperature range used, the relevant polarization phenomena observed is MWS.

Usually, $\varepsilon$ can be a tensor or a complex quantity, where the imaginary part represents energy dissipation during charge redistribution. The capacitance resulting from the application of a sinusoidal voltage $V$, with angular frequency $\omega$, to a capacitor, made up of two flat electrodes with parallel faces of area $S$ and separation $d$ in which there is a dielectric material, is a complex quantity, i.e., $C = C' + iC''$. By measuring $C'$, the real part of the dielectric permittivity can be calculated with:

$$C' = \frac{\kappa'\varepsilon_o(\omega)}{\kappa' \varepsilon_o + \kappa'' \varepsilon_o}$$

where $\kappa' = \varepsilon/\varepsilon_o$ is the relative dielectric permittivity.
4. Dielectric Permittivity of a Mixture

Understanding the behavior of polycrystalline and polyphasic ceramic materials [37] means analysing the dielectric properties considering the dielectric properties of the mixture and the effects produced by porosity and existing phases, such as MWS polarization because of components with different dielectric behaviors.

A dielectric mixture law aims at expressing the dielectric permittivity of a heterogeneous mixture in terms of permittivity and volumetric fraction of the components. For easier notation, we considered only the real parts of the permittivities, so that \( \kappa_m \) is the relative dielectric permittivity of the mixture, \( \kappa_a \) and \( \kappa_{cer} \) are the relative dielectric permittivities of air and ceramic respectively.

Mixtures in ideal dielectrics [37] can be regarded as simple models, considering that the different constituents are in layers to simulate a system in series or in parallel to the applied electric field. The following empirical relation is established:

\[
\kappa_m^n = \sum_i v_i \kappa_i^n
\]  
(7)

where \( n \) is a constant related to the system geometry, and \( v_i \) is the volumetric fraction of phase \( i \). When \( n = -1 \) (serial model), for a two component system (matrix + pores) the corresponding mixture law is:

\[
\frac{1}{\kappa_m} = \phi \frac{1}{\kappa_a} + (1 - \phi) \frac{1}{\kappa_{cer}}
\]  
(8)

where \( \phi \) is the air volumetric fraction or porosity. On the contrary, when \( n = 1 \) (parallel model), it is changed to:

\[
\kappa_m = \phi \kappa_a + (1 - \phi) \kappa_{cer}
\]  
(9)

and when \( n \to \infty \), \( \kappa_a \to 1 + \ln \kappa \) so that equation (7) for a two-component system can be written as:

\[
\ln \kappa_m = \phi \ln \kappa_a + (1 - \phi) \ln \kappa_{cer}
\]  
(10)

Assuming the possibility of considering an averaged electric field in a volume which is big compared to the distances at which the heterogeneous character of the medium can be appreciated, the mixture is an homogeneous and isotropic medium and can be characterized by effective permittivity values \( \epsilon_m \). In this context, Landau [38] derived a semi empirical mixture equation:

\[
\kappa_m = \phi \kappa_a + (1 - \phi) \kappa_{cer} + 2\phi(1 - \phi) \frac{\kappa_a \kappa_{cer} \cos(\delta/2)}{\cos \delta}
\]  
(12)

where \( \delta \) is the loss angle. In deriving this equation it was not taken into account the poral geometry, nor how pores are distributed inside the matrix.

The most commonly used mixing laws are those derived under the effective medium approximation (EMA) [14]. This theory is based on the polarization induced by an externally applied, uniform, electric field on isolated spherical inclusions located within a host material and the depolarization field due to the inclusions can be calculated [38]: equation (13) is obtained [14], where a volumetric fraction \( \phi (\phi < 1) \) of material with dielectric constant \( \kappa_a \) is immersed in a material of dielectric constant \( \kappa_{cer} \):

\[
\frac{\kappa_m - \kappa_a}{\kappa_m + 2\kappa_a} = (1 - \phi) \frac{\kappa_{cer} - \kappa_a}{\kappa_{cer} + 2\kappa_a}
\]  
(13)

This equation is known as the Clausius-Mossotti (CM) or Maxwell-Garnet [13] equation.

Other equation is the symmetrical effective medium (SEM) equation [13]. The symmetric term means that if the components are interchanged, interchanging also their respective volumetric fractions, the resulting mixture will have the same effective dielectric constant when compared to the original mixture [39,40]. Equation (14) is obtained:

\[
\phi \frac{\kappa_a - \kappa_m}{\kappa_a + 2\kappa_m} + (1 - \phi) \frac{\kappa_{cer} - \kappa_m}{\kappa_{cer} + 2\kappa_m} = 0
\]  
(14)

When non spherical inclusions are considered for deriving the "mixture law" equations, the depolarization factors can also be calculated [38] and the following equations are obtained:

**Needles as inclusions**

\[
\kappa_m = \frac{\kappa_a^2(\kappa_a + \kappa_{cer}) + 2\phi \kappa_{cer}(\kappa_a - \kappa_{cer})(5\kappa_a + 5\kappa_{cer})}{[9\kappa_{cer}(\kappa_a + \kappa_{cer}) - 6(\kappa_a - \kappa_{cer})(5\kappa_a + 5\kappa_{cer})]}
\]  
(15)

**Disks as inclusions**

\[
\kappa_m = \frac{\kappa_a^2\kappa_a + 2\phi \kappa_{cer}(\kappa_a - \kappa_{cer})(2\kappa_a + \kappa_{cer})}{[9\kappa_{cer}\kappa_a - 6(\kappa_a - \kappa_{cer})(2\kappa_a + \kappa_{cer})]}
\]  
(16)
Many other formulas have been previously obtained [12], but they are all empirical or semi empirical and derived for particular situations. In this work, we use equations (8) to (16) in order to evaluate the porosity of ceramic samples, knowing the permittivity of the components and measuring experimentally the permittivity of the mixture. However, these “mixture laws” do not provide satisfactory results. Hereafter, a general “mixture law” was developed, based on a mathematical model which describes better the fractal geometry of the porosity.


The frequency dependence of dielectric permittivity, for semiconductor and insulator materials, has often been described using empirical dielectric relaxation models such as the Debye model [41], the Cole-Cole model [35], and the Davidson-Cole [42] model. However, it has been observed that these materials show a “universal” behavior identified as a power-law behavior [43], i.e., the relaxation phenomena is not described with an exponential law, but with a potential one, representing a non-exponential decay function or an “anomalous” decay, which is slower than the exponential. An empirical function which has been studied [44,45,46] to describe this decay is the KWW function or also called “stretched exponential” function. This function is given by

\[ \psi(t) = \exp\left(-\frac{t}{\tau}\right)^\alpha \]  

(17)

where:

\[ <\tau> = \frac{\Gamma(1+\alpha)}{\alpha} \]  

(18)

\(<\tau>\) is the average relaxation time and \(\Gamma\) the gamma function [47]. Slow relaxation is represented by \(\alpha < 1\). For physical systems \(0 < |\alpha| \leq 1\). When \(\alpha = 1\), the relaxation decay is exponential and the behavior of the system is reduced to a Debye behavior.

Phenomenologically, equation (17) describes the retarded decay of the polarization of a dielectric after the removal of the electric field. Equation (17) is related to the following general equation by a Fourier transformation:

\[ \varepsilon'(\omega) = A\omega^{-\beta} \]  

(19)

where \(A\) is a constant and \(\beta\) apparently depends on the inclusion geometry, as it will be seen further. Both equations (17) and (19) represent a common characteristic of the dielectric properties in ceramic, insulator and semiconductor materials [21]. In disordered materials (heterogeneous) [31], this behavior is also observed. The existence of this relationship denominated “power-law” suggests similarity property as a characteristic of the physical process. A relationship with the dielectric relaxation process has been investigated as an explanation to the observed permittivity-frequency behavior [48,49,50].

The application of fractal geometry is performed through the Brownian movement of the charge carriers in the material, which is a process that has its own fractal dimension [31,51,52], also is realized through describing the medium as a fractal structure [9,43,20]. If the Brownian movement of charge carriers takes place over the fractal structure, the longitude \(L(t)\) covered by the movement of the charge carriers scales with time through the dimension \(D_w\) [31] is:

\[ L(t) = t^{1/D_w} = \omega^{-1/D_w} \]  

(20)

where \(D_w\) is the fractal dimension of the movement of charge carriers and \(1 < D_w < 2\). Beside, the conductivity of these charge carriers is related to the Brownian movement through the Einstein diffusion coefficient \(M(\omega)\) and can be written as [31]:

\[ M(\omega) \approx \frac{L^2(t)}{t} \approx \omega L^2(\omega) \approx \omega^{2-2/D_w} \]  

(21)

by using equation (20). The AC conductivity taking place in the fractal structure obeys then the following law [31]:

\[ \sigma(\omega) \approx (L(\omega))^{D_f-2} M(\omega) \]  

(22)

where the fractal dimension of the structure \(D_f\) satisfies \(2 < D_f < 3\). Then, substituting equation (21) in equation (22) we obtain:

\[ \sigma(\omega) \approx \omega^{1-D_f/D_w} \]  

(23)

According to Niklasson [31], if the charge transport takes place as a diffusive process in the fractal interface (which can be considered as a bidimensional discontinuity), we can take \(D_w\) tending towards 2, so it can take its limiting value, and the previous equation can be written as

\[ \sigma(\omega) \approx \omega^n \]  

(24)

where \(n=(D_f-1)/2\). In materials which exhibit a negligible DC conductivity at low frequencies and where the previous behavior is recognized - equation (24) -, the following empirical relations can be established from describing the behavior of dielectric permittivity [21]:

\[ \varepsilon'(\omega) = \varepsilon'(0), \varepsilon'(\omega) = \sigma_f/\omega \varepsilon_0 \quad \omega < \omega_c \]  

\[ \varepsilon'(\omega) = \varepsilon'(0) \omega^{n-1} \quad \omega > \omega_c \]  

(25)

where \(\sigma_f\) is the conductivity due to free charges and \(\omega_c\) is a “crossover frequency” where the “power-law”
behavior begins to be observed, and n is related to the fractal dimension through \( n = (D_r - 1)/2 \) and complies with \( 0 < n \leq 1 \). In addition, \( \omega_c \) identifies a region of fractal behavior which crosses over low frequencies to a non fractal behavior, i.e., the fractal structure persists until some “correlation longitude”, in which the structure is more regular. \( \omega_c \) then corresponds to the correlation longitude.

In experimental situations it is important to distinguish over which range of frequency prevails the fractal or “power-law” behavior. Using this fractal description of the dielectric relaxation process, it is possible to relate the fractal dimension of the structure to the porosity according to equation (4) where \( \Lambda = h/H \) defines the similarity range in the system, since h and H are the lower and upper limits of the similarity. Therefore a “mixture formula” based on the fractal description of the relaxation phenomena can be defined.

6. Sample Preparation and Dielectric Properties Measurements

Two groups of samples were prepared with the same constituents (20% Silica, 30% Kaolin, 25% Shale, 25% Feldspar – weight%) in order to simulate both porosity and chemical composition of reservoir rocks. Samples of the first group (A) are 25 mm diameter, 4mm height cylinders and were pressed in order to get a low connected porosity, varying pressure of forming and powders particle sizes distribution. Subgroup A1 samples were formed using particle sizes less than 38 mm and pressed under a 15, 20 or 25 ton load, while subgroup A2 samples were formed with particle sizes less than 48 mm under a 10 ton load. All these samples were sintered at 1250 °C for 1 1/2 hours.

Samples of the second group (B) according to a previous work [53], were formed by slip-casting to obtain a connected porous system and were sintered at 1200°C for 2 hours. Then, they were cut to obtain cylinders of 25 mm diameter and 4mm height. Both samples (from A and B group) presented the same phases. Beside, the particle size for A group samples was selected to get a total porosity less than 5% in volume due to the fact that “mixture law” formulas require the \( \kappa_{\text{cer}} \) value, i.e., the dielectric permittivity of the matrix which calculation implies \( \phi = 0% \). Afterwards porosity calculations were performed over all samples using Archimedes method [54] and picnometry.

Both group of samples were characterized by XRD to determine the present phases and to verify that the only difference between all samples was the porosity, so that comparisons of the dielectric properties could be performed.

The samples microstructure was studied with SEM photographies and determination of pore sizes was performed also from the images.

All samples were exposed to ultrasonic cleaning for 15 min in a water-acetone solution and then allowed to dry in a furnace at 100 °C for 24 hours. Immediately the conductivities and the complex permittivities measurements from 10Hz to 1MHz at room temperature were determined using impedance spectrometry with parallel electrodes technique. In this experiment, an Impedance Analyzer equipment was used (model 4192A, Hewlett-Packard). The conductance \( \sigma[S] \) and the capacitance \( C[F] \) were measured as a function of frequency. By using equation (6), the dielectric permittivity could be determined. Permittivity measurement of samples A1 allowed the obtaining of the \( \kappa_{\text{cer}} \) value by extrapolation. By measuring the dielectric permittivities of samples A2 and B the dielectric permittivity value \( \kappa_m \), can be determined.

7. Porosity Determination By Dielectric Properties Measurements

Determination of porosity using the “mixture law” formulas involves the values \( \kappa_{\text{cer}}, \kappa_m \) and \( \kappa_{\text{cer}} \) which is the value of \( \kappa_m \) for \( \phi = 0% \). Then, it is possible to estimate the total porosity \( \phi \) of the samples using equations (8) to (16). The permittivity-frequency response \( \varepsilon(\omega) \) of the samples can be fitted (determining \( \beta \)) to the equation (26):

\[
\varepsilon(\omega) = \omega^\beta
\]

where \( \beta = n - 1 \) is a parameter related to the fractal dimension through equation (25). Finally the fractal dimension can be associated to the total porosity through equation (4). In advance, the parameter \( \Lambda = h/H \) has to be determined, where \( h \) and \( H \) coincide with the lower and upper limits of similarity, i.e., they correspond to the frequency limits given by “the correlation length” \( \omega_c \) and \( \omega_0 \), in which the system experiences the fractal behavior. If the experiment were to determine the porosity from photographies, \( h \) represents the pore size and \( H \) is given by the sample size [20].

8. Experimental Results

In order to confirm the phases present in the samples, XRD analysis were performed to one sample of each group A1, A2 and B (figure 1). The phases found in all samples were quartz (SiO\textsubscript{2}) and mullite (Al\textsubscript{2}Si\textsubscript{2}O\textsubscript{5}). Consequently, it was possible to study the dielectric properties of the same materials, that so far is only dependent on the porosity.

The ceramics microstructure were analyzed by SEM (figures 2, 3 and 4).
In this case, pores are irregular in shape and apparently isolated (close porosity). Beside, a higher porosity than in sample A₁ (figure 2) can be evidenced, due to the fact that these samples had a particle size bigger and were pressed with a lower load (10 ton) than samples from group A₁.

Figure 2 exhibits the morphology of pores (dark zones); this belongs to a sample from group A₁. Notice that the pores are irregular and isolated (close porosity). Also it can be observed a uniform surface, due to an almost total sintering and to the apparition of a flowed vitreous phase. Figure 3 shows a sample from group A₂, where it can be observed the presence of dark zones, as pore evidence.

Fig. 1. XRD of ceramic samples a) A₁, sintered at 1250°C for 1.5 h b) A₂, sintered at 1250°C for 1.5 h C) B, sintered at 1200 °C for 2h. The same phases (mullite and quartz) were found in all samples.

Fig. 2. Photomicrography #1, ceramic sample A₁ sintered at 1250°C for 1.5 h. Augmented 350X. The darkest zones surrounded by clearer zones, are pores. Notice the irregular shape of pores. No open porosity was observed in these samples. This was corroborated by calculating the porosity by Archimedes method.

Fig. 3. Photomicrography #2, ceramic sample A₂ sintered at 1250°C for 1.5 h. Augmented 350X. The darkest zones surrounded by clearer zones, are pores. Also, notice the presence of a greater number of pores than in sample A₁, due to the lower load used to press these samples. However, it can be observed that almost all the porosity is closed. This was corroborated by calculating the porosity by Archimedes method. Also notice the irregular shape of pores.
Figure 4, corresponds to one sample of group B, where can also be seen dark zones, evidence of pores. In that case, irregular pores are interconnected. There are only a few closed pores. The great pore interconnectivity is due to the fact that these samples were all prepared by slip-casting.

Notice that at lower frequencies the conductivity in samples B is higher than in samples A. Samples B have a higher porosity.

The conductivity then grows from a constant value $\sigma_f$ (due to the free charge carriers) to a value at high frequencies given by $\sigma(\omega) = \sigma_f + \sigma_d(\omega)$, where $\sigma_d(\omega)$ is the conductivity due to bound charge carriers (displacement current). The differences may be explained by the difference of porosity. Subsequently, with the capacitance measurements, the real part of the dielectric permittivity $\varepsilon'\omega$ was calculated with equation (6). In figure 6, the behavior of the relative dielectric permittivity is shown as a function of frequency for 3 samples of group $A_1$ pressed at 15, 20 and 25 ton. The other samples of this group have a similar permittivity-frequency behavior.

Capacitance $C[F](\omega)$ and conductivity $\sigma[S](\omega)$ measurements were performed to determine the ceramic dielectric properties and to study its behavior as a function of porosity, from 10 Hz to 1 MHz at room temperature for each one of the samples from groups $A_1$, $A_2$ and B. Conductivity is similar for samples belonging to a same group, i.e., they have the same behavior. Figure 5 shows the relationship of conductance with frequency for a sample of each group: the conductivity of the samples is almost cero at low frequencies, as expected for ceramic materials.

Also in figures 7 and 8 the behavior of the relative dielectric permittivity as a function of frequency for some samples belonging to groups $A_2$ and B is shown. The other samples belonging to these groups have a similar behavior. Measured $\kappa'(\omega)$ is common with other ceramic materials and disordered materials [21]: it is typical of a power law behavior. Apparently, behaviors of this nature are associated with processes which take place over fractal structures [31]. Also at frequencies between 10 Hz and 100 Hz, is observed the so-called anomalous dispersion due to the bound water in the system (Maxwell-Wagner-Sillars polarization) [5], which makes the relative dielectric permittivity values (real part) to be higher to those expected at these frequencies. In any case, the dielectric permittivity reaches the maximum value at low frequencies, for higher values of frequencies the relative dielectric permittivity tends to diminish, due to the raise in the conductivity with a higher contribution of the displacement current.
calculated mixture permittivity and \( \kappa_m \) is the mixture permittivity experimentally measured.

Table I. Permittivity-Porosity relationship for different \( A_1 \) samples, for different frequency values.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \phi_{(total)} )</th>
<th>( \kappa' ) ( 10^7 )Hz</th>
<th>( \kappa'' ) ( 10^7 )Hz</th>
<th>( \kappa' ) ( 10^8 )Hz</th>
<th>( \kappa'' ) ( 10^8 )Hz</th>
<th>( \kappa' ) ( 10^9 )Hz</th>
<th>( \kappa'' ) ( 10^9 )Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>1.3</td>
<td>5.76</td>
<td>4.61</td>
<td>4.42</td>
<td>4.31</td>
<td>4.26</td>
<td></td>
</tr>
<tr>
<td>( A_1I )</td>
<td>1.5</td>
<td>5.76</td>
<td>4.32</td>
<td>4.09</td>
<td>3.91</td>
<td>3.89</td>
<td></td>
</tr>
<tr>
<td>( A_1I )</td>
<td>1.8</td>
<td>5.76</td>
<td>4.61</td>
<td>4.33</td>
<td>4.19</td>
<td>4.11</td>
<td></td>
</tr>
<tr>
<td>( A_1IV )</td>
<td>1.2</td>
<td>5.76</td>
<td>4.75</td>
<td>4.42</td>
<td>4.26</td>
<td>4.19</td>
<td></td>
</tr>
</tbody>
</table>

Notice that at 100 Hz the permittivity values are the same for all samples. As the frequency grows, the permittivity-porosity dependence also grows.

Table II. \( \kappa_{cer} \) values at different frequencies

<table>
<thead>
<tr>
<th>( \omega (\text{Hz}) )</th>
<th>( \kappa_{cer} )</th>
<th>( \Delta \kappa_{cer} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^2 )</td>
<td>5.76</td>
<td>±0.16</td>
</tr>
<tr>
<td>( 10^3 )</td>
<td>4.56</td>
<td>±0.09</td>
</tr>
<tr>
<td>( 10^4 )</td>
<td>4.47</td>
<td>±0.09</td>
</tr>
<tr>
<td>( 10^5 )</td>
<td>4.38</td>
<td>±0.09</td>
</tr>
<tr>
<td>( 10^6 )</td>
<td>4.25</td>
<td>±0.09</td>
</tr>
</tbody>
</table>

For the determination of \( \kappa_{cal} \) the equations (8), (9), (10), (11), (12), (13), (14), (15) and (16) were used. In table III, these values are shown (for a sample \( A_2 \) with \( \phi = 24\% \)) with their respective errors for some frequency values. The errors were calculated by the partial derivate method [55]. From table III, it can be observed the difference in the values of the permittivities of the mixture determined experimentally and calculated. The difference is lower at frequencies of 1 MHz, due to a lower dielectric dissipation. Of all of this “mixture law” formulas, the ones that describe better the experimental permittivity-frequency behavior are the formulas corresponding to the model of spherical inclusions (MG), landau (lan), symmetric effective medium (SEM) and logarithmic (log). However, when the porosity is calculated (table IV) using these models for 1 MHz (due to that \( \kappa' \) shows a bigger variation with porosity at this frequency), the difference of porosity obtained is between 5\% and 33\%.

Table IIIa. Permittivity (mixture) values vs. frequency for \( \phi = 24\% \). It is shown the experimental values, and those predicted by theory for the models: series(s), parallel (p), logarithmic (l), Landau(lan) y the refractive complex index method (crim).

<table>
<thead>
<tr>
<th>( \omega (\text{Hz}) )</th>
<th>( \kappa_{exp} )</th>
<th>( \kappa'_{s} )</th>
<th>( \kappa''_{s} )</th>
<th>( \kappa'_{p} )</th>
<th>( \kappa''_{p} )</th>
<th>( \kappa'_{1} )</th>
<th>( \kappa''_{1} )</th>
<th>( \kappa'_{lan} )</th>
<th>( \kappa''_{lan} )</th>
<th>( \kappa'_{crim} )</th>
<th>( \kappa''_{crim} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^2 )</td>
<td>5.04</td>
<td>4.61</td>
<td>2.68</td>
<td>3.77</td>
<td>4.10000</td>
<td>4.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 10^3 )</td>
<td>3.68</td>
<td>3.76</td>
<td>2.47</td>
<td>3.200</td>
<td>3.42000</td>
<td>3.51</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 10^4 )</td>
<td>3.49</td>
<td>3.60</td>
<td>2.42</td>
<td>3.090</td>
<td>3.29000</td>
<td>3.38</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 10^5 )</td>
<td>3.38</td>
<td>3.51</td>
<td>2.39</td>
<td>3.030</td>
<td>3.21000</td>
<td>3.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 10^6 )</td>
<td>3.32</td>
<td>3.47</td>
<td>2.28</td>
<td>3.000</td>
<td>3.18000</td>
<td>3.27</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Notice that difference between experimental and calculated values is less at 1 MHz, possibly due to lower dielectric dissipation at this frequency.

Table IIIb. Permittivity (mixture) values vs. frequency for \( \phi = 24\% \). Experimental values are shown, and predicted ones for the models: spherical inclusions (cm), disk inclusions (d), needle inclusions (a), and the symmetric medium formula (sem).

<table>
<thead>
<tr>
<th>( \omega ) (Hz)</th>
<th>( \kappa_{cm} )</th>
<th>( \kappa_{cm} )</th>
<th>( \kappa_d )</th>
<th>( \kappa_a )</th>
<th>( \kappa_{sem} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^2 )</td>
<td>±0.07</td>
<td>±0.36</td>
<td>±0.22</td>
<td>±0.15</td>
<td>±0.13</td>
</tr>
<tr>
<td>( 10^3 )</td>
<td>5.04</td>
<td>3.59</td>
<td>3.19</td>
<td>4.20</td>
<td>4.20</td>
</tr>
<tr>
<td>( 10^4 )</td>
<td>3.68</td>
<td>3.12</td>
<td>2.91</td>
<td>3.47</td>
<td>3.47</td>
</tr>
<tr>
<td>( 10^5 )</td>
<td>3.49</td>
<td>3.02</td>
<td>2.84</td>
<td>3.33</td>
<td>3.33</td>
</tr>
<tr>
<td>( 10^6 )</td>
<td>3.38</td>
<td>2.97</td>
<td>2.80</td>
<td>3.26</td>
<td>3.26</td>
</tr>
<tr>
<td>( 10^7 )</td>
<td>3.32</td>
<td>2.95</td>
<td>2.79</td>
<td>3.23</td>
<td>3.23</td>
</tr>
</tbody>
</table>

Notice that the difference between experimentally determined and calculated values is less for \( \omega = 1 \) MHz, possibly due to dielectric dissipation is less at this frequency.

Table IV. Porosity values obtained the mixture formula that best describe the system, for \( \omega = 1 \) MHz.

<table>
<thead>
<tr>
<th>( \phi ) (Arch.)</th>
<th>( \phi ) (mg)</th>
<th>( \Delta \phi ) (mg)</th>
<th>( \phi ) (lan)</th>
<th>( \Delta \phi ) (lan)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.245</td>
<td>0.16</td>
<td>33.13</td>
<td>0.21</td>
<td>14.39</td>
</tr>
<tr>
<td>0.266</td>
<td>0.25</td>
<td>8.86</td>
<td>0.30</td>
<td>12.52</td>
</tr>
<tr>
<td>( \phi ) (Arch.)</td>
<td>( \phi ) (sem)</td>
<td>( \Delta \phi ) (sem)</td>
<td>( \phi ) (log)</td>
<td>( \Delta \phi ) (log)</td>
</tr>
<tr>
<td>0.245</td>
<td>0.22</td>
<td>9.04</td>
<td>0.17</td>
<td>29.24</td>
</tr>
<tr>
<td>0.266</td>
<td>0.32</td>
<td>17.07</td>
<td>0.26</td>
<td>5.13</td>
</tr>
</tbody>
</table>

Notice that difference in porosity between Archimedes and the dielectric permittivity method using the mixture formulas is between 5% - 33%.

The results in table III and IV, show that none of these “mixture law” formulas describes adequately the behavior \( \kappa' (\omega) \) and/or \( \kappa (\phi) \). This is due to:

These equations were formulated empirically for particular situations.

Were formulated for simple geometries, and also for isolated inclusions.

It is clear that from the permittivity-porosity relationship for a particular frequency, and from the permittivity-frequency relationship for a given porosity that an adequate "mixture law" formula must be a function of the frequency and the porosity simultaneously, i.e., \( \kappa (\phi, \omega) \)

In order to obtain, a “mixture law” formula which takes into account an irregular non isolated pore structure and the behavior of \( \kappa (\phi, \omega) \), a fractal model of dielectric permittivity was used. From the permittivity-frequency response \( \varepsilon (\omega) \), experimentally measured, a data fit to the equation \( \varepsilon (\omega) = \varepsilon_0 \phi \) was made, determining the parameter \( \beta \). Table V shows the \( \beta \) values and also the parameter \( n \), the fractal dimension \( D_f \), the parameter \( \Lambda \) and the porosity \( \phi \) (%) values, according with equation (4). In the porosity calculations using the fractal model, the \( h \) (lower limit of similarity) and \( H \) (upper limit of similarity) must be known.

In advance. In this work, the lower limit of similarity is taken as the crossover frequency \( \omega_c \) - equation (25) - and the upper limit at \( \omega = 1 \) MHz, where it is assumed that the fractal behavior of the system is in this frequency range. These limits were obtained from the graphics of relative dielectric permittivity as a function of frequency for each sample, and the following criteria was used: the similarity range chosen was that corresponding frequency range, where the power law behavior was observed, i.e., the frequency range where the data fit made to the experimental data had the best correlation with a potential function.

Table V. Exponent (\( \beta \)) values, fractal dimension (\( D_f \)) and porosity (\( \phi \)), determined by dielectric permittivity measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \beta )</th>
<th>( n )</th>
<th>( D_f ) (h/H)</th>
<th>( \phi ) (%)</th>
<th>( \phi ) (%)</th>
<th>( \Lambda )</th>
<th>Arch. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>-0.4681</td>
<td>0.5319</td>
<td>2.0638</td>
<td>0.01</td>
<td>1.34</td>
<td>1.3</td>
<td>3</td>
</tr>
<tr>
<td>AII</td>
<td>-0.4465</td>
<td>0.5535</td>
<td>2.1070</td>
<td>0.01</td>
<td>1.64</td>
<td>1.5</td>
<td>8</td>
</tr>
<tr>
<td>AIII</td>
<td>-0.4285</td>
<td>0.5715</td>
<td>2.1430</td>
<td>0.01</td>
<td>1.93</td>
<td>1.8</td>
<td>7</td>
</tr>
<tr>
<td>AIV</td>
<td>-0.4761</td>
<td>0.5239</td>
<td>2.0478</td>
<td>0.01</td>
<td>1.25</td>
<td>1.2</td>
<td>4</td>
</tr>
<tr>
<td>AV</td>
<td>-0.1448</td>
<td>0.8552</td>
<td>2.7104</td>
<td>0.01</td>
<td>26.35</td>
<td>26.1</td>
<td>1</td>
</tr>
<tr>
<td>AVII</td>
<td>-0.1432</td>
<td>0.8568</td>
<td>2.7136</td>
<td>0.01</td>
<td>26.75</td>
<td>25.3</td>
<td>5</td>
</tr>
<tr>
<td>AVIII</td>
<td>-0.1512</td>
<td>0.8488</td>
<td>2.6976</td>
<td>0.01</td>
<td>24.85</td>
<td>23.8</td>
<td>4</td>
</tr>
<tr>
<td>AVIII</td>
<td>-0.1337</td>
<td>0.8663</td>
<td>2.7327</td>
<td>0.01</td>
<td>20.29</td>
<td>27.6</td>
<td>6</td>
</tr>
<tr>
<td>BI</td>
<td>-0.3138</td>
<td>0.6862</td>
<td>2.3725</td>
<td>0.1</td>
<td>23.58</td>
<td>20.0</td>
<td>15</td>
</tr>
<tr>
<td>BII</td>
<td>-0.0994</td>
<td>0.9006</td>
<td>2.8012</td>
<td>0.001</td>
<td>25.33</td>
<td>24.5</td>
<td>3</td>
</tr>
<tr>
<td>BIIIII</td>
<td>-0.1021</td>
<td>0.8979</td>
<td>2.7957</td>
<td>0.001</td>
<td>24.39</td>
<td>24.3</td>
<td>0.37</td>
</tr>
<tr>
<td>BIV</td>
<td>-0.0999</td>
<td>0.9067</td>
<td>2.8135</td>
<td>0.001</td>
<td>27.57</td>
<td>25.8</td>
<td>6</td>
</tr>
</tbody>
</table>

The fractal dimension was calculated using \( D_f = 2n + 1 \), where \( \beta = n - 1 \). Notice that obtained values of \( D_f \) from dielectric permittivity measurements are greater than 2, i.e., they are bigger than the dimension of a surface y lower than a volume dimension (3). Beside, the difference in porosity between Archimedes method and fractal model is between 0.37%-15%.

9. Conclusions

Porosity could be considered as a feature more than a defect in porous rocks. The conventional mixture laws could not describe porosity as expected. Also, Archimedes method fails to measure small pores in rocks and ceramics. Dielectric permittivity measurements can be used to determine the total porosity of ceramic materials. This can be done effectively by describing the porous medium as a fractal structure instead of estimating the porosity with the common "mixture law" formulas. It was observed that electric conductance grows with a raise in porosity and also with a raise in the fractal dimension of the structure. Beside, the electric conductivity and dielectric...
permittivity follows a “power-law” relationship. The fractal method allows a higher precision and thus, the detection of smaller pores.

10. References

36. Ibidem [5].
54. The American Society for testing and materials, # ASTM-C373-72, 1982.