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Electrical Properties of Moist Limestone Samples In The Frequency Range 1Hz-10^7Hz From Abu Rawash Area

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Abstract: The dielectric constant and electrical resistivity of Abu Rawash limestone samples are measured at some different atmospheric relative humidity and room temperature ($\approx 22C^0$) in the frequency range (1Hz-10^7Hz). Little increase in the atmospheric humidity can vary resisitivities by 4 orders or more of magnitude. Variations in the dielectric constant of the same order can also be obtained. Frequency dependent impedance measurements indicate that the overall electrical response of a rock sample is controlled by one or more of three conduction mechanisms, which can be identified as, (i) conduction through adsorbed water layer on solid surfaces, (ii) conduction through mass transport or diffusion through pore spaces filled with water, and (iii) high frequency (radio frequency and higher) conduction. Cation exchange capacity (CEC) plays the essential role in defining electrical properties of the solid-solution interfaces. Mass transport or diffusion impedance is affected by measuring electrode properties, it may be also called diffusion controlled impedance. It takes place at frequencies lower than the chemical reaction. The high frequency conduction mechanism is controlled by the intrinsic properties of the sample constituents.

Key words: Moist limestone, electrical properties, Abu Rawash, Egypt

INTRODUCTION

The dielectric constant and resistivity of moist limestone samples show a great dependence on water content. Study of the effect of water content on the electrical properties of limestone is of great importance in many fields. Electrode effect may be of reasonable effect in the obtained data. A study is made on some limestone samples at different relative humidities to identify the effects of water content, as well as electrode effect. Reasonable electrode effects may be noticed partially at higher water content. A trial is done to minimize such effects or to subtract it. High values of dielectric constant and conductivity were obtained at relatively high water content. The data is represented in the impedance plane to identify the assumed mechanisms that take place within sample-water mixture. Three mechanisms are traced, Warburg (diffusion) impedance, chemical reaction impedance, and bulk material impedance. The first mechanism (Wrburg impedance) takes place at frequencies lower than 500Hz. The second mechanism (chemical reaction impedance) takes place at higher frequencies, but lower than radio frequencies(Husain, S.A., 1983; Macdonald, J.R., 1985), the third mechanism (bulk material impedance) that takes place at radio frequencies and higher, is beyond the scope of this work. The chemical reaction impedance takes place at frequencies lower than the radio frequencies and higher than 100 Hz and depends mainly on the sample nature and water content in pore spaces. It describes electrically the chemical reaction that takes place at water-grain interfaces. The Warburg or mass transport impedance, on the other hand takes place at frequencies lower than that in chemical reaction impedance. It represents diffusion or transport of products from grain interface to the bulk of solution filling pore spaces between grains.

In the present work A.C measurements of electrical impedance are made over a frequency range 1-10^6Hz. Measurements of this type, can be referred to as impedance spectroscopy, are used in a variety of fields because of the wealth of information that can be gained about the material under investigation including the number and arrangement of conduction mechanisms (i.e., series versus parallel conduction), microstructural properties (including distribution, geometry, and interconnectedness of conducting phases), and grain boundary properties (Macdonald, J.R., 1985; Knight, R., 1984). Impedance spectroscopy has also been used to determine whether a material undergoing chemical reaction, such as corrosion and ion exchange in clays and soils (Olhoeft, G.R., 1979).

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MATERIALS AND METHODS

Previous Work:

Studies regarding the electrical properties of partially saturated rocks have been carried out by a number of authors. Knight (Knight, R., 1991), and Knight and Nur (Knight, and A. Nur, 1987), investigated the electrical resistivity and dielectric response of partially saturated sandstone at room temperature. They found that the dielectric response of fully and partially saturated sandstone in the frequency range of 60 KHz to 4MHz is determined predominantly by the presence of 2 nm of water coating the surface of the pore spaces. The amount of surface water in a sandstone sample has been found to determine the magnitude of the frequency dependence and hence, in this frequency range the value of the dielectric constant. The surface area -to- volume ratio of the pore space determines the amount of surface water making this parameter (which describes the microgeometry of pore space) the essential material property governing the dielectric response of a sandstone (Knight, and A. Nur, 1987). Knight and Dvorkin (1992), suggested that a few mono-layers of water on mineral grain surfaces in sandstone marks the transition between adsorbed water and bulk water. The saturation at which this transition occur is important because many other physical properties, such as thermal conductivity, diffusivity, and permeability, change rapidly above or below this saturation. Robert and Lin (1997) measured the electrical properties of Tuff as a function of water saturation at 23 and 40 C^0. Complex impedance measurements indicate three 3 distinct regions of conductivity based on the number of impedance arcs that occur at a given saturation. For the 23 C^0 case there is an impedance arc related to material properties, between 0 and ≈ 15% saturation, between 15 and ≈35% saturation there are 2 impedance arcs, and about 35% saturation there is 1 impedance arc. In the lowest range of water content (between 0 and ≈15%) conduction is primarily through layers of adsorbed water on the internal surface. In the medium range of saturation (between 15 and ≈35%) two impedance arcs in series are obtained which Robert and Lin(1997) interpret to be isolated regions of bulk water that is bundler rings and mix. The decrease in the resistivity with increasing saturation is the smallest for higher saturation (above 35%). Their results and interpretation are in general agreement with the model of Knight and Dvorkin(1992).

Theoretical Consideration and Equivalent Circuit:

A rock sample impedance is a complex quantity, generally expressed as a real component (R) and imaginary component (1/wC). In rocks, impedance normally contains both resistive (real part) and capacitive (imaginary part) components. The impedance is given by

$$Z = R_s + \frac{1}{J\omega C_s} \quad (1).$$

The complex conductivity (σ*) of a rock sample is also represented as :

$$\sigma^* = \sigma' + J\sigma'' \quad (2)$$

Where

$$\sigma' = \omega\varepsilon'' \quad (3)$$

$$\sigma'' = \omega\varepsilon' \quad (4)$$

ω is the angular frequency, and ε' and ε" are the dielectric constant and the dielectric loss of the measured sample respectively. The complex relative dielectric constant can be written as

$$\varepsilon^* = \varepsilon' - J\varepsilon'' \quad (5)$$

The response of LCR – meter which is an auto-balancing bridge that measures R and C, where R is the parallel resistance and C is the is the parallel capacitance is given by:

$$Z = \frac{R_p}{(\omega C_p R_p)^2 + 1} + \frac{\omega C_p R_p^2}{(\omega C_p R_p)^2 + 1} = = \mathrm{Re}Z + \mathrm{Im}Z \quad (6)$$

The response of equation (6) and that of the rock when plotted in the impedance plane is represented by a semicircular arc with a centre on the real axis.

Robert and Lin (1997), stated that the R_0 value returned by the bridge is the value of the intersection of this arc with the real axis at the low frequency side and is also the width of the arc (fig.1 in Robert and lin[9] they added that it can be verified by noting fig.1 that in the impedance plane at least 2 impedance arcs (or portion of impedance arcs) separated in frequency are observed. The higher frequency portion corresponds to material properties. It can be studied in the frame of chemical reaction or ion exchange between water and surfaces of rock grains. The resistive (R_r) and capacitive $1/\omega C_r$ components of the reaction impedance Z_r are given by (Saadl, A. Khalil, and Marzouk M. Bekhit, 2003).

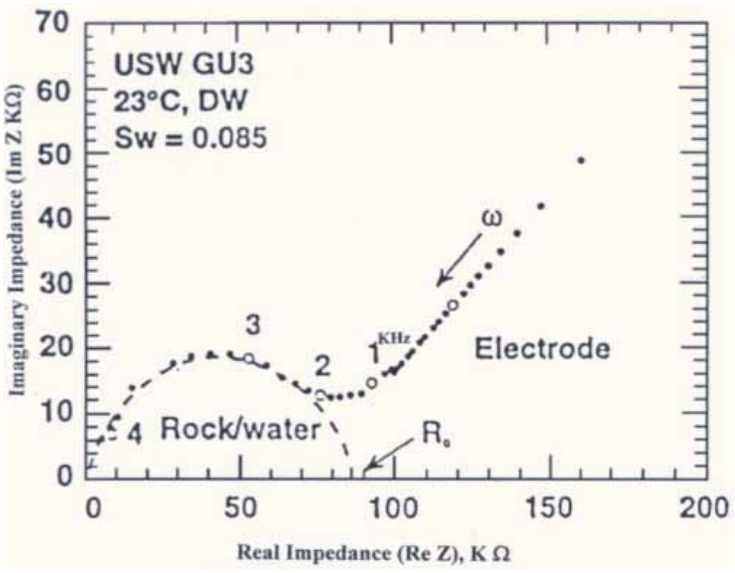

Fig. 1: Relationship between real and imaginary impedances (after Robert and Lin, 1997).

$$\mathrm{Re}\,Z_r = R_0 X \frac{1}{1+\left(\frac{\omega}{K}\right)^2} = R_r = \frac{1}{\omega C_r}$$

and (7)

$$\mathrm{Im}\,Z = \frac{1}{\omega C_r} = R_o X \left(\frac{\frac{\omega}{K}}{1+\left(\frac{\omega}{K}\right)} \right)$$

i.e, an equation of half circle

$$(\mathrm{Re}\,Z_r - \frac{R_0}{2})^2 + (\mathrm{Im}\,Z_r)^2 = (\frac{R_0}{2})^2$$

where R_0 is the intersection of the semicircular arc (Rock/water reaction) with the real axis (X-axis) at the low frequency side and K is the reaction rate (Saadl, A. Khalil, and Marzouk M. Bekhit, 2003). Such half circle corresponds to the rock-water monolayer conduction(Roberts, J.J., W. Lin, 1997).

It is important to consider the ion exchange between the surface monolayer and the rest of the pore water. The surface monolayer leads to a Debey behavior for the impedance (half circle). Pore water or bulk

electrolyte effect gives rise to a volume diffusion which in turn leads to an impedance containing the well known Warburg impedance behavior.

If we consider one dimensional diffusion of charge carriers (in the X-direction), the charge distribution takes the form (Vetter, 1967):

$$N = Ae^{-\gamma x} \quad (8)$$

Where N is the ionic density

$$\gamma = \frac{J\omega}{D} = (1+J)\frac{\omega}{2D} \quad (9)$$

D is the diffusion coefficient

$$J = \sqrt{-1} \quad (10)$$

This attenuated wave has a characteristic length L for the diffusion cloud given by:

$$L = \sqrt{\frac{2D}{\omega}} \quad (11)$$

As ω decreases the diffusion cloud extends a larger distance.

Usually diffusion processes are expressed electrically (charged particles) by the well known Warbug impedance (Vetter, K.J., 1967). The Warburg impedance is represented by a series circuit consisting of frequency dependent resistance $R_\omega(\omega)$ and a frequency dependent capacitance $C_\omega(\omega)$, and both the real part ($R_\omega(\omega)$) and the imaginary part ($1/\omega C_\omega(\omega)$) are equal.

$$R_{(\omega)}(\omega) = \frac{1}{\omega C_\omega(\omega)} \text{ , where} \quad (12)$$

$$R_\omega(\omega)\alpha\frac{1}{\sqrt{\omega}} \text{ , and} \quad (13)$$

$$C_\omega(\omega)\alpha\frac{1}{\sqrt{\omega}} \quad (14)$$

RESULTS AND DISCUSSIONS

Some limestone samples from Abu Rawash area west Cairo are studied in the present work in the frequency range 1 – 10^7 Hz. Measurements are carried out under some controlled atmospheric relative humidities from nearly dry sample (relative humidity ≈ 10%) up to 50%. The samples have thicknesses of about 3mm. and a diameter about 5cm. The measurements were carried out using Hioki bridge for measuring samples in the frequency range 100Hz up to 5MHz, and Q-meter bridge for measuring the samples up to 10 MHz.

Fig.(2) shows variation of capacitance (C_x) and conductance (G_x) for nearly dry sample (R.H. ≈10%) in the frequency range 1-10^7Hz. No dispersion is noticed in C_x in the frequency range of measurement. The sample conductance (G_x) on the other hand shows a frequency dependence which can be approximated as G_x α ω.

With increasing the relative humidity up to 35% the sample capacitance increases from about 100 in the dry state (fig.2) to about 10^3 at frequency 10 Hz. (Fig.3). Dispersion can be noticed here in the sample capacitance. The sample conductance (G_x) on the other hand shows a very little dispersion in the low frequency range (lower than 10^5 Hz), and relatively more dispersion at higher frequencies (higher than 10^5 Hz)

As the atmospheric relative humidity is increased to reach 50% the obtained data is shown in fig. (4). A great dispersion is noticed in C_x which can be described by C_x α 1/ω while G_x shows no dispersion.

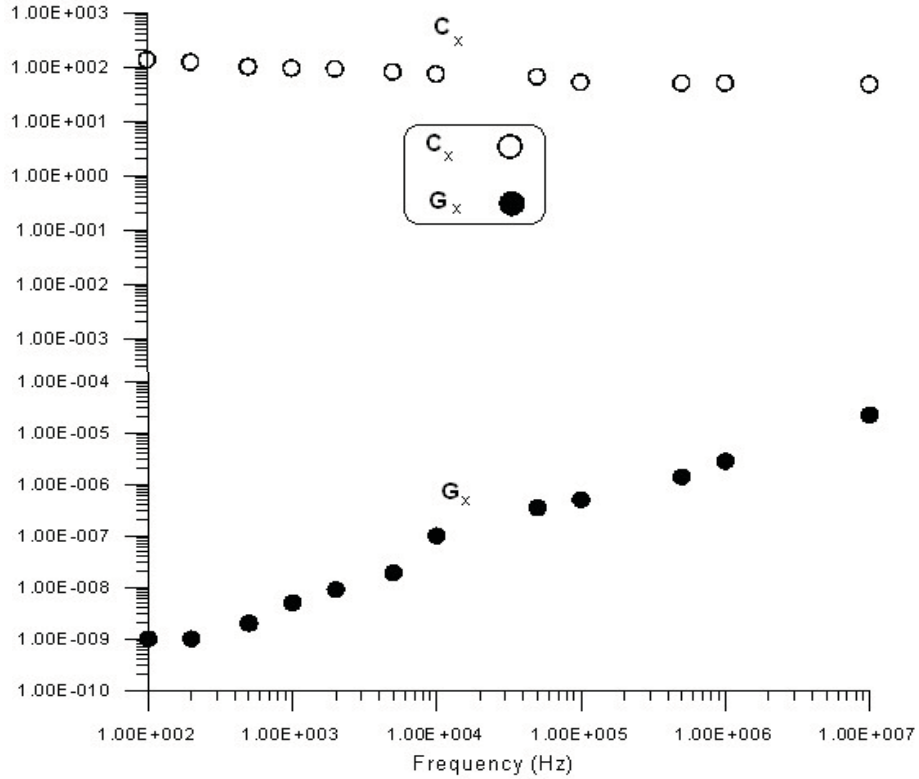

Fig. 2: Relationship between capacitance Cx, conductance Gx and frequency F for limestone sample (R.H. 10%)

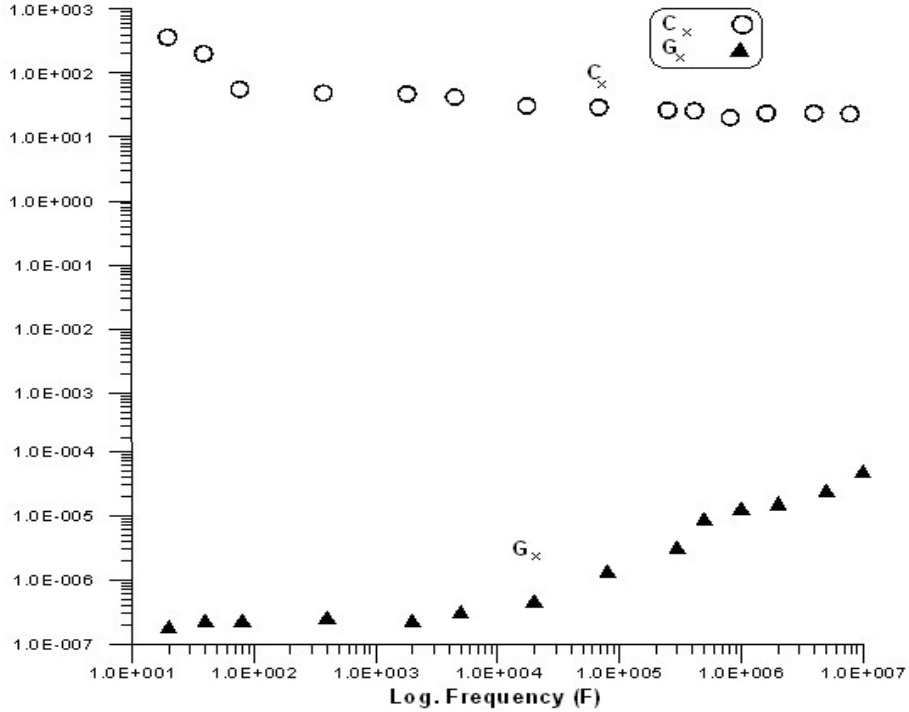

Fig. 3: Relationship between capacitance Cx, conductance Gx and frequency F for limestone sample (R.H. 35%)

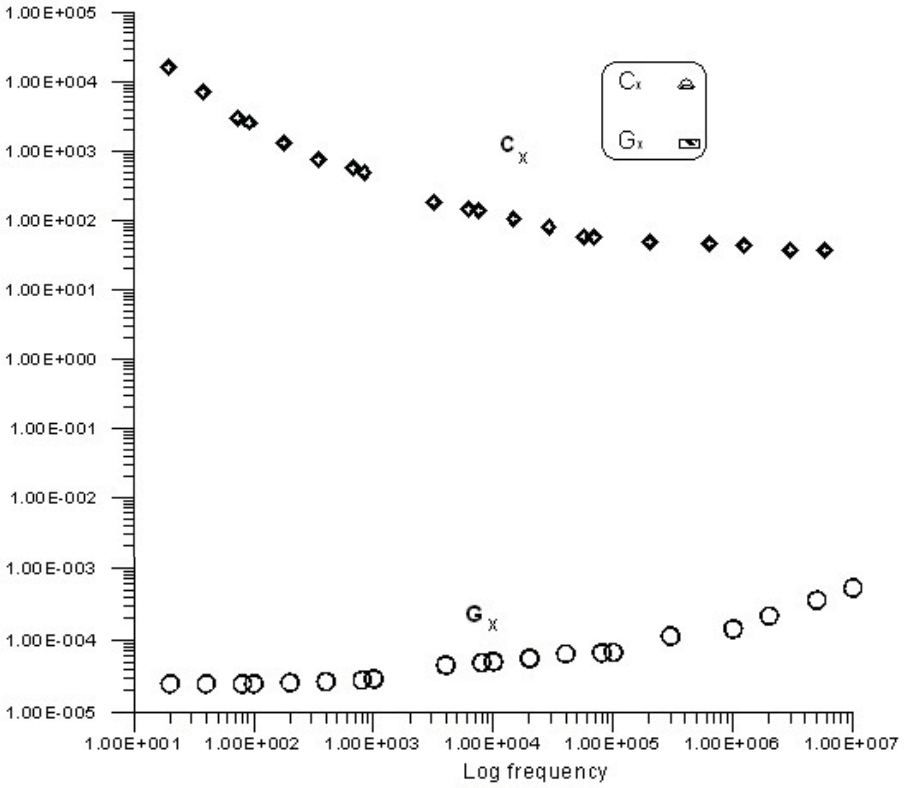

Fig. 4: Relationship between Cx, conductance Gx and frequency F for limestone sample (R.H. 50%)

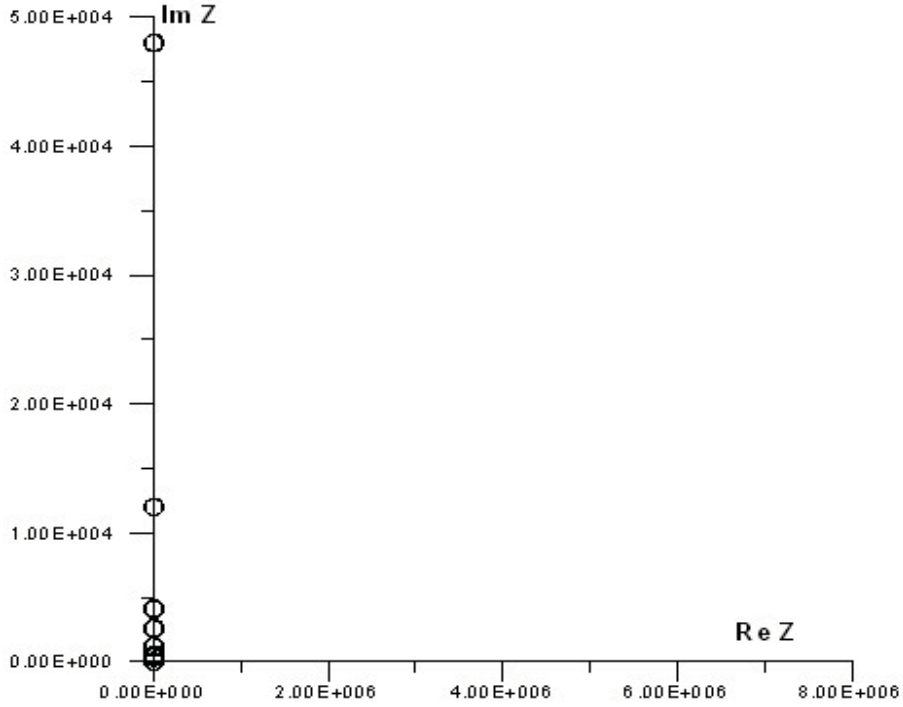

Fig. 5: Relationship between Re Z and lm Z for limestone sample at (R.H. 10%)

In the impedance plane, fig.5 the data obtained from the dry sample shows a straight line. Such straight line is ascribed to the presence of interfaces between limestone grains and air filling the pore spaces. Such interfaces lead to the formation of the electrical double layer (Mazouk, M. Bekhit, 1999) which in turn increases the capacitive part relative to the resistive part of the impedance and gives the behavior shown in fig.5.

An equivalent circuit is deduced (fig.6) to represent the behavior of such system. Here, Z_i represents the interfacial impedance. C_g, is the geometrical capacitance of the sample and, R_∞, is the high frequency resistance. The interfacial impedance Z_i, is given by

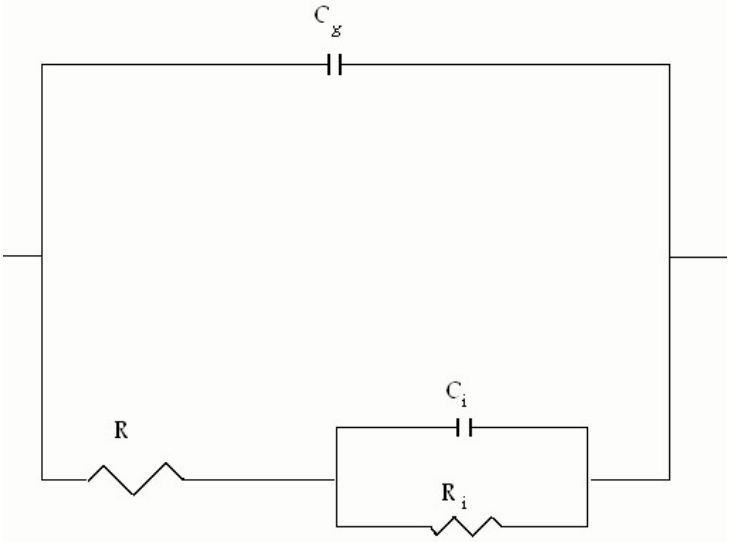

Fig. 6: Equivalent circuit assumed to represent grain surface-water Interaction (C_i and R_i)

$$Z_i = R_i + \frac{1}{J\omega C} \qquad (15)$$

R_i, is a frequency dependent interfacial resistance, and C_i is a frequency independent interfacial capacitance (fig.6).

As the atmospheric relative humidity of the measured sample is increased, the obtained data are shown in the impedance plane (fig.7). A half circle with a peak at a frequency of ≈ 500Hz is noticed which can be ascribed to water-grain interface (Schwaz, G.A., 2005).

An equivalent circuit is shown in fig. (8) to represent the behavior of the sample under such condition. At the interface between the sample grains and the surrounding water films, ion exchange or chemical reaction may take place, such chemical reaction have a rate (k) which defines the peak frequency (F_m) of the semicircle, i.e $F_m = 1/k$.

Data obtained at relative humidity up to 50% are shown in fig.9. The behavior of the sample can be divided into two regions, low frequency region (audio frequency range and lower) which is characterized by a straight line behavior. Such response is defined by Robert and Lin to be an electrode effect (Robberts, J.J. and W. Lin, 1997) It can be ascribed to diffusion of charge carriers from the sample grains through pore spaces which are filled partially or completely with water to the bulk of pore water or even the electrode and discharge there. When the straight line given makes an angle of 45^0 with the positive direction of the real axis, the impedance is called Warburg impedance.

The high frequency region, on the other hand was ascribed by Robert and Lin (1997) to rock-water monolayer conduction, which is generally a half circular shape, or an arc of a sphere with a peak at ≈100KHz (fig.1).

A general circuit is proposed in fig. (10) to examine systems in which diffusion (Z_D) and transport (Z_t) impedances are significant or in which bulk (C_g and R_∞)and reaction (C_R and R_R) effects are not well separated. The total impedance (Z_T) of the system which can be represented by this equivalent circuit (fig.10) is given by :

$$Z_T = Z_\infty + Z_R + Z_D + Z_t \qquad (16)$$

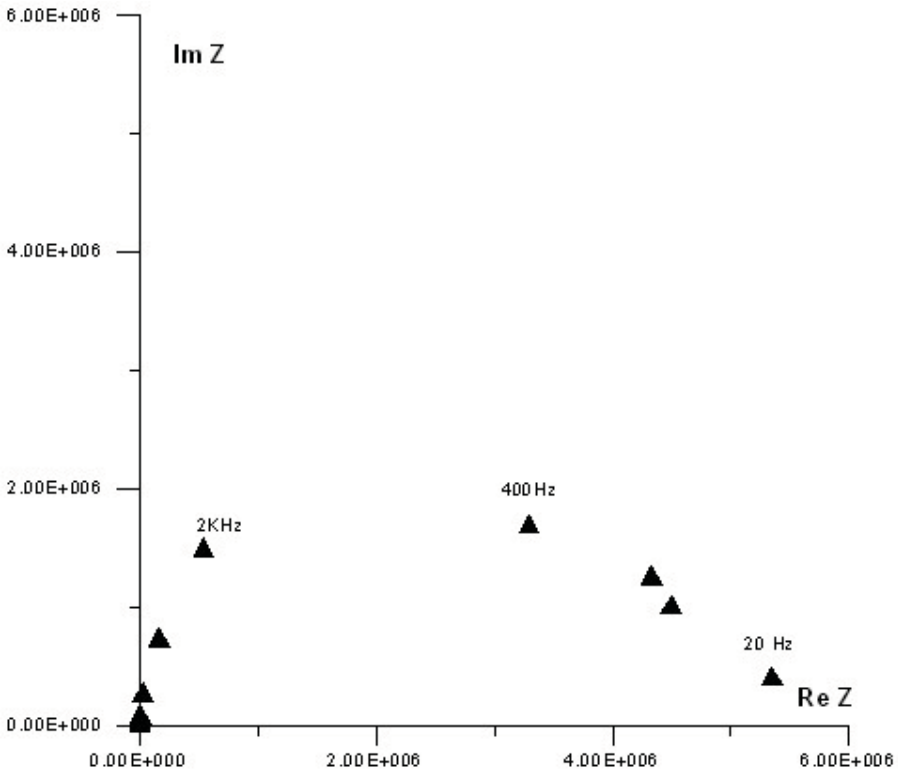

Fig. 7: Relationship between Re Z and lm Z for limestone sample at (R.H. 35%)

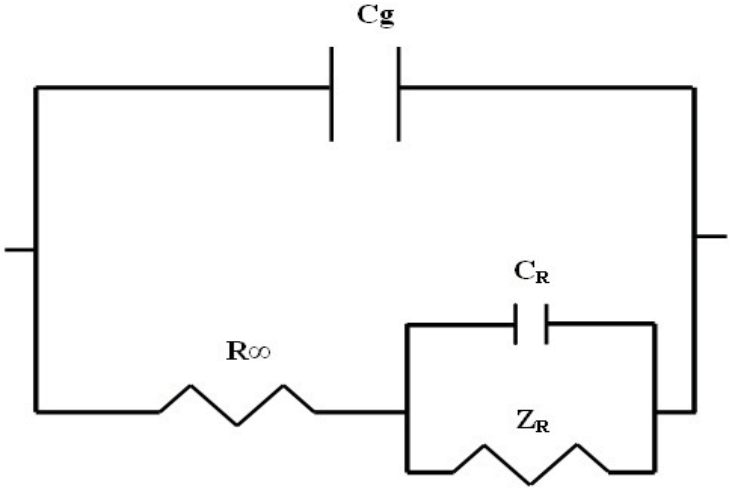

Fig. 8: Equivalent circuit assumed to represent interfacial (chemical reaction) impedance (Z_R).

Because of the hierarchical form of this equivalent circuit it insures experimental observations that bulk effects occur at higher frequencies than reaction effects (1 MHz and higher), and reaction effects at higher frequencies than diffusion and transport mechanisms (10^2 – 10^5 Hz). Diffusion and transport ones occur at frequencies lower than 10^2Hz. Anyhow the appearance of one or more of these mentioned processes is controlled essentially by the level of water content in the sample as well as the frequency range of the applied electric field.

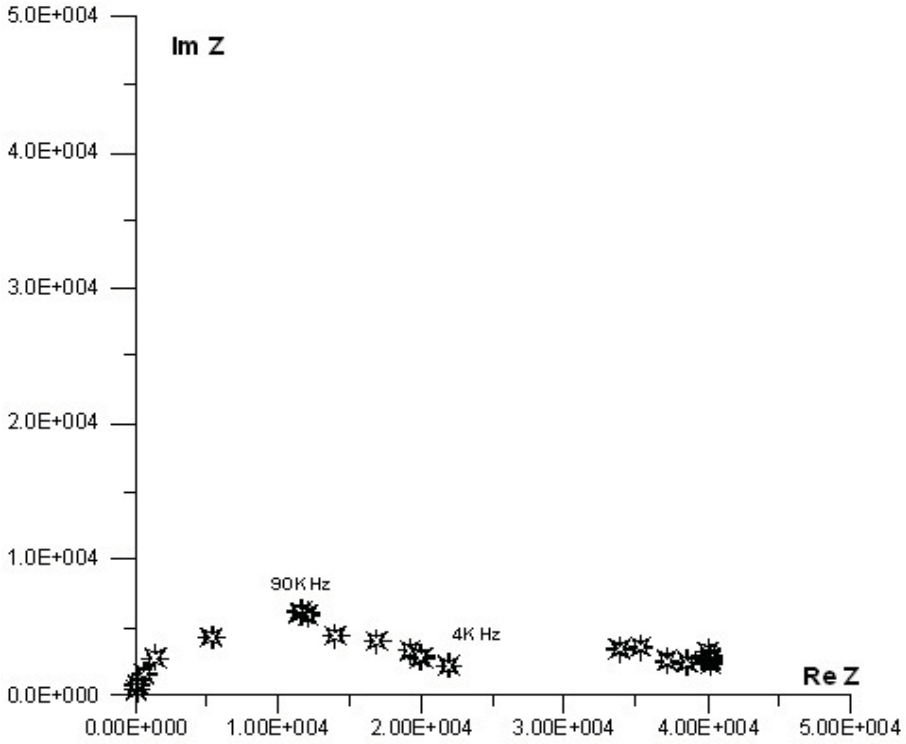

Fig. 9: Relationship between Re Z and lm Z for limestone sample at (R.H. 50%)

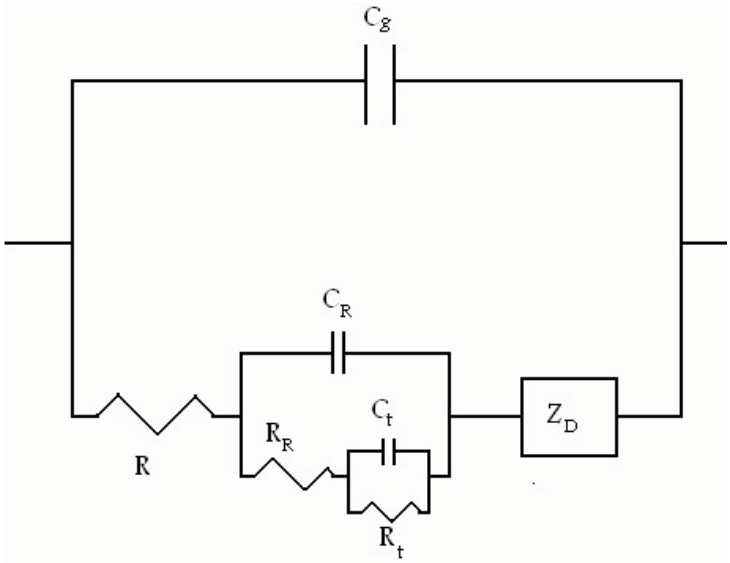

Fig. 10: Equivalent circuit assumed to represent diffusion impedance (Z_D) and transport behavior (C_t and R_t)

Conclusion: Studies on the electrical properties of water bearing porous medii in the frequency range $1 - 10^7$ Hz reveals many physical processes, which are induced in rocks by the application of an alternating current of varying frequencies.

At frequencies lower than 10^7 Hz surface processes make significant and often dominant contributions to polarization (capacitance), and conductance of water bearing rocks. Experimentally it can be noticed that there are two means relaxation times induced by surface polarization.

- Relatively fast relaxation (in the frequency range $10^3 - 10^5$ Hz) caused by the interaction between grain surface and solution in the pore spaces surrounding it giving rise to chemical reaction or ion exchange impedance (Macdonald, J.R., 2005)
- Slow diffusion controlled process due to mass transport to and from electrode and bulk water in the pore spaces. Such diffusion process may behave under certain conditions as Warburg impedance (ReZ = ImZ)

Qualitative theories of dielectric polarization allow one to predict the principle parameters of electrical spectra (i.e to solve the forward problem); asymptotic values of ε' and σ at the low and high frequency limits and relaxation times. Solving the inverse problem can provide information on the electrical properties of rock components, the microstructure of pore spaces, the state of water, the geometrical and electrical roughness of the surface and the surfaces charge. As the equivalent circuit technique does not give information on the nature of physical processes producing particular spectra, the role of physical experiments and their optimal planning is of great importance in solving the inverse problem.

The high sensitivity of the electrical properties at different frequencies of rocks to content, state and composition of pore fluid and the microstructure of the porous spaces allow one to determine the above-mentioned properties of water bearing porous system. The diagnostics may be effective in mineral, water and oil prospecting, exploration of geothermal energy, well logging, monitoring of the stress stored within the earth's crust, earthquake prediction and assessment of the safety of toxic and radio active waste repositories.

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