

Interfacial Effects on the Electrical Properties of Humid Limestone

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Abstract: The simple Archie's equations relate the average conductivity to average porosity and average saturation and seem to work when the fluctuations of local porosity and local saturation are small. The presence of conducting minerals and grains or pore-surface conduction produces, in addition to Archie's suggested mechanism conduction, a second conducting component. Modification of the classical Archie's relation is carried out. Since carbonate rocks are of special importance in the petroleum as well as underground water explorations, samples of limestone rock are studied under varying conditions of atmospheric relative humidity to identify their interfacial effects. Power law is discussed as an empirical relationship for describing the experimental results. Debye behavior is also noticed under particular conditions.

Key words: Humid limestone, interfacial effects, electrical properties, Egypt

INTRODUCTION

In recent years, research work has been carried out for the development of geophysical methods for the purpose of determining electrical properties (dielectric constant and conductivity) of fluid-saturated porous rocks occurred in a borehole. It was shown that, the measurement of electrical parameters can provide useful information about the physical properties of porous medium. This technique, also, provides a potential approach for measuring the water saturation and may be used directly to distinguish the oil from water in a formation having unknown water salinity. In boreholes drilled with non conducting mud, the dielectric constant logging is a useful tool to differentiate the water saturated formations from shale. For normal drilling mud, it appears to be possible to determine the oil saturation, nature of fluid, and to detect the permeable zones (Reveul, A., and Glover, P.W.J., 1998). In a historical paper about the electrical conduction in clean sands, Archie (Archie, G.E., 1942) suggested that, the conductivity of the brine saturated rock is proportional to brine conductivity, and also the specific resistivity of water saturated rock is proportional to the specific electrical resistivity of the brine. The historical importance of the Archie equation results from the fact that, it gave the first practical relationship between the measurable conductivity and an important reservoir property (porosity).

The classical discussion of experimental results and theories for clean rocks (e.g. pure sand) are based on two-component models (Schon, J.H., 1996):

- Conducting component: water.
- Non-conducting component: solid matrix material, oil, and gas.

The presence of conducting minerals and grain-or pore surface conduction produces a second conducting component and, therefore, the given equations must be modified. It was stated that "current was being carried through the core by some medium other than the saturating solution" (Revil, A., and Glover, P.W.J. 1998). Limestone, clay and grain surface phenomena create interfacial conductivity. The contribution of each process to the conductivity of the system is controlled greatly by external atmospheric condition e.g. relative humidity. Such interfacial behavior is the goal of this work.

It can be stated that, the simple Archie's equations relate the average conductivity to average porosity and average saturation and seem to work when the fluctuations of local porosity and local saturation are small. In general, carbonates and clays are extremely complicated and the Archie's relation fails to give unique solution. The saturation exponent in Archie's relation can depend on the saturation itself, and can be anomalously small or large.

A study of some varying models such as the power law and its development, as well as Cole-Cole model will be discussed here in terms of the obtained experimental data. Complex dielectric constant ϵ^* and complex

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impedance (Z^*) will be measured for the limestone samples derived from Gebel Mokattam at low relatively atmospheric humidity in the frequency range $\approx 20-10^5$ Hz. However, the impedance measurements offer a further method for separating the electrical volume and interface effects in the radio frequency range and lower ($F \leq 10^6$ Hz).

The two Archie's exponents are the subject of numerous investigations with regard to various parameters (texture, pressure, etc.), and also their theoretical derivation (Schon, J.H., 1996).

The complex resistivity data for the oil /water experiment was modeled in an effort to characterize the effect of interfacial polarization through the frequency dispersion. Given the absence of clay from the Ottawa sand, only a small relaxation (Piggott, S.D., 1999) would be expected, due to the local buildups of charge at the sand grain water interfaces (Piggott, S.D., 1999; Piggott, S.D., *et al.*, 1999)

MATERIALS AND METHODS

Theoretical Considerations:

In a historical paper on electrical conduction in clean sand, Archie suggested that the conductivity of the brine saturated rock is proportional to the brine conductivity (Archie, G.E., 1942). Archie put the relation:

$$\sigma = \frac{\sigma_{water}}{F} \quad (1)$$

Where F is the formation factor = $\frac{1}{\phi^m}$

Where ϕ is the porosity and m is an empirical quantity, known is cementation factor.

The presence of conducting minerals and grain- or pore surface conduction produces a second component and therefore, the last equation "Archie" must be modified. Modification of such equation was firstly detected and described by Patnode and Wyllie (Patnode, W.H., and Wyllie, M.R.J., 1950) they found Archie's relationship did not apply to shaly sand cores, and laboratory made clay slurries, and wrote "it was apparent, that current was being carried the core by some medium other than the saturating solution. They called this additional conduction: conductive solids which include clay component in the form of disseminated particles or shale streaks (Schon, J.H., 1996).

The electrical behavior of a rock sample was described as follows (Schon,1996):

$$\sigma_{electrolytic} + \sigma_{interface} = \frac{\sigma_{water}}{F} + \sigma_{interface} \quad (2)$$

Where σ_0 is the total conductivity of the rock sample, $\sigma_{electrolytic}$ is the conductivity given by Archie's equations, and equals $\frac{\sigma_{water}}{F}$

The electrolytic component given by the Archie's equation δ in equation (2) is considered a simple value. In rocks and generally in heterogeneous media, it is difficult to assume that, σ is a simple component. It is more reasonable to consider that; σ is a complex quantity i.e.

$$\sigma^* = \sigma' + j\sigma'' \quad (3)$$

$$\text{Where } \sigma^* = j\omega(\epsilon' - j\epsilon'') \quad (4)$$

Comparison of equations (3) and (4) shows that, the following relation holds:

$$\sigma' = \omega\epsilon'' \quad (5)$$

$$\sigma'' = \omega\epsilon' \quad (6)$$

Where: ϵ' is the dielectric constant given by:

$$\epsilon' = \frac{C_x}{C_0}$$

Where $C_0 = 8.85 \times 10^{-12} \times A/d$ Farad

A is the cross-sectional area of the studied sample in meters, and d, is the thickness of the sample in meters, and ϵ'' is the dielectric loss given by:

$$\epsilon'' = \frac{\sigma}{\omega \epsilon_0}$$

Where $\epsilon_0 = 8.85 \times 10^{-12}$ Farad/meter, σ is the conductivity ($\text{Ohm}^{-1} \cdot \text{m}^{-1}$), and ω is the angular frequency.

$$J = \sqrt{-1}$$

Also
$$\sigma = \frac{1}{\rho}$$

Where: ρ is the resistivity ($\text{Ohm} \cdot \text{m}$).

It is generally used to describe the electrical properties of a rock sample in terms of its impedance Z, complex resistivity ρ^* , or complex dielectric constant ($\epsilon^* = \epsilon' - j\epsilon''$)

where

$$\begin{aligned} Z_t &= Z_1 + Z_2 + Z_3 \\ \rho^* &= \rho_1 + \rho_2 + \rho_3 \\ \sigma^* &= \sigma_1 + \sigma_2 + \sigma_3 \end{aligned} \quad (7)$$

or

Where: Z_t is the total impedance of the sample, Z_1 , Z_2 and Z_3 express three different mechanisms that contribute to the total impedance of the sample. Z_3 represents the impedance of the sample at high frequency range (radio frequency range and higher), where the interfacial effects are neglected and the electrical properties of the sample are controlled by the bulk properties of the constituents. Z_1 and Z_2 , on the other hand, are controlled by interfaces between pore spaces and solid matrix, as well as the intrinsic properties of the fluid filling such pore spaces. In ideal cases, these three impedances can appear simultaneously when the sample is studied in a wide frequency range.

When the sample is subjected to a very low atmospheric relative humidity, a water mono-layer is attached strongly to the grain surfaces, giving rise to a cloud of ions due to the ion exchange occurred between fluid and grain surface, which in turn is controlled by cation exchange capacitance. The mobility of such ions in the cloud surrounding a grain is limited or even blocked. So, the sample total impedance is controlled by ion exchange process or chemical reaction impedance. Such impedance is composed of an ohmic and a capacitive component.

The ohmic and capacitive components of the reaction impedance are connected in series as follow;

$$R_R = R_0 \frac{1}{1 + (\omega/k)^2} \quad (8)$$

$$\frac{1}{\omega C_R} = \nu^2 R_0 \frac{\omega/k}{1 + (\omega/k)^2} \quad (9)$$

where: k is the reaction rate (ion exchange reaction), which shows an equation of a half- circle:

$$\left[\operatorname{Re} Z_R - \frac{R_0}{2} \right]^2 + (\operatorname{Im} Z_R)^2 = \left[\frac{R_0}{2} \right]^2 \quad (10)$$

where $Z_R = \operatorname{Re} Z_R + \operatorname{Im} Z_R = R_R + \frac{1}{j\omega C_R}$

In addition to the previously presented model (mechanism), a model which taking into consideration the conduction and diffusion processes in the electrolyte filling the pore spaces surrounding the grain particles, is considered. While the reaction impedance leads to Debye behavior (half circle) as shown in equation (10), the volume diffusion leads to the well known Warburg impedance.

Diffusion processes (charged particles transfer) are usually expressed electrically by the well known Warburg impedance (Vetter, K.J., 1967). The Warburg impedance is represented by a series circuit consisting of a frequency-dependent resistance $R_w(\omega)$ and a frequency-dependent capacitance $C_w(\omega)$, in which both the resistance and reactance are shown as follows:

$$R_w(\omega) = \frac{1}{\omega C_w(\omega)} \quad (11)$$

$$R_w(\omega) \propto \frac{1}{\sqrt{\omega}} \quad (12)$$

$$C_w(\omega) \propto \frac{1}{\sqrt{\omega}} \quad (13)$$

Laboratory Works:

Solid specimens of limestone of varying sand and clay contents are prepared as flat rounded discs. The thicknesses of these discs range between 2.5 and 3.5 mm, to give reliable data. The diameter of these specimens is prepared to be slightly larger than the diameter of the condenser electrodes, to diminish the error due to the surface leakage over the edge of the sample (Marzouk, M. Bekhit, *et al.*, 2005), and due to fringing the electric field. The discs are then covered by aluminum foils mounted with vacuum grease. The foils are smoothed into place with a small pad, so that any air gap is excluded. The main capacitor electrodes are then made to cover the foils, when the specimen is in position. The condenser is then put inside a dissector containing magnesium chloride solution, to give the desired humidity (32%). The two leads of the condenser come out of the dissector are connected to a Hioki LCR-meter, to measure the samples in the frequency range (20 Hz – 10⁵ Hz).

RESULTS AND DISCUSSIONS

The study of interface phenomenon opens the possibility for determination and characterization of pore geometry properties, using electrical methods. In particular, specific internal surface and grain size (porosity) are properties related to hydrodynamic permeability, which is of fundamental importance for all fluid motion processes (Schon, J.H., 1996).

Fig. (1) shows the behavior of the tested sample, when subjected to a low atmospheric relative humidity 32% (Saad, A. Khalil and Mazrouk, M. Bekhit, 2003). The sample behavior is controlled by the activity of each of its constituents (water and solid grain materials), i.e. ion exchange at the interfaces between the fluid filling pore spaces and the solid grains. Such behavior gives rise to a half- circle in the impedance plane representation with a relaxation time at frequency 2 KHz. Such half-circle is described by equation (10).

Fig. (2) shows the behavior of the same sample, when the atmospheric relative humidity is increased to 50 %. A second mechanism is appeared in the low frequency range, which can be represented by a straight line. Under certain atmospheric conditions “relative humidity”, this straight line makes an angle of 45° with the positive direction of the Re Z axis (Marzouk, M. Bekhit, and Safwat, A. Hussain, 1999). This behavior is well-known as diffusion effects. The impedance is thus called Warbuge impedance (Safwat, A. Hussain, 1980). When other effects such as DC

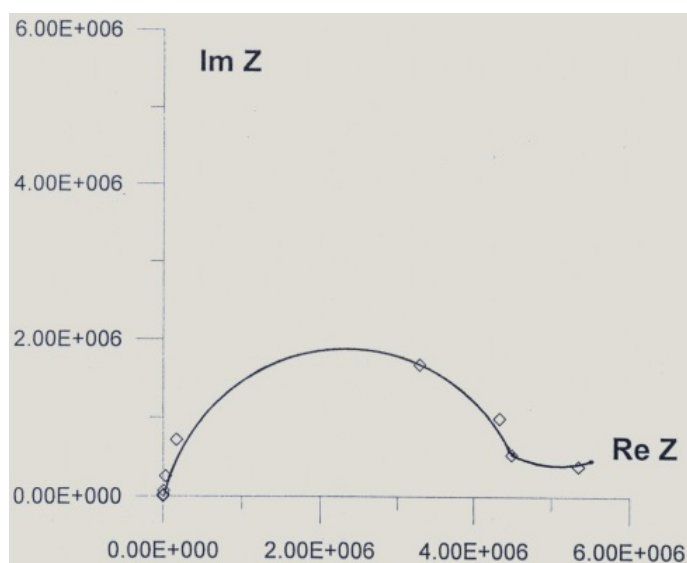


Fig. 1: Shows the relationship between the real impedance (Re Z), and the imaginary impedance (Im Z) at relative humidity 32% (After Saad et al. 2005).

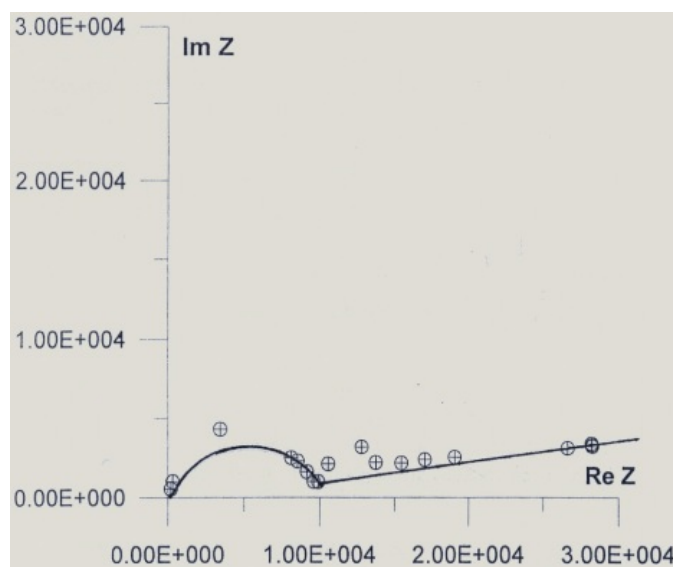


Fig. 2: Shows the relationship between the real impedance (Re Z), and the imaginary impedance (Im Z) at relative humidity 50% (After Marzouk et al. 2003).

conduction are superimposed on Warbug impedance, the straight line makes an angle less than 45° . Such dc conduction can be described by Archie's relation. It dominates under special conditions, which are difficult to be achieved in natural rock samples due to interfacial effects.

In all cases, the peak of the half-circle (chemical reaction or ion exchange impedance) is shifted in the direction of high frequency, to be of the order of ≈ 6 KHz in comparison with its value in Figure 1, where the peak lies at the frequency of ≈ 2 KHz.

Fig. (3) shows the relationship between ϵ' and $\log F$ for three limestone samples subjected to low relative humidity level ($\approx 18\%$). The behavior of ϵ' against $\log F$ can be described by the well-known power law relation; $\epsilon' \propto \omega^{-n}$, where the exponent $n \leq 0.2$. The dielectric constant of the measured samples shows a small dependence on frequency ($\omega = 2\pi F$). The dielectric loss (ϵ'') shows the same behavior, i.e. a small dependence in F is noticed (Fig.4). The exponent n has nearly the same value ($n \leq 0.2$).

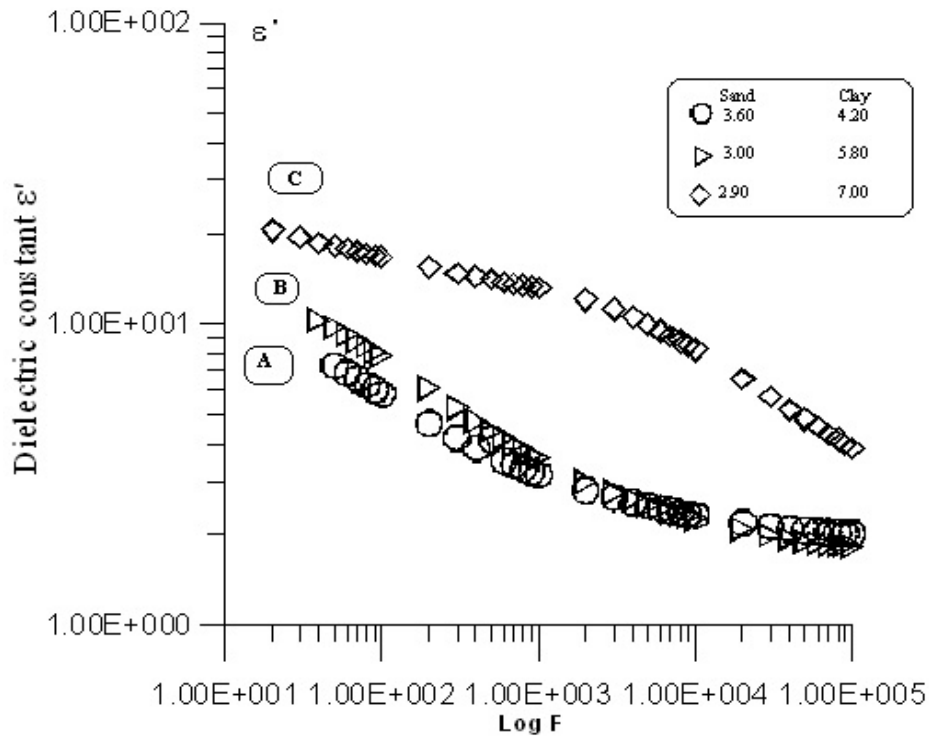


Fig. 3: Shows the relationship between the dielectric constant ϵ' , and the frequency F for 3 limestone samples different in sand and clay content.

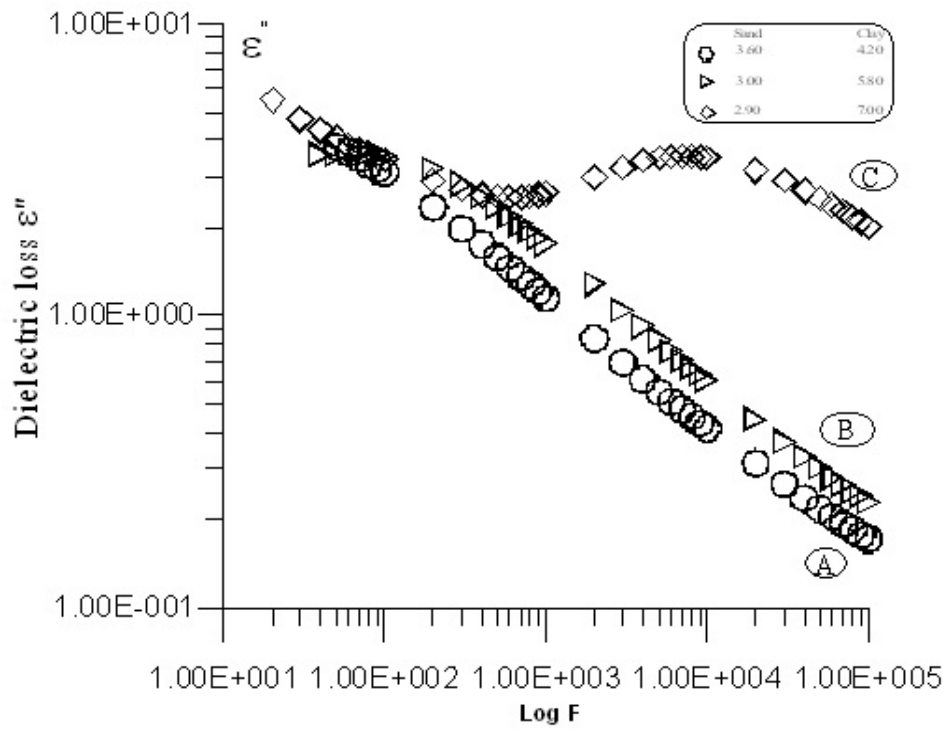


Fig. 4: Shows the relationship between the dielectric constant ϵ'' , and the frequency F for 3 limestone samples different in sand and clay content.

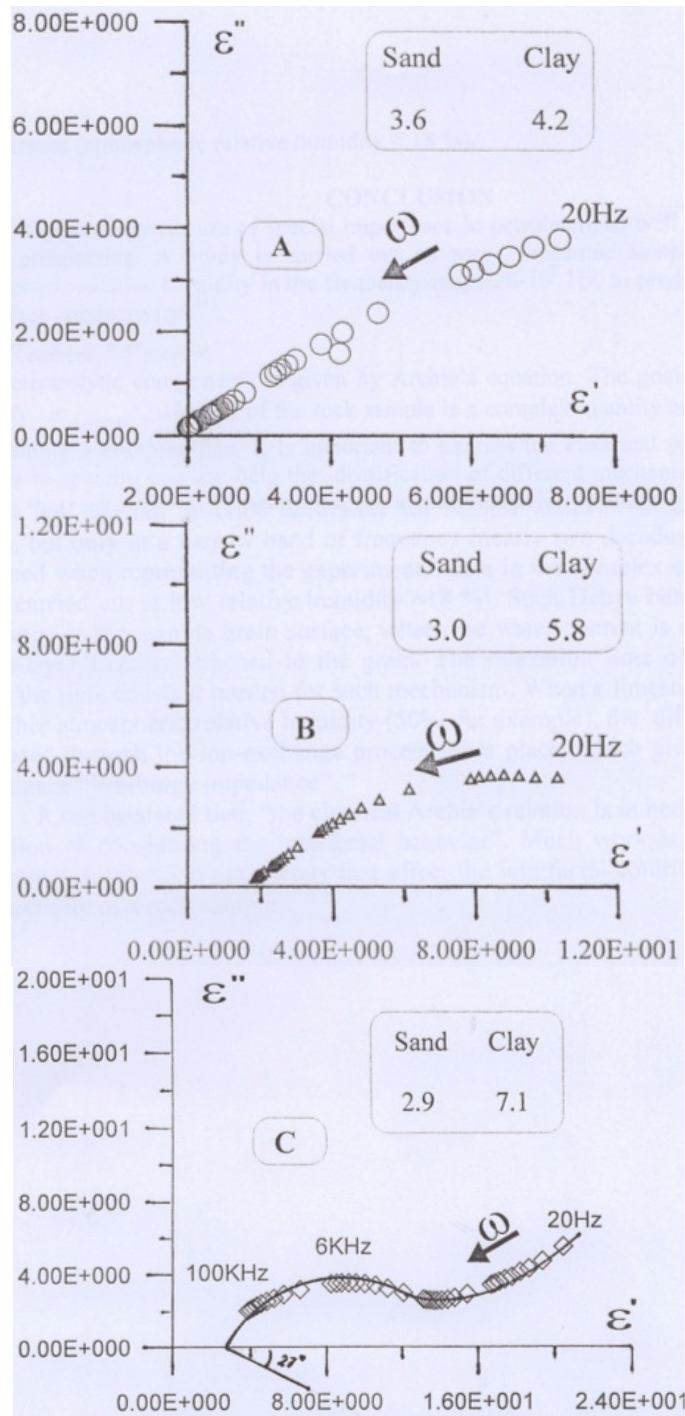


Fig. 5: Shows the relationship between the dielectric constant ϵ' and the dielectric loss ϵ'' for 3 limestone samples different in sand and clay content.

From petrophysical point of view, it can be stated from Figures (3 & 4) that, the most effective parameters in defining the electrical properties are the clay content and simultaneously the sand content. The increase in clay content (increasing the interfacial activity), which is accompanied by a decrease in the sand content, gives rise to an increase in the dielectric constant and dielectric loss. The decrease in clay content (decreasing the interfacial activity), which is accompanied by an increase in the sand content, gives rise to a decrease in the

dielectric constant and dielectric loss. This means that, the induced polarization of the sample increases with the increase of clay content, in particular, when the sample is humid.

A Debye model (Von, Hipple, 1954), is one of the simplest and common models describing the polarization accompanied by losses and having a single relaxation time τ . The Debye model leads to the frequency dependent ϵ' and ϵ'' as given by:

$$\epsilon' = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{1 + (\omega\tau)^2} \quad (14)$$

and
$$\epsilon'' = (\epsilon_s - \epsilon_{\infty}) \frac{\omega\tau}{1 + (\omega\tau)^2} \quad (15)$$

This leads to an equation of half-circle relating ϵ' and ϵ'' , when plotted in the complex (ϵ^*) _ plane (Safwat, A. Hussain, 1980).

Cole-Cole (Von, Hipple, 1954) modified the Debye model to describe the results, when a distribution of relaxation time is involved. It can be put in the form:

$$\epsilon^* = \epsilon_{\infty} + \frac{(\epsilon_s - \epsilon_{\infty})}{1 + (j\omega\tau)^{1-\alpha}} \quad (16)$$

Its representation in the ϵ^* - plane shows an arc of a circle, whose centre is depressed by an angle $\alpha \pi/2$ from the real (ϵ') axis (Fig.5C). The empirical constant α , which may vary between 0 and 1, describes the broadening of the relaxation region. In this case, the relaxation time τ becomes a mean time constant, around which other time constants are spread. The spreading factor α can be determined as ($1 \geq \alpha \geq 0$) (Fig. 5C).

The Cole-Cole expression of equation (16) corresponds to the general equivalent circuit shown in Fig. (6), in which C_g is the capacitance at infinite frequency, and C_D is the Debye capacitance. The Debye resistance is replaced by the interfacial impedance $Z_i = Z_{(\omega)} e^{i\alpha \frac{\pi}{2}}$. Such interfacial impedance describes the power law and controls the sample behavior. It may be ascribed to the ionic clouds surrounding the sample grains, due to the wettability with water traces (atmospheric relative humidity $\approx 18\%$).

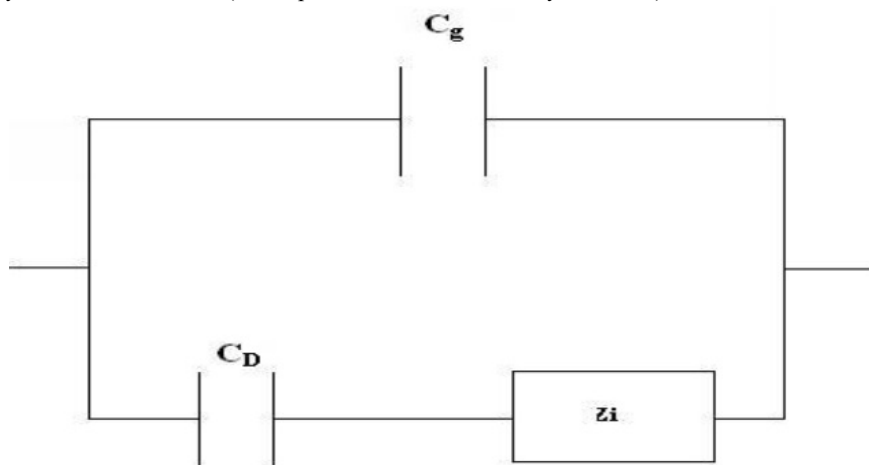


Fig. 6: Shows an equivalent circuit representing the studied samples.

Conclusion:

Carbonate rocks are of special importance in petroleum, as well as in underground water prospecting. A study is carried out on some limestone samples under varying atmospheric relative humidity in the frequency range 20-10⁵ Hz, to predict the well-known “interface conductivity”⁽¹⁾.

$$\sigma_t = \sigma_{electrolytic} + \sigma_{interfacial}$$

“The electrolytic component” is given by Archie’s equation. The goal of this work is to identify $\sigma_{interfacial}$, where σ of the rock sample is a complex quantity and the resistivity is accordingly a complex one. It is important to express the electrical properties of a rock sample in specific ways to help the identification of different mechanisms that take place within the rock sample. In describing the sample behavior (ϵ' and ϵ'') against $\log F$, the power law can not describe accurately the sample behavior in the complete frequency range, but only in a narrow band of frequency (nearly two decades). Debye behavior was obtained when representing the experimental data in the complex ϵ^* plane (measurements were carried out at low relative humidity $\approx 32\%$). Such Debye behavior describes the ion exchange in the sample grain surface, where the water content is enough only to make a mono-layer fiercely attached to the grain. The relaxation time of such Debye behavior gives the time constant needed for such mechanism. When a limestone sample is measured at higher atmospheric relative humidity (50%, for example), the diffusion of charge carrier produced through the ion-exchange process takes place, which gives rise to the diffusion impedance “Warburg impedance”.

It can be stated that, “the classical Archie’s relation is in need to development in the direction of considering the interfacial behavior”. Much work is needed to identify the different petrophysical parameters that affect the interfacial contributions to the electrical conductivity of a rock sample.

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