

# CHARACTERISATION OF PRESSED CLAY PRODUCTS BY ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

N. Vancaster, G. Moortgat, F. Cambier

Belgian Ceramic Research Centre  
4, Avenue Gouverneur Cornez - 7000 MONS - BELGIUM

## SUMMARY

*To avoid defects due to the shaping processes it is important to reduce the production costs in ceramic industries. In this paper, we discuss mainly the determination of the pressed pellets water content to obtain a product exhibiting good properties.*

*In pressed samples, there is not enough water to use classical electrochemical measurements because, in such conditions, owing to the large ohmic loss, electrochemical phenomena are hidden. Therefore, to approach the surface reaction mechanisms during pressing, the impedance measurement technique is used.*

*The impedance spectrum is a characteristic of the material and the corresponding equivalent circuit parameters allow to determine the optimum moisture content of the powders mix to process the pressed tile.*

*The variation of these characteristic parameters and the physical meanings of the different elements of the equivalent circuit are discussed.*

## 1. INTRODUCTION

During pressing, green density of sample increases implying the rearrangement of the particles. Such a variation leads often to the formation of cracks and defects due to the difference of friction coefficient between the particles according to the grain size distribution. These effects can be reduced by the addition of a small quantity of water. So, the lubricant content is an important experimental parameter, but the effect of the shaping conditions and the particle surface have also to be taken into account. In the ceramic industry, the shaping process parameters are fixed and cannot be easily changed. Only the moisture content can be adapted to improve the powder mix properties and to optimise its behaviour during pressing.

The optimal water concentration is not only proportional to the specific surface area of the clay based powder, other factors depending on water content such as the surface charges of the particles on ionic force are also significant.

To solve these problems and to detect the surface reaction mechanisms, we propose to use the impedance spectroscopy technique. In this paper, the impedance diagrams have been fitted using an equivalent circuit and the evolution of the characteristic parameters are studied to explain the behaviour of the samples.

## 2. EXPERIMENTAL PROCEDURE

### 2.1. PRINCIPLES OF THE ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS) TECHNIQUE

The EIS is a method to determine the structure of materials by using the alternative current or tension frequency response of the material electrical impedance. If a variable (AC) voltage is applied to the material, the ratio of voltage to current ( $E/I$ ) is known as the impedance. In many materials, the impedance varies with the frequency of the applied voltage, in a way that is related to the physical structure of the material, to chemical processes within it, or to a combination of both.

A great advantage of EIS is that, according to appropriate data analysis, it is often possible to characterise the different regions in a material, both qualitatively by demonstrating their existence and quantitatively, by measuring their individual properties.

In the EIS method, absolute impedance  $Z(\Omega)$ , phase angle  $\phi(^{\circ})$ , real part of the impedance  $\text{Re}(Z)(\Omega)$  and imaginary part of the impedance  $\text{Im}(Z)(\Omega)$  can be obtained and the relationships among these parameters are given by :

$$|Z| = \sqrt{\text{Re}(Z)^2 + \text{Im}(Z)^2} \quad \text{and} \quad \phi = \tan^{-1} \frac{\text{Im}(Z)}{\text{Re}(Z)}$$

Two diagrams can be used for the impedance analysis. One is a complex plane plot of  $\text{Re}(Z)$  and  $\text{Im}(Z)$  named Nyquist diagram and the other is a Bode diagram of  $Z$  and  $\phi$  as a function of the frequency. Figure 1 illustrates the complex plane plot and Bode diagram in the case of a R(resistance -  $\Omega$ ) - C(capacitance - F) parallel circuit.

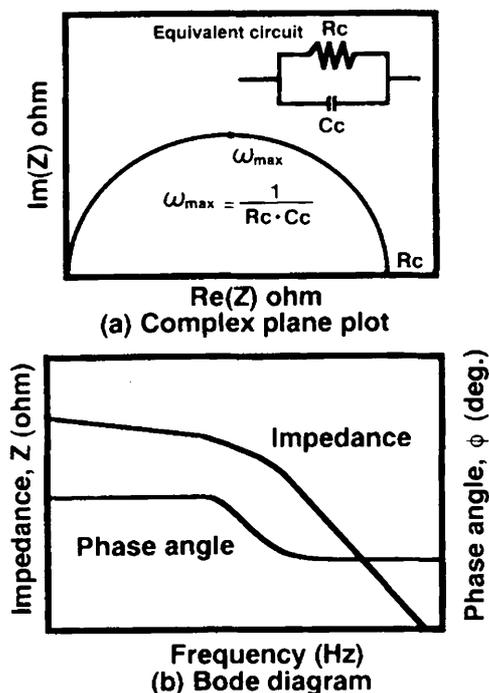


Figure 1. Schematic (a) complex plane plot and (b) Bode diagram of impedance behaviour for a R-C parallel circuit.

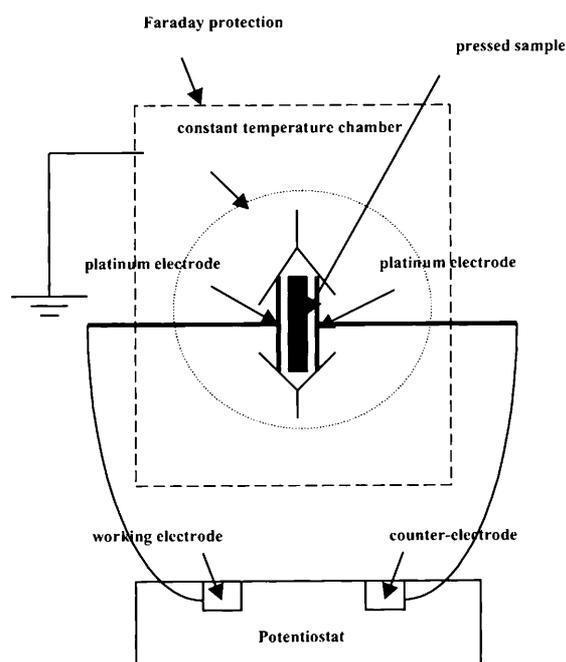


Figure 2. Schematic layout of the sample holder.

## 2.2. DATA ANALYSIS USING ELECTRICAL EQUIVALENT CIRCUIT

The electrochemical impedance spectroscopy (EIS) measurements offer the possibility of a comprehensive characterisation of green ceramics (pressed samples for instance). The knowledge of the microstructure of the material is, of course, important but the link between the microstructure and the electric properties is not always obvious.

To characterise the different regions contributions to the global response signal, the research of an equivalent circuit is necessary. The equivalent circuits allow the physical interpretation of the experimental results.

There are some difficulties in selecting the most appropriate equivalent circuit. In fact, it is often possible to find more than one circuit to fit the impedance curves and there is no a priori way to tell which one is the more suitable. The solution is to use a pragmatic approach and to adopt a circuit which the scientist believes to be most appropriate, given their knowledge of the physical behaviour of the studied material.

The fitting of the impedance results using equivalent circuit is a way in finishing off an analysis, in checking the physical interpretation of the samples microstructure.

### 2.3. RAW MATERIAL CHARACTERISATION AND SAMPLES PREPARATION

The clay based raw material used for the preparation of the pressed samples is a mix usually used to process industrial tiles, obtained by spray drying, with an average diameter of 540  $\mu\text{m}$ .

A mineralogical analysis of the clay fraction ( $< 2 \mu\text{m}$ ) showed that the raw material is mainly a kaolinite based clay.

The specific surface area measurement was performed by nitrogen adsorption under liquid nitrogen. The values have been calculated using the B.E.T. method. The specific surface area value is 21  $\text{m}^2/\text{g}$ .

The cylindrical pressed samples (diameter : 2.5 cm ; high : 1 cm) were prepared using 8 g of clay based powder and the pressing conditions used for shaping are 40 kN with a rate of 200 N/s.

The composition of the samples varies from 3 to 8 weight percent of water.

The EIS measurements were performed 24 hours after the pellets shaping in order to obtain the equilibrium in the electrochemical system.

### 2.4. PROCEDURE OF IMPEDANCE MEASUREMENTS

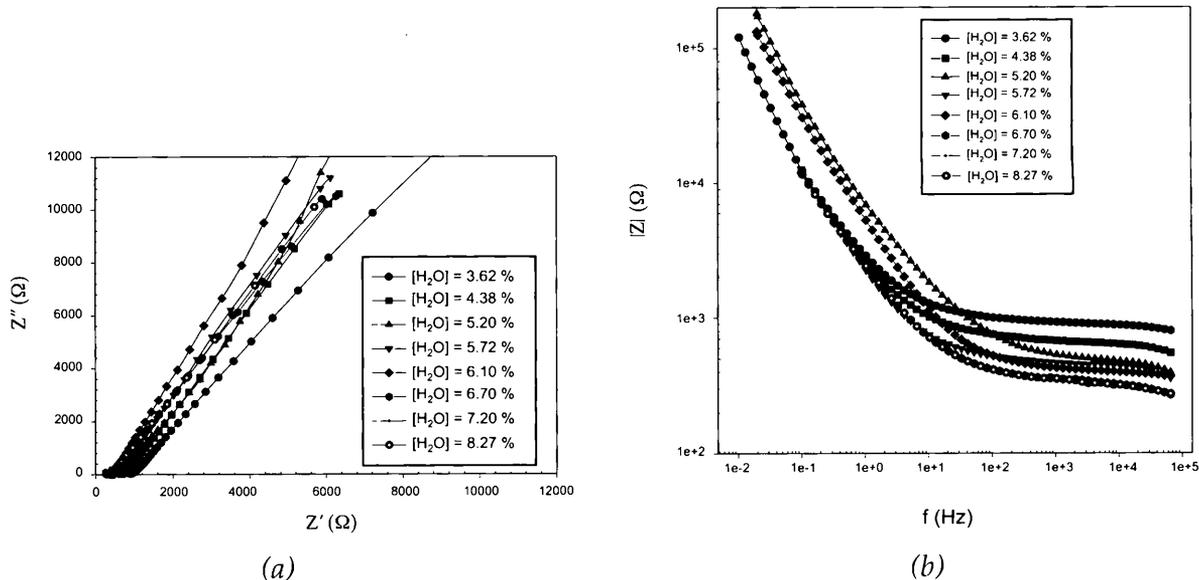
The impedance is measured by a two contact platinum electrodes system. A schematic illustration of the sample holder used for the impedance measurements is shown in figure 2. The two electrodes are cylindrical and symmetrical in order to ensure parallel current lines in the sample. They are connected to a potentiostat/galvanostat (Radiometer Analytical PJT 35/2). The latter is connected (via a programmable interface (Radiometer Analytical IMT 102)) to a tension amplifier (Radiometer Analytical PLA 102) and a Frequency Response Analyser (Solartron FRA 1250) able to measure the electrical properties.

As a result of the variation of moisture content during the measurements which causes a significant variation in the impedance spectra, the specimens are protected from environment.

A voltage of only 20 mV over the rest potential in order to avoid any electrochemical reactions in the system and a range of the swept frequencies from 10 mHz to 65 kHz are applied.

### 2.5. EXPERIMENTAL DATA

Complex plane plots and Bode diagrams as a function of the different compositions are shown in figures 3.a. and 3.b.



Figures 3.a. and 3.b. Complex plane plots(a) and Bode diagrams (b) for the different compositions

The resulting complex plane plots can be divided in two parts : one corresponding to high frequencies and the other to medium and low frequencies.

In the region of high frequencies, we can observe, in figure 4, a shift of the curves to lower values of the real part of impedance ( $Z'$ ) with increasing water concentration. The phenomenon can also be shown using the Bode representation (figure 5) : an increasing moisture content leads to a decrease of the absolute value of impedance  $|Z|$ .

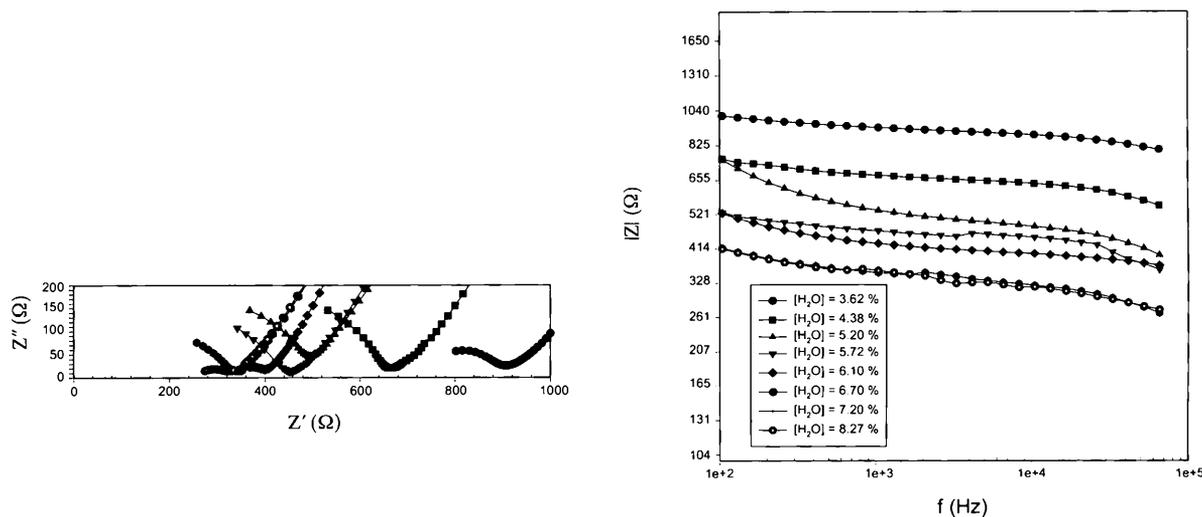


Figure 4. Complex plane plot diagrams for the different compositions at high frequencies.

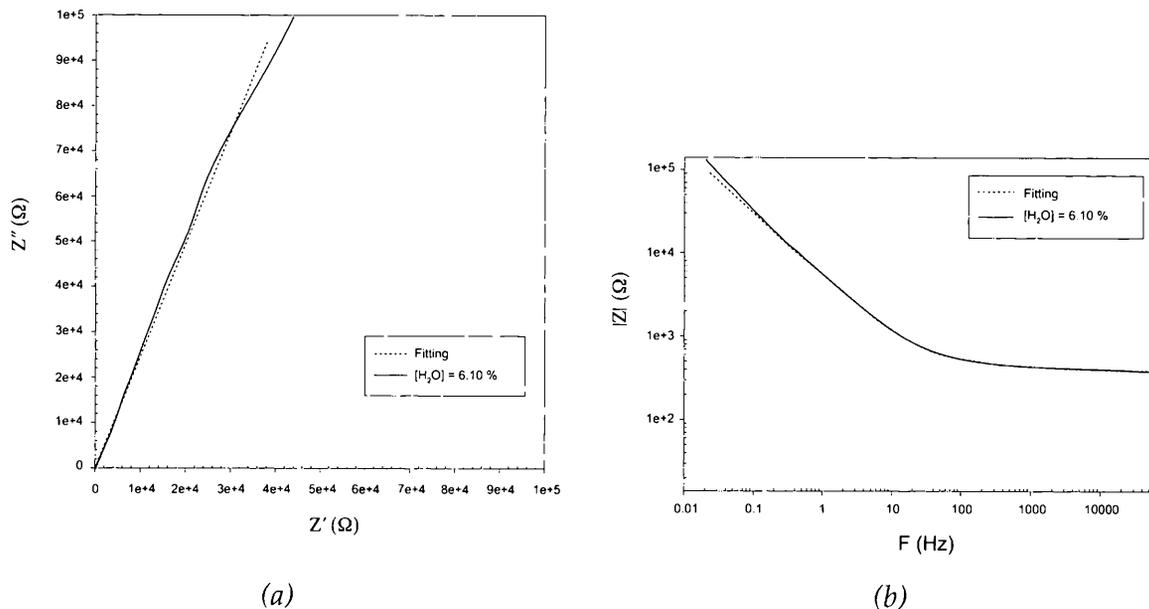
Figure 5. Impedance absolute value for the different compositions at high frequencies.

On the other hand, a change of impedance spectra behaviour at medium and low frequencies for the component containing 6.1 % of water can be observed in figure 3.

The impedance spectra were fitted using "Zview" software (Solartron). The first step of the fitting procedure is to divide the electrochemical impedance curves in two

parts and to fit them separately. The software proposes an instant fit and the operator can adapt it in order to obtain the best simulation of the experimental data. Eventually, when the optimum equivalent circuits are obtained for both parts of the curve, a last fitting is done, taking into account the whole experimental data.

The example of an experimental curve and its fitting resulting curve of the green pressed sample containing 6.1 % of water are plotted in figure 6.a. and 6.b.



Figures 6.a. and 6.b. Comparison of the fitting curve and the experimental curve for the pellet containing 6.1 % of water. (a) : complex plane plot diagram, (b) :absolute value of the impedance as a function of the frequency

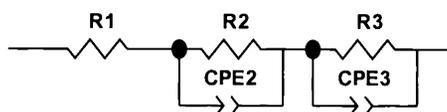


Figure 7. Equivalent circuit for the studied system

The “Zview” software calculates the characteristic parameters of the equivalent circuit and the relative error on each of them as well as the  $\chi^2$ .

All the experimental impedance curves were fitted, one by one, using the equivalent circuit composed of a resistance ( $R_1$ ) in series with two identical elements, each one being constituted by a resistance ( $R_2$  and  $R_3$ ) in parallel with a constant phase element ( $CPE_2$ -T,  $CPE_2$ -P,  $CPE_3$ -T,  $CPE_3$ -P) as illustrated in figure 7. The first resistance corresponds to the intersection of the fitted curves with the real axis in the Nyquist diagram (complex plane plot diagram) at an infinite frequency value. The second element ( $R_2$ ,  $CPE_2$ ) is attributed to the semi-circle corresponding to the impedance results in high frequencies and the third one ( $R_3$ ,  $CPE_3$ ) to the medium and low frequencies values as shown in the theoretical example of the figure 8.

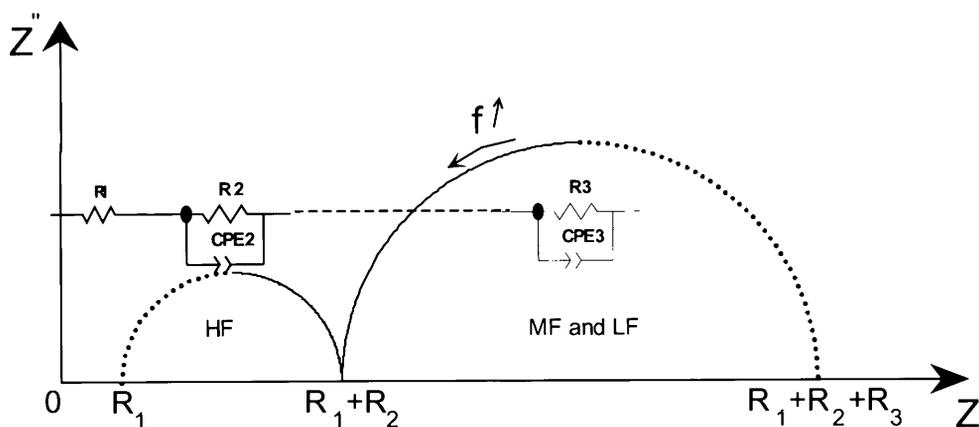
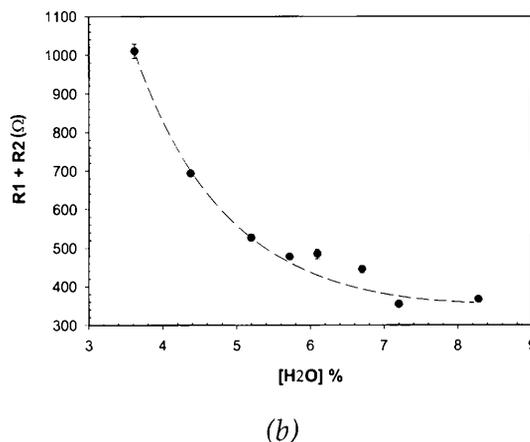
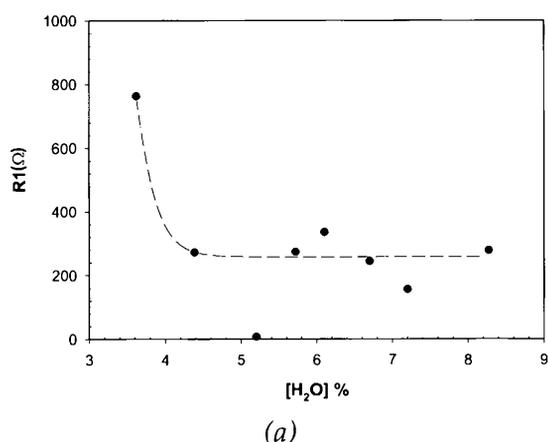


Figure 8. Theoretical representation of the semi-circles in a complex plane plot

The evolution of some characteristic parameters like the ohmic loss ( $R_1$ ), the impedance value corresponding to the intersection between the two semi-circles ( $R_1+R_2$ ) and the two phase angles ( $CPE_2-P$  and  $CPE_3-P$ ) as a function of the pressed samples composition are reported in the figures 9, 10 and 11.



Figures 9.a. and 9.b. Evolution of the characteristic parameter  $R_1$  and the sum ( $R_1+R_2$ ) as a function of the water concentration in the pellets

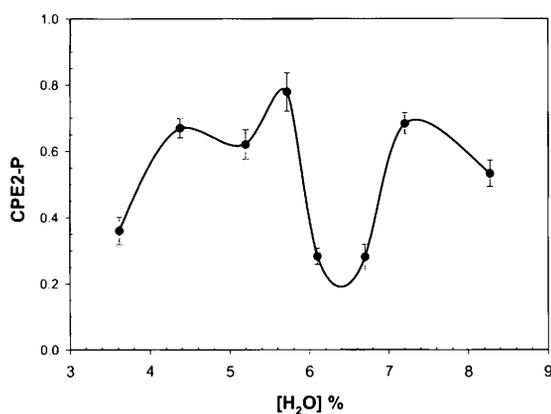


Figure 10. Evolution of the characteristic parameter  $CPE_2-P$  as a function of the water concentration in the pellets.

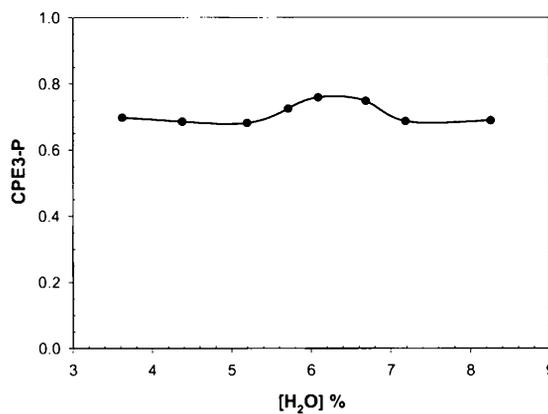


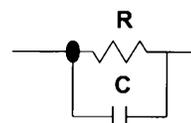
Figure 11. Evolution of the characteristic parameter  $CPE_3-P$  as a function of the water concentration in the pellets.

### 3. RESULTS AND DISCUSSION

The association of a resistance in parallel with a constant phase element (CPE) is represented in a Bode diagram by a semi-circle which is not centred on the  $Z'$  axis. The CPE represents the discrepancy from an ideal Debye-like behaviour of the pressed samples and describes the "power-law" dependence of the impedance components on frequency. The phase angle CPE-P is representative of the angle between the straight line linking the semi-circle centre and the origin of the graph (CPE-P is equal to 1 when the centre of the semi-circle is on the X-axis and to 0.5 when it is on the Y-axis).

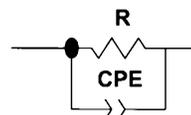
In its simplest form, the equivalent circuit for an "ideal", Debye-like, system is represented by a single parallel R-C element and the impedance and the admittance are given by :

$$Y = (Z)^{-1} = \frac{1}{R} + j\omega C \quad \text{where} \quad j = \sqrt{-1}$$



The CPE describes the "power-law" dependence of the impedance components on frequency and the equivalent circuit is modified and represented by a R-CPE element obeying to:

$$Y = \frac{1}{R} + A\omega^n + jB\omega^n$$



For  $n = 1$ , the equation corresponds to a Debye-like equation (R-C) and for  $n = 0.5$ , the impedance corresponds to a diffusion reaction and is called "Warburg impedance".

The non-Debye behaviour is mainly due to a physical phenomenon : the polarisation of the particles induces discontinuous jumps in charge transport and a finite number of dipoles cannot follow the polarisation changes due to the alternative current. Practically, the samples, hold between the two electrodes, form a porous dielectric element and the liquid fill more or less in the pores. Each constituent, acting like a dipole, reacts differently under the alternative current.

In the pressed samples, the use of non-Debye capacities in the equivalent circuit means that the charge transport is mainly due to a charge transfer across the particles.

The experimental curves, drawn in figure 3, can be described by the equivalent circuit shown in figure 7. This equivalent circuit is composed of three parts :  $R_1$  (the ohmic loss),  $R_2$  and  $CPE_2$  corresponding to the semi-circles in the high frequencies range and  $R_3$  and  $CPE_3$  representing the semi-circles in the medium and low frequencies domain.

When submitted to a high frequency polarity variation, all the components of the system cannot follow the switch; only the more movable elements can respond to the movement. So, the second element ( $R_2, CPE_2$ ) of the suggested equivalent circuit can be attributed to the amount of water in the prepared pellets and to the filling of the pores.

The semi-circles at high frequencies do not exhibit a change of behaviour for a particular composition of the green pressed samples but are proportional to the quantity of water added.

On the other hand, at medium and low frequencies, the semi-circles, simulated by the third part of the equivalent circuit ( $R_3$ ,  $CPE_3$ ), shows a key value for the pressed sample containing 6.1 % of water. At medium and low frequencies, even the water molecules dipoles forming the Helmholtz layer are able to follow the polarity change of the imposed sinusoidal tension. This third element can be interpreted as the image of the behaviour of the part of the double layer being responsible of the interaction between the solid particles and the water. This interaction water-solid particles is attributed to cohesion forces between the clay based particles and ensure the mechanical resistance of the green pellets. The optimal value corresponds then to a material containing 6.1 % of water.

### 3.1. OHMIC LOSS

The value of the resistance  $R_1$ , representing the ohmic loss of the system at an infinite value of the frequency, decreases with the addition of water in the pressed samples. This parameter is therefore an image of the global conductivity of the system. The resistance  $R_1$  decreases more slowly and tends to a constant value when the amount of water increases (figure 9.a.).

In fact, for the lower amounts of water in the pressed samples, the ohmic loss can be considered as the sum of three terms : the resistance of the solution (water in this case), the solid particles and the air in the porosity of the system. When the pressed samples contain enough water (more than about 6 %) to ensure the mobility of the free ions between the particles, there is no more air in the pores and the conductivity is mainly due to the conductivity of water (which is larger than the conductivity of air) and becomes more stable.

The value of the resistance  $R_1$  (at an infinite frequency) (figure 8) is a calculated value for the proposed equivalent circuit by the software and a fitting error has to be charged to  $R_1$ . This parameter is then an approached value. If the sum ( $R_1+R_2$ ), which is in fact the impedance absolute value corresponding to the intersection between the two semi-circles, is plotted as a function of the water contained in the pressed samples, the curve exhibits the same shape but the values are experimental ones and then, more representative of the real behaviour of the system (figure 9.b.).

### 3.2. PHASE ANGLES $CPE_2$ -P AND $CPE_3$ -P

The figures 10 and 11 represent the evolution of the phase angles of the two successive constant phase elements  $CPE_2$ -P and  $CPE_3$ -P with the composition of the green pellets. The two plots exhibit an optimum for the sample containing 6.1 % implying a change of behaviour of the studied system.

As said previously, the use of a non-Debye capacity (CPE) implies that the charge transport is due to a charge transfer reaction. In the high frequencies range, the corresponding part of the equivalent circuit is composed of  $R_2$  and  $CPE_2$ .

The phase angle,  $CPE_2$ -P (figure 10) plot can be divided in two parts delimited by the key concentration of 6.1 % of water. In pressed samples prepared with low concentrations of water, the charge transfer is performed by the water molecules fixed on the surface of clay based particles in the Helmholtz layer and the studied system is composed of water and solid particles but also of air.

An instability appears for the value of 6.1% of water due to the fact that all the pores are filled and the charge transfer is suddenly disturbed and ensured by the particles in the double layer as well as by dissolved ions in the free water. Over that value, the system becomes again stable.

The signification of the phase angle is commonly described as the image of instability and inhomogeneity in the studied system. The sudden jump of the  $CPE_2$ -P phase angle to a lower value can be explained by the transformation of the ternary system (solid particles-water-air) to a binary system (disappearing of air in the green pressed pellets).

The third element phase angle plot ( $CPE_3$ -P), corresponding, as said before to the interaction between the solid particles and the water, is reported in figure 11 and the points coordinates are more constant and closer to 1 because the system ( the fixed molecules of water on the surface of particles) is stable and exist even at low concentrations of water. A small variation in the curve can be observed for the same key value as previously observed in the  $CPE_2$ -P plot and is due a rearrangement of the particles and the dissolved ions in the free water (the dissolved ions can move through the free water because of the disappearance of air in pressed samples containing more than 6.1%).

#### 4. CONCLUSIONS

The impedance spectroscopy technique can be successfully applied to analyse the green pressed samples properties. The main conclusions of this study are the following ones:

(a) the impedance spectra can be fitted using an equivalent circuit composed of three impedance elements; the use of constant phase elements explaining the charge transfer phenomenon;

(b) the analysis of experimental impedance spectra allows us to understand the physical behaviour of the green samples. The two semi-circles plotted using the experimental data can be attributed to the filling of the pores and to the influence of the cohesion forces between the Helmholtz layers of the solid particles;

(c) the characteristic parameters evolutions exhibit a key-value of the water concentration in the samples of 6.1%. This amount of lubricant is the minimum value to allow a complete filling of the porosity and then, to ensure a good homogeneity. When the quantity of water is higher, the cohesion forces between the particles are not large enough to ensure the handiness of the product after pressing. This composition also corresponds to the best industrial results.

The impedance spectroscopy is then a practical method to analyse the internal structure and the properties of green pressed samples but also to determine the water

amount giving the adequate properties to the clay based product which is prepared; the shaping step can then be successfully achieved without any appearance of defects.

## 5. ACKNOWLEDGEMENTS

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