Pergamon

Cement and Concrete Research, Vol. 27, No. 8, pp. 1191–1201, 1997

0008-8846/97 $17.00 + .00

PII S0008-8846(97)00117-8

IMPEDANCE MEASUREMENTS ON CEMENT PASTE

M. Keddam and H. Takenouti
UPR15 CNRS, Université Pierre et Marie Curie, 75252 Paris Cedex 05, France

X.R. Nóvoa
Universidad de Vigo, E.T.S.E.I., Lagoas-Marcosende, 9; 36280 Vigo, Spain

C. Andrade and C. Alonso
Instituto Eduardo Torroja, C.S.I.C., Apartado 19002, 28080 Madrid, Spain.

(Refereed)
(Received April 8, 1996; in final form June 17, 1997)

ABSTRACT

The present paper is devoted to the study of the high frequency region of the impedance spectrum, and focused at determining the origin of the time constants in the impedance and their relation to the dielectric properties of cement paste. The origin of the intermediate frequency capacitive range was investigated by intercalating polyester sheets between the paste sample and the graphite electrodes. It was concluded that the dielectric constant of cement paste can be determined only when impedance measurements are performed to frequencies higher than 10 MHz. Oven dried cement paste presents a single almost perfect capacitive behaviour with a dielectric constant, ε, below 10. In partially moistened cement paste the higher frequency range gives a reasonable ε ($\approx$80) for awater containing material. It is concluded that the interpretation of the high values of ε in terms of the DAF effect does not seem correct. © *1997 Elsevier Science Ltd*

Introduction

Electrochemical techniques are currently used to study the corrosion of reinforcements embedded in concrete. D.C. techniques such as the so called Polarization Resistance Method have been the most widely used (1-3). The use of A.C. ones, namely Electrochemical Impedance Spectroscopy (EIS), have steadily increased during the last decade (3-5).

The EIS data obtained from steel bars embedded in concrete are usually represented as Nyquist and/or Bode plots. These plots show in general more than one time constant, often three which leads to differentiate consequently three main regions: high, medium and low frequency regions. The high frequency region corresponding to frequencies higher than several tens of hertz, the medium frequency region being in the range of several hertz, and the low frequency region corresponding to the part of the spectrum at frequencies lower than several tenths of hertz.

The response of the system in the medium frequency region was attributed to the corrosion process, while the response in the low frequency region would correspond to a redox process taking place in the steel passive layer (6). The response in the high frequency region was related either to the bulk concrete properties (7-8) or to the interfacial (4) properties of the concrete.

The high frequency region was studied with interest in the last few years because some authors tried to correlate the electrical response of the concrete to physical characteristics of its micro-structure (9-11). However, while in some cases reasonable values for the dielectric constant of the concrete are reported (8) much higher values of the dielectric constant, in the range of 10^2-10^5 are also found (9-11). Obviously, such high values are well beyond the expected range for a material as concrete and were tentatively accounted for on the basis of a Dielectric Amplification Factor (DAF) mechanism (9).

The present paper is devoted to the study of the high frequency region of the impedance spectrum, and focused at determining the origin of the time constants in the impedance and their relation to the dielectric properties of cement paste. An explanation will be given for the anomalous dielectric constant values reported in the literature for the concrete bulk. Furthermore, an estimation of what seems the correct dielectric constant of the concrete has been performed.

Experimental

Specimens. Cement paste of water/cement (w/c) ratio = 0.4 was cast in mould of 4 × 4 × 16 cm and cured during 24 hours in atmosphere having relative humidity (RH) > 95%. Afterwards the specimens were held in plastic bags until testing in order to avoid premature drying.

Before testing, the specimens were cut in slices of different thickness, although the present results deal only with those one centimeter thick. The samples were then abraded until obtaining perfectly parallel plane specimens of 4 × 4 × 0.8 cm.

Flexible graphite square sheets of 4 cm side were used as electrodes to apply the electric signal through the 0.8 cm specimen. The graphite/cement/graphite specimens were tightly pressed to avoid air trapping at the specimen/graphite interface during impedance measurements.

To eliminate any faradaic contribution due to the conducting electrodes, a series of experiments were performed by intercalating polyester sheets 100 μm thick between the specimen and the graphite electrodes, as shown in Figure 1.

The specimens were then conditioned at different R.H. However, due to the aim of the present paper, only the results at R.H. ~ 50% and ~ 0% will be discussed. These two testing conditions correspond respectively to the room temperature and one hour oven drying at 150°C then cooled at room temperature.

Technique and Equipment. Impedance measurements were performed with the two-electrode arrangement depicted in Figure 1. This measuring cell was directly wired to a Impedance/Gain-Phase Analyser (HP 4194A). This apparatus allows to measure capacitance in the range of 10 fF to 100 mF having a maximum resolution of 0.1 fF.

Data Processing. The impedance data have been fitted using the impedance function, Z, defined in equation 1 which corresponds to the circuit displayed in Figure 2:

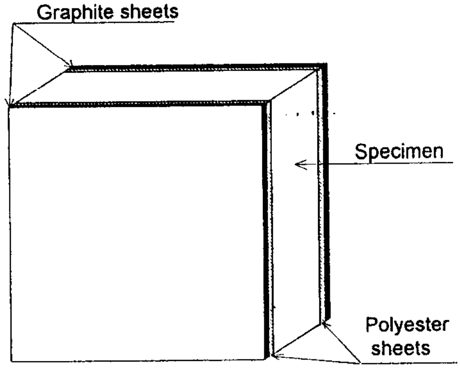

FIG. 1.
Schematic representation of the electrode arrangement for impedance measurements. Polyester sheets are removed in some experiments.

$$Z = R_c + \sum_{i=1}^{3} \frac{R_i}{1+\left(j\omega R_i C_i\right)\alpha_i} \tag{1}$$

R_c being the contact resistance, $j = \sqrt{-1}$, $\omega = 2\pi f$, C_i the capacitance and α_i the degree of dispersion of the time constant R_iC_i (12). $0 \le \alpha_i \le 1$.

It is important to note that:

a) The minimum number of time constants R_iC_i necessary to reproduce properly the experimental data are used,
b) For the fitting calculation, the not in use R_i and C_i are set to such values that they do not contribute to the overall impedance (low R_i and high C_i values).
c) The equivalent circuit in Figure 2 is one of the several possible equivalent circuits able to fit the impedance data. However, the arbitrary selection of the circuit in Figure 2 does not affect the conclusions of the present paper.

The fitting procedure is based on the algorithm by Nelder and Mead (13) which uses the SIMPLEX method to find the minimum of a function. For the present case, the function to minimise, χ^2, is defined as:

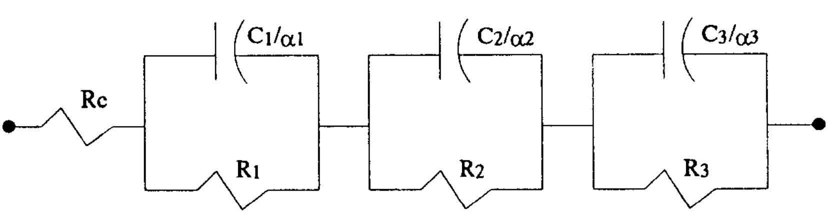

FIG. 2.
Equivalent circuit used to fit the different experimental impedance data. C/a characterizes a Constant Phase Element (CPE).

$$\chi^2 = \sum_{i=1}^{N}\left[\left(\frac{a_{ei} - a_{ci}}{0.01\,|\,Z_{ei}}\right)^2 + \left(\frac{b_{ei} - b_{ci}}{0.01\,|\,Z_{ei}}\right)^2\right] \tag{2}$$

where N is the total number of scanned frequencies; a_{ei} and b_{ei} the real and imaginary parts of the experimental impedance Z_{ei}, $|Z_{ei}|$ the experimental impedance modulus at frequency **i**, and a_{ci} and b_{ci} the corresponding real and imaginary parts of the calculated impedance at frequency **i**. Equation 2 implies that the experimental error is estimated as 1% of the impedance modulus and randomly distributed in the real and imaginary parts. If these hypotheses are fulfilled, then the fitting quality factor, **q**, will be close to 1, being:

$$q = \sqrt{\frac{\chi^2}{2N - Np}} \tag{3}$$

where N is the total number of scanned frequencies, and Np the number of variables in equation 1 to be fitted.

Results

Figure 3a shows the impedance spectrum for the cement of RH ~ 0%. The experiment was performed without polyester sheets in the cement/graphite interface. Only one capacitive branch can be identified. The experimental data were fitted using a single parallel RC circuit. The results of parameter fitting are given in Table 1 and the comparison of experimental and fitted data are shown in Figure 3b. If this time constant is assumed to correspond to the dielectric characteristics of the cement paste, the fitted capacitance value (0.84 pF/cm^2) should correspond to the capacitance, C, of a parallel plate capacitor for which equation 4 is applicable:

$$C = \frac{\varepsilon \cdot \varepsilon_0 \cdot S}{d} \tag{4}$$

S stands for the surface area of the plates, **d** the distance between the plates, $\boldsymbol{\varepsilon_0}$ the vacuum permitivity ($8.854\ 10^{-14}$ F/cm) and $\boldsymbol{\varepsilon}$ the relative dielectric constant of the material between plates.

As for the studied specimen $d = 0.8$ cm, a value of $\varepsilon = 7.6$ is obtained using equation 4. A dielectric constant value below 10 seems reasonable for a material as dry cement. Strictly speaking, C is a constant phase element, that is, the C value is depending on the frequency at which the capacitance is determined according to equation 5.

$$C = C_0 \cdot \left(\frac{\omega}{\omega_0}\right)^{\alpha - 1} \tag{5}$$

ω is the angular frequency, and the subscript "0" refers to the frequency at which the capacitance is determined. However the value of α is close to one (0.97), i.e., the frequency dependence of C is negligibly small in the present case. It is important to stress the fact that only one time constant is found in the frequency range explored while several capacitive

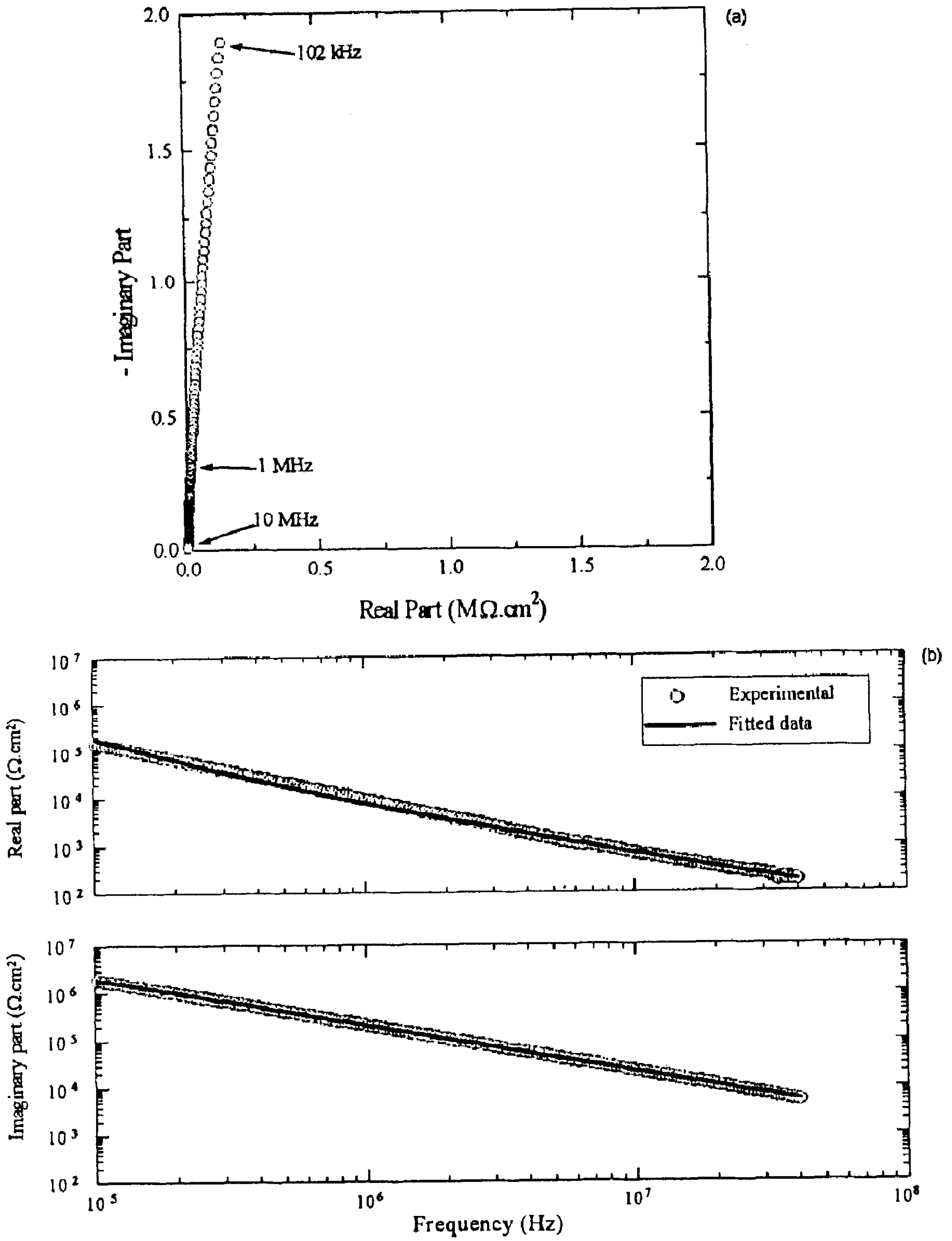

FIG. 3.
a) Impedance spectrum in Nyquist plane for the oven dried specimen (one hour at 150°C).
b) Comparison in Bode plane of experimental (circles) and fitted (solid line) data displayed in Figure 3a. The fitting parameters are given in Table 1.

TABLE 1

Fitting Parameters Obtained Using Equation 2 for the Different Model Circuits Used to Fit the Data in Figures 3, 4 and 7. The Impedance for the Different Model Circuits is Defined in Equation 1. The Fitting Quality Factor, q, is Defined in Equation 3

	Rc $\Omega.cm^2$	R_1 $\Omega.cm^2$	C_1 $pF.cm^{-2}$	α_1	R_2 $\Omega.cm^2$	C_2 $nF.cm^{-2}$	α_2	R_3 $M\Omega.cm^2$	C_3 $\mu F.cm^{-2}$	α_3	q
Fig. 3	11.0	$29 \cdot 10^6$	0.84	0.97	-----	-----	-----	-----	-----	-----	1.29
Fig. 4	299	3542	9.5	0.89	19600	0.53	0.52	31	0.53	0.64	2.01
Fig. 7	0.03	5900	8.3	0.90	$1 \cdot 10^{18}$	2.0	0.90	----	----	----	0.91

loops in the Nyquist plane are found for ceramic materials (14). This difference can be attributed to the colloidal nature of hydrated cement phases which form a continuous bulk (gel) without defined grains, as it is the case for the referred ceramic materials.

When the specimen is held at room RH, the response to the A.C. perturbation is shown in Figure 4. The comparison between the spectra in Figures 3a and 4 shows a dramatic change in the response of the system due to the different degree of RH. In Figure 4, instead of one capacitive branch, a capacitive arc centred at about 8 MHz, followed by another capacitive loop, though not clearly distinguished, around 100 kHz and a tail for frequencies lower than 10 kHz are observed. These results are consistent with the previous one (15). This impedance spectrum was fitted with three series RC circuits (Figure 2), and fitted results are displayed in Table 1. In the literature work, often the frequency range is limited up to a few MHz and the time constant appeared at higher frequencies was regarded as irrelevant to the paste properties (9). Determining the dielectric constant on the basis of C_2 provides a value in the order of 16.10^3. Whilst, if C_1 is used, $\varepsilon = 85.8$ is obtained, a value far more consistent for a moistened cement paste.

At the same room R.H. the experiments were repeated after introducing the polyester sheets between the specimen and the graphite foils (Fig. 1) to avoid any contribution of faradaic effects at the graphite surface in the overall impedance. The result is depicted in Figure 5. Again, a marked difference is observed compared with the results in Figure 4. Solely one capacitive branch with a inflection around 1 MHz is observed.

Additionally, the polyester sheets were tested alone, Figure 6 summarizes these results. As expected, a nearly purely capacitive behaviour is revealed.

Since the polyester sheets are placed in series with the specimen, their own contribution to the overall spectrum in Figure 5 can be removed by direct subtraction of impedance data in Figure 6 from those in Figure 5. The result is expected to correspond to the impedance of the cement paste in the presence of an electrically (ionic and electronic) blocking boundary on both faces of the sample. Figure 7 displays the result, the shape of the Nyquist plot remains roughly similar to that in Figure 5.

The impedance data in Figure 7 can be fitted using two time constants. The fitted parameters are given in Table 1. In this calculation, the value of R_2 is fixed arbitrary (not adjusted) to 1.10^{18} to match the blocking character of the observed impedance. Using the C_1 value, a dielectric constant $\varepsilon = 75$ can be obtained, which continues being compatible with a moistened cement paste.

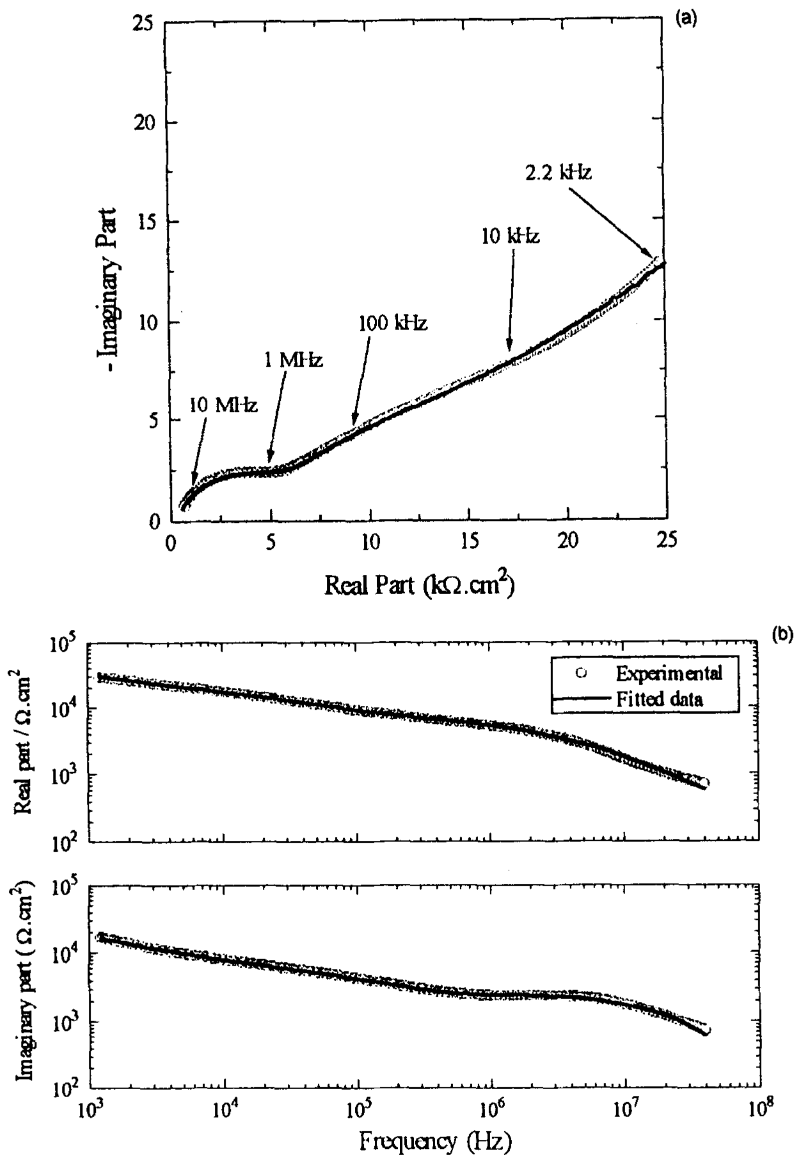

FIG. 4.

a) Impedance spectrum for the specimen at room RH. Experimental (circles) and fitted (solid line) data are presented. The fitting parameters are given in Table 1. b) Comparison in Bode plane of experimental and fitted data displayed in Figure 4a.

Discussion

Impedance of the oven-dried specimen (Fig. 3a) shows only one capacitive branch corresponding to a dielectric constant of $\varepsilon = 7.6$. However, this is not the case of the wetted specimen (Fig. 4a) which shows, in the high frequency domain, the typical depleted semicircle reported by other authors (7-9). The origin of this depletion was investigated by interca-

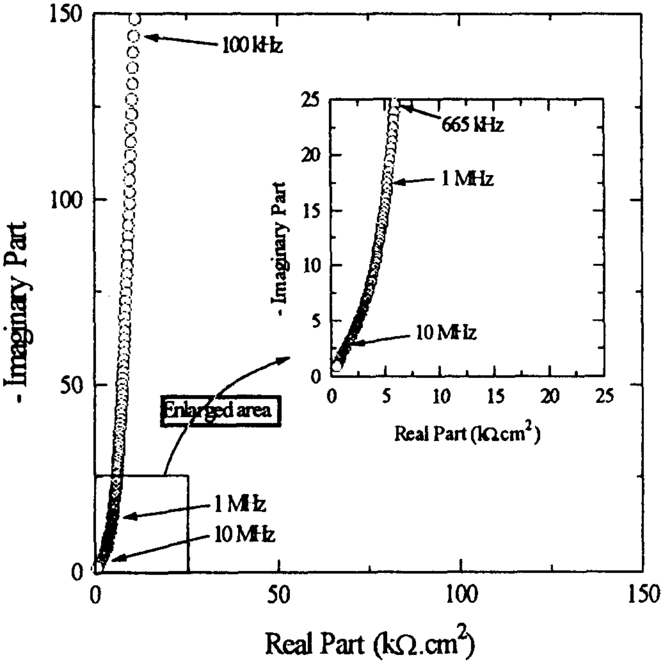

FIG. 5.

Overall impedance spectrum for the specimen at room RH. Polyester sheets are introduced at the graphite/specimen interface, as shown in Figure 1.

lating polyester sheets between the paste sample and the graphite electrodes. If a single time constant is assumed, an abnormally large dielectric constant calculated from this capacitive response, ranging 10^2-10^5 is found. This large value has been tentatively explained by the so-called (DAF) (9). However, present results show that this response dramatically changes if polyester sheets are intercalated between the paste sample and the graphite electrodes. This fact suggests that the high frequency response, attributed to the cement paste (9), actually results from the combination of two different time constants: one corresponding to the paste bulk (that at frequency range around MHz) and the other one to the paste/electrode interface (1MHz to 100 KHz in Figure 4).

This last time constant appears to be due to some interfacial effect still not well understood. It cannot be due to the electrode double layer, as its response appears at lower frequencies and is well characterised by the R_3C_3 time constant in present results (Fig. 4). It can be neither attributed to any paste bulk feature, as wall pore roughness, (the DAF effect). However, the roughness of the paste/electrode interface may play a role.

The interfacial origin is confirmed by impedance measurements on the wet sample insulated from conductive electrodes by the polyester sheets (Fig. 7a). Only the high frequency arc was obtained. As expected, in series with this high frequency arc a capacitance is observed due to the charge build-up at the blocking interfaces of the polyester. The corresponding R_1 and C_1 are close to their values for the same sample contacting metallic electrodes (Fig. 4a and Table 1). These results suggest that the interpretation of the high values of the dielectric constant, claimed in the literature by a DAF effect, is not correct.

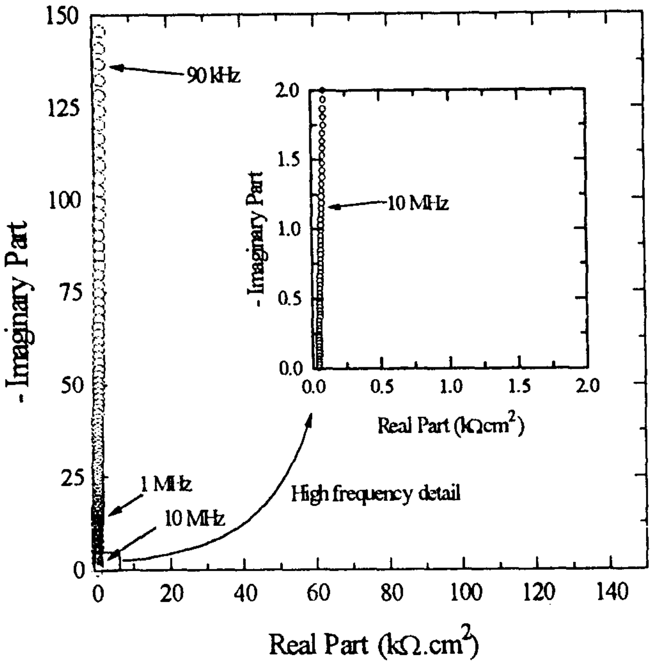

FIG. 6.
Impedance spectrum for the polyester sheets.

Conclusions

The results reported in the present work have enabled drawing up the following conclusions:

1.) The dielectric constant of cement paste can be determined only when impedance measurements are performed to frequencies higher than 10 MHz.
2.) Oven dried cement paste presents a single almost perfect capacitive behavior with a dielectric constant below 10.
3.) In agreement with literature data, partially moistened cement paste presents several capacitive time constants. Again, the higher frequency range gives a reasonable dielectric constant (≈80) for a water containing material. The large capacitance in the mid-range frequency, (1MHz-100KHz) recently ascribed to the composite properties of the moistened paste through the DAF model, is much more likely arising from some interfacial phenomenon as shown by using insulated electrodes. This aspect of the present work will be further investigated in a forthcoming paper.

Acknowledgements

The authors are grateful to the French Program Picasso and the Accion Hispano-Francesa for having supported their joint cooperation.

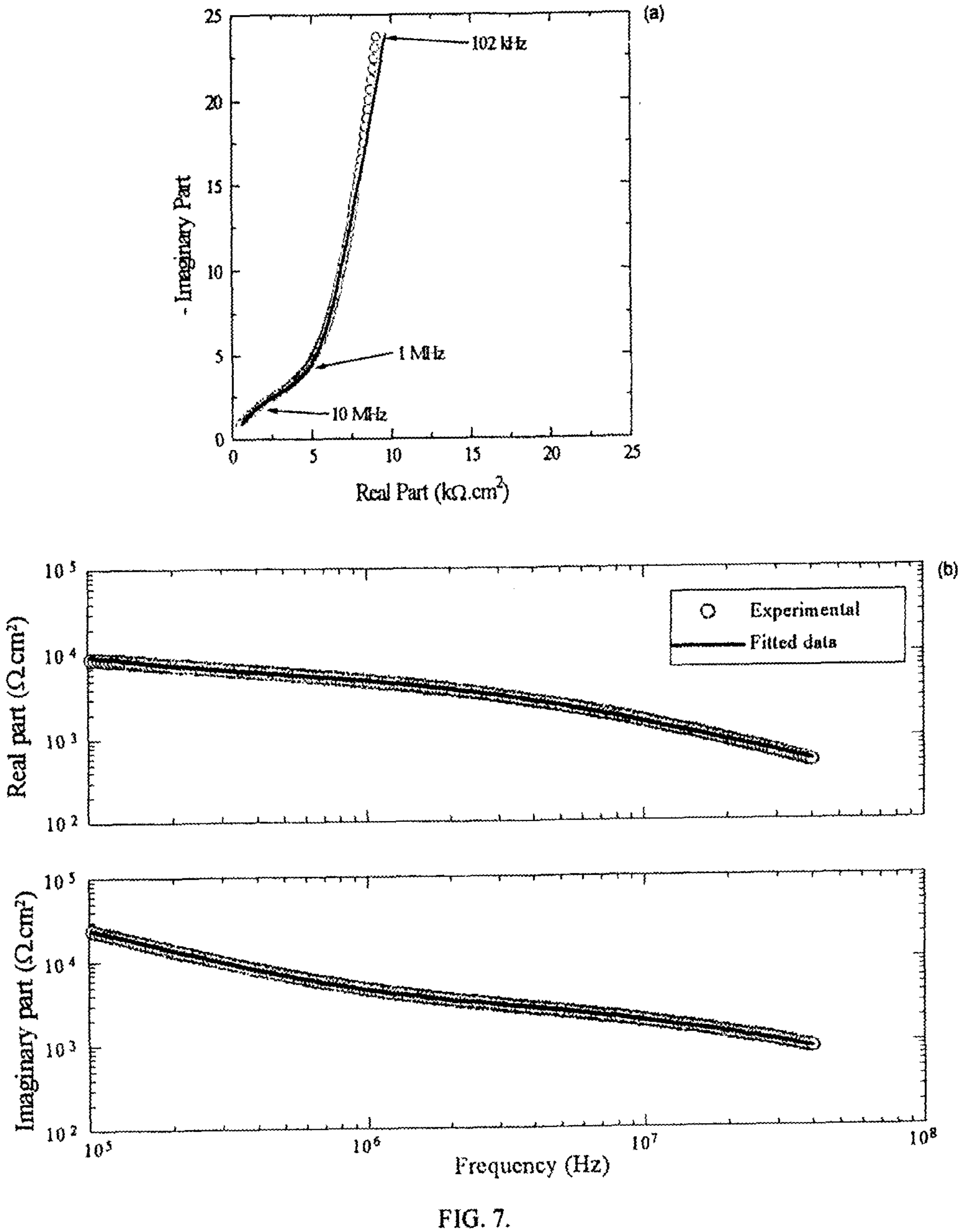

FIG. 7.

a) Impedance spectrum for the specimen at room RH after subtracting the polyester sheets contribution. Experimental (circles) and fitted (solid line) data are presented. The fitting parameters are given in Table 1. b) Comparison in Bode plane of experimental and fitted data displayed in Figure 7a.

References

1. C. Andrade, J.A. González, Werkst. Korros. 29, 515 (1978).
2. P. Lambert, C.L. Page, P.R.W. Vassie, Mater. Struct. 24, 351 (1991).

3. A. Sagüés, NACE-Corrosion 87, 118 (1987).
4. D.E. John, P.C. Searson, J.L. Dawson, Br. Corros. J. 16, 102 (1981).
5. C. Andrade, V. Castelo, C. Alonso, J.A. González, ASTM STP 906, 43, ASTM, New York, 1986.
6. C. Andrade, P. Merino, X.R. Nóvoa, M.C. Pérez, L. Soler, Mater. Sci. Forum, 192-194, 891 (1995).
7. W.J. McCarter, R. Brousseau, Cem. Concr. Res. 20, 891 (1990).
8. Zhongzi Xu, Ping Gu, Ping Xie, J.J. Beaudoin, Cem. Concr. Res. 23, 853 (1993).
9. B.J. Christensen, R.T. Coverdale, R.A. Olson, S.J. Ford, E.J. Garboczi, H.M. Jennings, T.O. Mason, J. Am. Ceram. Soc. 77, 2789 (1994).
10. B.J. Christensen, T.O. Mason, H.M. Jennings, J. Am. Ceram. Soc. 75, 939 (1992).
11. Ping Gu, Ping Xie, Yan Fu, J.J. Beaudoin, Cem. Concr. Res. 24, 86 (1994).
12. J.R. Macdonald, W.B. Johnson, Impedance Spectroscopy, 90, J.R. Macdonald Ed., J. Wiley, New York, 1987.
13. J.A. Nelder, R. Mead, Computer Journal 7, 308 (1985).
14. P. Durán, J.R. Jurado, C. Moure, Mater. Chem. Phys. 18, 287 (1987).
15. W.J. McCarter, S. Garvin, J.Phys. D: Appl. Phys. 22, 1773 (1989).