Use of impedance spectroscopy to determine the displacement of water in cement paste under small loads

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Abstract

The effect of mechanical loading in concrete structures may cause deformation by creeping. The physical origin of this phenomenon is not well known, but water seems to play an essential role in it. Impedance spectroscopy in the high frequency region can detect water movements towards empty pores, even when the applied load is small. In this paper a system for application of mechanical loading compatible with simultaneous impedance spectroscopy measurements is presented. The effect of several parameters (ageing, water to cement ratio, water content) on cement paste samples' performance under mechanical loading is analysed through the corresponding impedance spectra.
Keywords: impedance spectroscopy, cement paste, microstructure, dielectric properties, mechanical loading.

1 Introduction

Real concrete structures are designed to be mechanically loaded. The effect of the deformation of a structure under a constant load is called creeping and is a classical phenomenon well described in the literature [1, 2]. This effect has a great dependency on some factors such as temperature and relative humidity [1, 3]. The microstructural mechanism that leads to the effect of creeping is still not well known, although water plays an essential role in almost every theory on

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the subject [4]. This phenomenon is related to microstructure of cementicious materials. In recent years impedance spectroscopy has been adopted as a technique to study the microstructure of cementicious materials, due to the possibility of correlating dielectrical and mechanical properties [5, 6]. Even though the first works on this field considered de presence of only one time constant in the high frequency loop of the impedance spectra [7, 8] it has been shown that two time constants are present [9]. This has been done using a numerical technique, differential impedance analysis, which does not require previous knowledge about the material studied [10, 11]. The two time constants have been associated to the two phases present in the material. The high frequency time constant was associated to the solid phase, while the low frequency one was associated to the electrolyte filling the pores. This association has been proved using different experiments [12]. If water has something to do with creeping, then the time constant associated to the electrolyte will vary during loading and unloading of samples. A work published in 2003 showed the effect of mechanical loading on the dielectric properties of cement pastes [13]. This effect consisted in an increase of the capacitance and a decrease of the resistance associated to the electrolyte in pores, and was interpreted in terms of water displacements to empty spaces in the microstructure of the material.

In this work, some parameters of the samples are varied and the effect of loading is studied. The load was applied using a new system designed for this application.

2 Experimental

2.1 Sample preparation

Samples were prepared using CEM I 52.5R cement according to the Spanish standard UNE 80303:96. Two different water to cement ratios, 0.5 and 0.7, were employed. The mixtures were cast in cylindrical moulds of 5.9 cm diameter and 20 cm height. Samples were kept in 100% RH chamber and demoulded after one day setting. Several discs, thickness form 3 to 10 mm, were cut from those cylinders for the impedance spectroscopy measurements. The remaining material was used for mercury intrusion porosimetry determinations.

2.2 Mercury intrusion porosimetry

Mercury intrusion porosimetry (M.I.P.) was used to determine the time evolution of the microstructure of cement paste samples, in order to validate the microstructural modifications detected with the impedance spectroscopy measurements. Even though there are many facts suggesting that this technique is not optimal for pore size measurement [14, 15], it is widely used to determine pore sizes and distributions.

The pore structure of different samples, at different time of exposure to chloride migration was determined using this technique, which is based on the

Washburn law, where a relation between applied pressure, P, and pore diameter, D, is given, under the hypothesis of cylindrical pores, by Equation (1).

$$D = -\frac{4\gamma\cos\theta}{P} \tag{1}$$

where γ is the surface tension of the mercury (0.485 $N \cdot m^{-1}$, at room temperature) and θ is the contact angle. There has been recently some discussion on the effect that different types of drying have on the MIP measurements [16, 17]. In this work samples were vacuum dried for 48 hours and then kept in oven at 50ºC. This procedure assures that no structural water is evaporated. With this preparation, the chosen value for the contact angle was 130º. To ensure that samples used for this measurements were representative they were cut off core cylinders with irregular and random shapes.

The porosimeter employed was an AUTOPORE IV 9500 from Micromeritics. This porosimeter allows pore diameter determination in the range from 5 nm to 0.9 mm. It has to be considered, as reported by Diamond [14, 15], that only the dimensions of the pore superficial structure can be detected by MIP, and the irregularities in pore shape cannot be determined. Nevertheless, information on the possible tortuosity of pore network can be obtained from the mercury retained in the sample after the end of the porosimetry measurement.

The experiment is quite simple, after getting high vacuum in the recipient containing the sample, the reservoir is filled with mercury, and the intrusion step starts. The pressure applied on the mercury is fixed by the user, and that value of pressure is hold for 10 seconds to permit the mercury filling the pores having the corresponding diameter. The measurement of the volume that penetrates for each pressure gives the amount of pores with the corresponding size [18].

The analysis of the curve in which the logarithmic differential intrusion volume is plotted vs. pore size (or applied pressure), shows the size ranges where pores appear. It is possible to determine the number of pore families that exist in the sample, and the contribution of each one to the total porosity of the sample. A first step consists in fitting the experimental curve to a function including a number of Gaussians equal to the number of peaks present in the curve. The result of this fitting is the central pore diameter for each pore family. The area under each Gaussian curve is related to the contribution of the corresponding pore family to the total porosity. The intrusion curve allows one to determine the volume of mercury intruded in the sample in a particular pressure range. The division of this volume by the overall intrusion volume gives the contribution of the corresponding pore family to the total porosity of the sample.

2.3 Impedance spectroscopy

Impedance spectra of samples were obtained using the method that avoids contact between sample and electrodes, as described in [13].

The electrodes used were of flexible graphite, attached on copper plates of 4 cm diameter, and a foil of polymer was interposed between the graphite sheet and the sample. The thickness of this foil was 100 μm. The impedance analyzer used was an HP4194-A. It permits the measurement in a frequency range from

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100 Hz to 40 MHz. The impedance analyzer allows measurements in a capacitance range from 10^{-14} F to 0.1 F with a precision of 10^{-15} F. The impedance spectra measured are almost purely capacitive, as can be seen in fig. 1(A). A more clear representation corresponds to the Cole-Cole transformation given in fig. 1(B). The equation for this transformation is eq (2).

$$C(\omega) = \frac{1}{j \cdot \omega \cdot Z(\omega)} \tag{2}$$

The impedance spectra in their Cole-Cole representations were fitted to the equivalent circuit already proposed [13]. The fitting to the model was done using a simplex method already described [19].

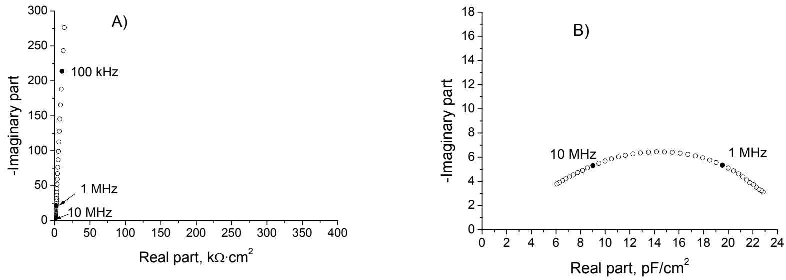


Figure 1: (A) Impedance spectrum obtained for a cement paste sample with w:c ratio of 0.5 and 0.4 cm thickness. (B) Cole-Cole diagram corresponding to (A).

2.4 Mechanical loading system

The objective of this work makes necessary the design of a system to apply mechanical load in a controlled way during the impedance spectroscopy measurements. The main problem that appears when the impedance spectra are measured at such high frequencies comes from the wire's inductance. This fact makes necessary to use connecting cables as short as possible. Thus, it is necessary to design a mechanical loading system to be placed close enough to the impedance analyzer, and that permits the application of known loads. The system designed for that purpose is shown in Figure 2(a). A steel spring is mounted on a mobile screw. A first step consisted in the determination of the elastic constant of the spring. For that purpose, the spring was compressed using a universal testing machine. The values of force and the reduction of length were registered and are shown in Figure 2(b). As it can be seen, the data show linear behaviour, and the slope corresponds to the elastic constant of the spring.

So, just measuring the distance that the spring has moved, with a calibre of 10 μm precision, the applied force can be easily obtained using Hook's law.

The stress is applied to the sample moving a certain distance the screw and the force is applied through the electrodes used for the impedance spectroscopy measurements. The stress applied can be calculated using equation (3)

$$\sigma = \frac{k \cdot \Delta x}{S} \tag{3}$$

where x is the compression of the spring, in mm, S the electrode surface (12.56 cm^2 in this case)

The application of load during the impedance spectra measurements is done in the growing sense. The first impedance measurement is obtained at 0 MPa load, calculated as explained before. Then pressure is applied at regular steps until the end of the experiment.

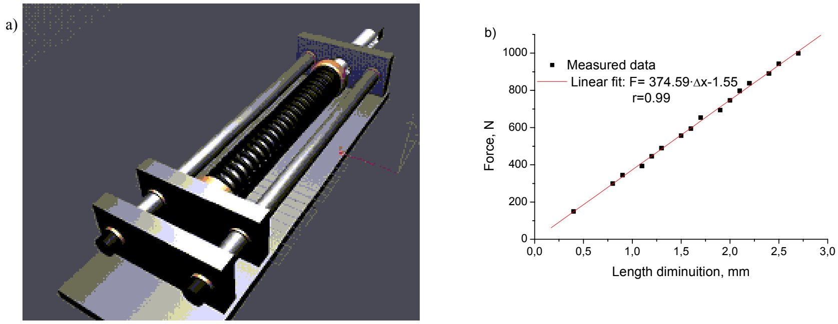


Figure 2: Loading system used and calibration employed for the calculation of the elastic constant.

3 Results and discussion

Three variables have been taken into account to validate the hypothesis of water moving to empty pores. These parameters are water to cement ratio, sample thickness and age of the sample. The effect of each of these parameters has been analysed. The evolution of the microstructure during setting and hardening was followed using mercury intrusion porosimetry.

3.1 Mercury intrusion porosimetry results

Mercury intrusion porosimetry measurements were done on cement paste samples of water to cement (w:c) ratios of 0.5 and 0.7. The results for the total porosity are shown in Figure 3. As it is easily seen, the value of the porosity is always higher for the w:c ratio of 0.7 and has a clear decreasing tendency with time for both ratios.

The analysis of the logarithmic differential intrusion volume as a function of the pore diameter shows the presence of four different pore families for the w:c=0.5, and 3 families for samples with w:c=0.7. The evolution of the central diameters for each family, and the contribution to the total porosity are shown in Figure 4. The central pore sizes have in general a slightly deceasing tendency, but the most important fact that can help us in the understanding of the dielectrical behaviour of samples is the observed change in the contribution to the total porosity of the families for w:c=0.7. The family with the biggest size and the one with the smallest one change their relative contribution at about the

10th day. This result will be used during the discussion of the effect of age on the influence of the mechanical loading on the impedance spectra of cement paste samples.

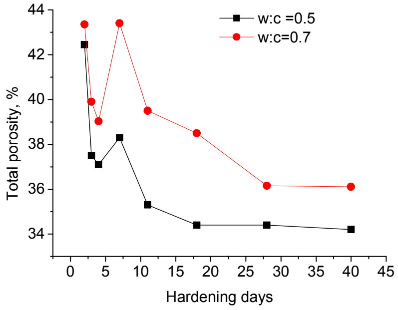


Figure 3: Evolution of the total porosity with the age of cement paste samples.

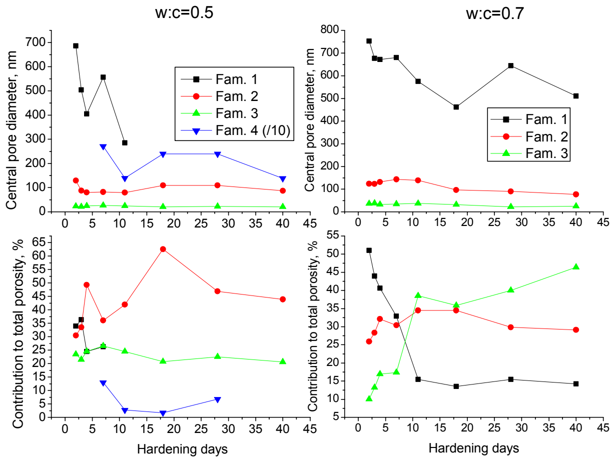


Figure 4: Evolution with time of pore diameters and contribution of each family to the total porosity.

For the w:c ratio 0.5, 4 pore families can be found. An important result is that family four has pore sizes greater than any pore present for w:c ratio 0.7, but the contribution to the overall porosity is not important.

These results will be used for the interpretation of the impedance spectra of cement paste samples under mechanical loading.

3.2 Impedance spectroscopy results

The influence of each one of the factors has been studied separately. The main results are presented in the following subsections.

The variations of all the parameters present in the equivalent circuit have been studied. As expected, the high frequency capacitance C_1, associated to the solid phase, do not vary with applied load, as it has already been reported [13]. A common point for all samples is that the capacitance C_2 increases and R_2 decreases as the mechanical load applied to the sample increases. This fact has been explained in terms of water movement to the empty pores [13]. The influence of sample thickness and w:c ratio was studied with daily impedance measurements. For the sake of simplicity only the evolution of C_2 will be discussed.

3.2.1 Influence of hardening time.

The evolution of the variations of the dielectric parameters was followed during the first 40 days hardening. The effect can be seen in figure 5 for both w:c ratios tested. The effect of loading decreases as hardening progresses, except for day 2 with the w:c ratio of 0.5. This result matches with M.I.P. The decrease in the value of total porosity means that the space occupied by empty pores decreases, and the influence of loading is not so important.

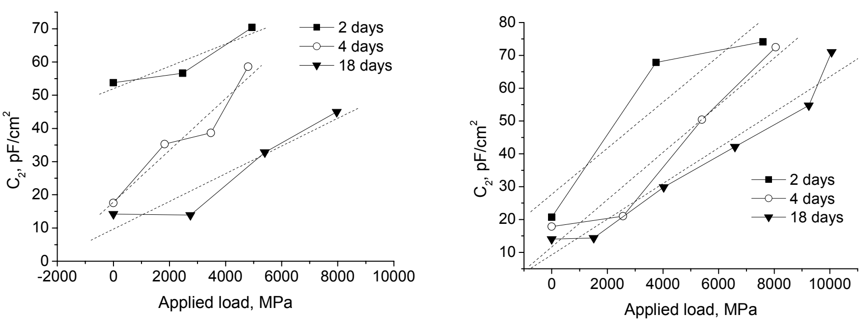


Figure 5: Effect of hardening age on the influence of mechanical loading on the dielectrical properties of cement paste samples. w:c ratio of 0.5 was used for the sample on the left, while 0.7 was the w:c for the sample on the right.

Another factor that can be taken into account is that during the hardening processes structures with higher resistance to load are developed, and in consequence the transmission of loading is less effective.

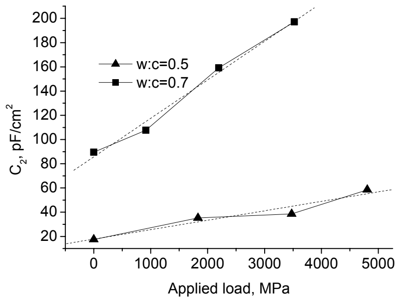
The effect observed for the w:c=0.5 at the second day can be justified in terms of the fraction of empty pores that can contribute to the increase in C_2. The value obtained for the capacitance is really high, much higher than for the 4^{th} and the 18^{th} days. This means, as the results are depicted for the same sample, that at day 2 the sample is almost water-saturated, as proved by the high value obtained for the capacitance C_2 without applied load.

3.2.2 Influence of water:cement ratio

The first factor that has a clear influence on the dielectric response of the samples, is the w:c ratio, and in consequence the sample porosity.

Figure 6 shows the influence of w:c ratio on the effect of mechanical loading for two different ages. The first one corresponds to 2 days maturing age, while the second one corresponds to 40 days age.

As it can be observed in both figures, the value of C_2 is greater for 0.7 w:c ratio than for w:c=0.5. This result can be easily explained in terms of porosity. The volume of pores is greater at any age for w:c=0.7, and the capacitance C_2 has been associated to the interface solid-electrolyte. The greater the porosity is, the more surface of pores exists in the sample. It also coincides with the theory of water movement. The more electrolyte is in the sample, the higher the possibility of water movement.



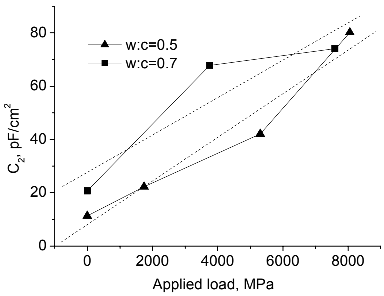


Figure 6: Effect of water:cement ratio on the changes observed in the low frequency capacitance, C_2, at two different ages, 2 days (left) and 40 days hardening (right).

At 45 days age the slopes of the capacitance vs. load for both w:c ratios are more similar. This result coincides with the classical theory for creeping in concrete, which predicts a smaller influence of load on hardened concrete, and also coincides, with the decrease in the total porosity. The slope found for w:c=0.7 is smaller than for w:c=0.5, in agreement with mercury intrusion porosimetry results, that showed a change in the relative contribution of the different pore families. After the 10^{th} day the smallest pore family increases its contribution to the overall porosity. So, most of the porosity is distributed on small pores, that have a smaller contribution to the variations of this capacity, because the space reachable by water in movement is not very big.

3.2.3 Influence of the sample thickness

Samples of different thickness were studied, for the same w:c ratio, and at the same age. It has already been shown [9] that the value of the capacitance C_2 increases as the thickness of the sample does. This means that this capacitance is not of dielectric nature. The influence of sample thickness when the sample is subjected to mechanical loading can be seen in Figure 7.

As it could be expected, an increase in sample thickness leads to smaller influence of mechanical loading on the low frequency capacitance. It is easily explainable in terms of the water movement towards empty pores. The mechanical stresses have more difficulty to transfer when the sample is thicker. This fact has been proved for both w:c ratios.

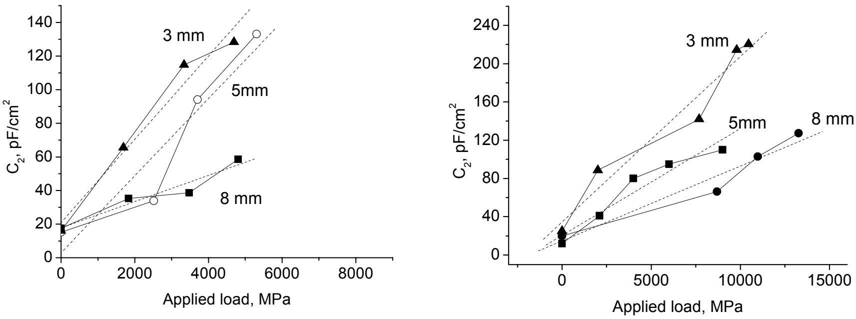


Figure 7: Effect of sample thickness on the changes observed in the low frequency capacitance, C_2, at two different ages, 2 days (left) and 40 days hardening (right).

4 Conclusions

The main conclusions that can be obtained from the results previously discussed can be summarized as follows

- A system for applying a known load allowing simultaneous high frequency impedance measurements has been designed and proved.
- The role of water is important in the creeping of cementitious materials. Several factors have been modified to study their influence on material's dielectric properties under mechanical loading.
- The effect of the possible water movements decreases with the hardening time.
- The effects of loading on dielectric properties are more important for more porous samples (higher w:c ratio).
- Sample's thickness is also of importance as it concerns the effect of mechanical loading. The effect decreases in thicker samples.

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