

# Effect of Fly Ash on Chloride Transport through Concrete: Study by Impedance Spectroscopy.

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## Abstract

In this work we studied the effect of the replacement of Portland cement by different percentages of fly ash. The study covers two points of interest: the microstructure of the mortar, and its resistance to chloride ingress from the environment. The study of the microstructural evolution is done using the impedance spectroscopy technique, which has the main advantage of being non destructive. The diffusion coefficients of chloride ions through mortars are obtained using a well known accelerated migration test. This method permits the calculation of both stationary and non stationary diffusion coefficients in only one experiment. The impedance spectroscopy is also used during the forced migration experiments to determine the variations in the microstructure during the test.

## 1.-Introduction

In recent years the use of active additions on concrete has become quite popular. The particular case of fly ash, and the effect on the properties of the cementitious materials is a topic of study [1, 2]. They are known to reduce the diffusion coefficient of chlorides in concrete.

Chloride ions are responsible of many of the corrosion problems of steel embedded in reinforced or prestressed concrete [3]. These corrosion phenomena can lead to early deterioration and risky situations for the stability of structures. The economical costs of the possible reparations are also important.

Chlorides arrive to the armatures from the environment through the pore paths of concrete most of the times. Though several ingress mechanisms may operate, depending on the environmental conditions, the most studied is diffusion [4, 5]. Big efforts have been made to design test methods of chloride ingress into concrete [6-11]. Some of these methods intend to determine Cl-diffusion coefficient through mortar or concrete. Transport parameters in conjunction with chloride transport models, can be used for service life estimations of new or existing structures [12].

Pure diffusion tests are time consuming and involve big experimental effort for chemical analysis of Cl- content of many samples. Different forced migration tests, based on the application of electrical fields, have been proposed to speed up the transport of ions through concrete specimens [6, 10]. In addition to the

time reduction, this methods permit the determination of both steady-state and non steady-state ionic diffusion coefficients.

In recent years it has been shown that impedance spectroscopy is a powerful technique to study the microstructure and mechanical properties of cement paste, mortar and concrete. It is due to the possibility of correlating dielectrical and mechanical properties of cementitious materials [13-15].

For the concrete-steel system a complete impedance spectra has been described in a previous work [16]. As stated in that work the dielectric properties of concrete appear in the high frequency range (~MHz). The key point in the interpretation of the impedance spectra is the determination of the time constants present in this high frequency range. The differential impedance analysis, proposed by Stoynov [17], applied to the high frequency loop of cementitious materials shows the presence of two time constants [18]. This result confirms the hypothesis proposed in previous works [19, 20] against those who proposed models including only one time constant [21-23]. Impedance spectroscopy allows to follow changes in microstrutrure of cement paste and mortar, using quite simple equivalent circuits to represent the behavior of the material [15]. The non destructive character of this technique, and the possibility of being used in situ, makes it very adequate for the determination of the modifications that occur, during the hardening process and also the modifications induced by forced migration tests, as shown in a recently published work on this field [24].

## **2.- Experimental setup.**

### **2.1.- Sample preparation.**

Mortar samples were prepared using two different types of fly ash cement, with different content in fly ash. Cements used were type CEM II B-V 32.5 R and CEM IV B(V) 32.5 N, both supplied by "Cementos Alfa, Spain". The percentage of fly ash is for CEM II a 25% and for CEM IV a 45%.

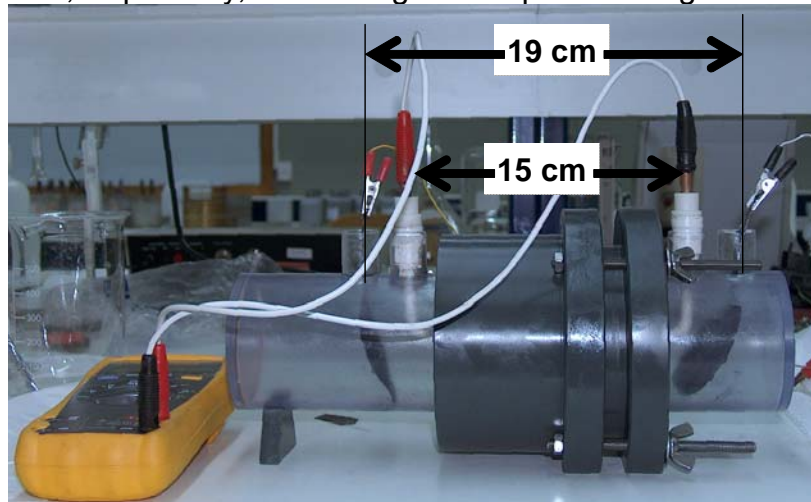
The mortars were prepared with a water:cement ratio of 0.4 and an aggregate:cement ratio of 3:1. After accurate mixing they were cast in cylindrical moulds of 10 cm high and 10 cm diameter. The samples were kept in moulds per 24 hours in a 95% humidity chamber. After demoulding two type of slices were cut off. For the impedance spectroscopy measurements there were taken 4 slices from each mortar type, with different thickness from 0.7 to 1.0 cm. For the forced migration experiments 9 slices of each mortar type were obtained with a thickness of 1.5 cm.

These slices were identified, and kept in the humidity chamber until they were tested.

### **2.2 Forced migration measurements**

The forced migration experiments have been performed following essentially an experimental procedure described in [10], which is based on monitoring the

conductivity of the anolyte. This procedure allows one to obtain both the steady-state and the non steady-state diffusion coefficients with only one experiment. Three mortar samples of each cement type were preconditioned previously to the migration tests, following a standardized water saturation procedure [25]. A typical migration cell is shown in Fig. 1. Each electrolyte container has about 400 ml of capacity and the concrete sample is placed in between with two silicone rings, leaving exposed circular faces of 6.5 cm diameter for the migration test. The driving electrical field is established using circular graphite sheets, to ensure a greater uniformity of the electric field. This kind of electrodes also prevents the formation and deposition of corrosion products from the driving electrodes. The electrodes are placed in the outer orifices of the cell, being 19 cm the distance between them. The inner orifices are used for the electrodes of the impedance measurements, and to measure the potential drop through the sample. After checking the absence of liquid leaks between both electrolyte chambers, the catholyte and anolyte chambers are filled with a 1 M NaCl solution and with distilled water, respectively, and the migration experiment begins.



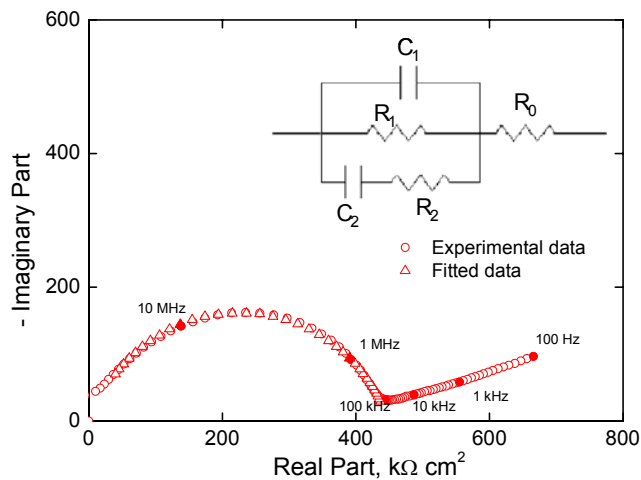
**Figure 1:** Experimental setup used for the forced migration tests. The driving electrodes are placed in the outer orifices and the copper electrodes used to measure the potential drop on the sample in the inner orifices.

The applied driving voltage is 12 V, although the effective potential drop between both sides of the concrete disc is measured periodically by means of two copper rigid electrodes. The electrodes have the right curvature to reach the neighborhoods of the sample without touching it. The experimental configuration is shown in Figure 1. The conductivity measurements of the anolyte solution were performed each 12 hours. These measurements were performed with a Crison GLP31 conductimeter (Barcelona, Spain), with automatic compensation of the readings to 25°C standard temperature. Temperature data of the electrolytes were also recorded. In order to get a more complete information also the conductivity of the catholyte, and the pH of both anolyte and catholyte were recorded every 12 hours.

### 2.3- Impedance spectroscopy measurements

The impedance spectra were obtained using a HP 4294 A impedance gain/phase analyzer. This impedance analyzer permits the measurement in the range from 10-14F to 0.1F having a maximum resolution of 10-15F. The maximum frequency range available is from 40 Hz to 110 MHz

As has already been described (15, 18), different dispositions between the electrode and the sample can be used for the obtention of the impedance spectra. In this case we used a disposition that consists in two circular electrodes, of 7cm diameter in contact with the sample. To achieve a good contact a sheet of flexible graphite was interposed between each copper electrode and the sample. The frequency range used was from 100 Hz to 100 MHz. Even though it has been demonstrated that the better electrode-sample dispositions are those that avoid the contact, and in addition the interfacial effects [18, 20], in this work the contact has been chosen for two main reasons. The first one is that this disposition permits the determination of the conductivity of the sample, a parameter that can be related to the diffusion coefficient. The second reason is that the impedance spectra obtained during the forced migration test always have the electrolyte in contact with the sample, and there is no other possibility to obtain the impedance measurement. So these two reasons justify the choice of the experimental setup.



**Figure 2:** Impedance spectra obtained (circle) for a mortar sample made with CEM II, at the age of 7 days. The thickness of the sample was of 0.8 cm. The equivalent circuit used for the fitting is also depicted, and the result of the fitting. The best fitting parameters are:  $R_0=2986.9 \Omega \cdot \text{cm}^2$ ,  $R_1=445560 \Omega \cdot \text{cm}^2$ ,  $C_1=2.03 \text{ pF/cm}^2$ ,  $\alpha_1=0.798$ ,  $R_2=201.21 \Omega \cdot \text{cm}^2$ ,  $C_2=0.589 \text{ pF/cm}^2$ , and  $\alpha_2=0.799$

A typical example of the impedance spectra obtained is shown in Fig. 2. The impedance spectra were fitted using an equivalent circuit that contains two time constants in the high frequency loop, according to the previously published results [18]. This fitting was made using a Simplex optimization method, well described elsewhere [19]. In Fig. 2, both the equivalent circuit employed as a

model, and the result of the fitting for that spectrum are depicted. The equation that represents the circuit can be written as follows:

$$Z(\omega) = R_0 + \frac{Z_1 \cdot Z_2}{Z_1 + Z_2} \quad (1)$$

$$\text{where } \left( Z_1 = \frac{R_1}{1 + (j\omega R_1 \cdot C_1)^{\alpha_1}} \text{ and } Z_2 = R_2 \cdot (1 + (j\omega R_2 \cdot C_2)^{-\alpha_2}) \right)$$

During the forced migration experiments the impedance spectra was also measured. To obtain the impedance spectrum of the system sample+electrolyte two stainless steel electrodes were used, and placed in the inner orifices of the forced migration cell. The impedance spectra were obtained in the range from 100 Hz to 100 MHz. this measurement was done every 12 hours in coincidence with the conductivity and pH measurement. Some researchers have proposed a modification of the equivalent circuit for the fitting of this kind of impedance spectra [26] including a new time constant  $R_3C_3$  that takes into account the interface electrolyte- sample. The model does not vary much, and for a shake of simplicity only the results of the rest of the parameters will be studied, because no interest has been found on these two parameters.

### 3.- Results and discussion

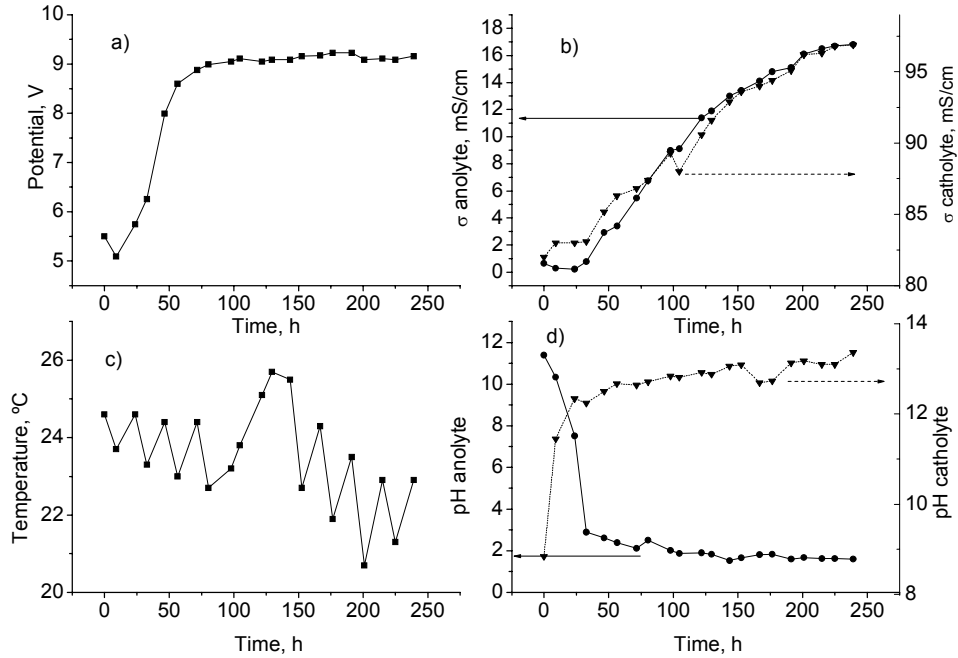
#### 3.1 Forced Migration experiments results

As has already been exposed, after cutting the samples, properly identified, were kept in a 95% RH chamber until they were used for the forced migration experiments. The ages of samples were of 14 days, 28 days, and 45 days after preparing the mortars. Three samples of each type of mortar studied were used for the migration test at every age. The conductivity, pH and temperature of anolyte and catholyte were measured two times a day. Results of the evolution of all these parameters are shown in Figure 3.

The conductivity of both anolyte and catholyte has the same behavior. After a initial stage where the conductivity does not vary much, and after some hours the conductivity starts to increase linearly. These two steps have been well described [10], and the first step corresponds to the time that chlorides need to fill the sample (time lag), while the step when conductivity increases linearly corresponds to the constant chloride flux regimen. The analysis of the time lag gives the value of the non stationary diffusion coefficient, and the slope of the conductivity curve in the linear region gives the value for the stationary diffusion coefficient. The equations that permit the calculation of both diffusion coefficients are the following ones:

$$D_{NS} = \frac{2x^2}{\tau v^2} \left[ v \coth \frac{v}{2} - 2 \right]; \quad v = \frac{zF \Delta \phi}{RT} \quad (2)$$

$$D_s = \frac{JRTx}{zFC_1\gamma\Delta\phi} \quad (3)$$



**Figure 3:** Evolution with the forced migration time of different parameters a) potential drop through the sample. b) conductivity of the anolyte (circle) and catholyte (triangle) c) temperature, d) pH of the anolyte (circles) and the catholyte (triangles), for a sample of mortar made with cement type CEM II, of 1,48 cm thickness. The forced migration test started after 28 days hardening.

$x$  corresponds to sample thickness,  $\tau$  is the time lag, calculated as the time elapsed until the conductivity starts to increase in the anodic compartment.  $\Delta\Phi$  is the mean value of the potential difference between both sides of the sample.  $J$  is the flux of ions in stationary state and it is calculated from the slope of the conductivity versus time in the linear region.  $C_1$  is the  $\text{Cl}^-$  initial concentration in the catholyte (1 M).  $\gamma$  corresponds to the activity coefficient of the catholyte solution (0.656), and finally  $T$  is the average temperature recorded during the experiment.

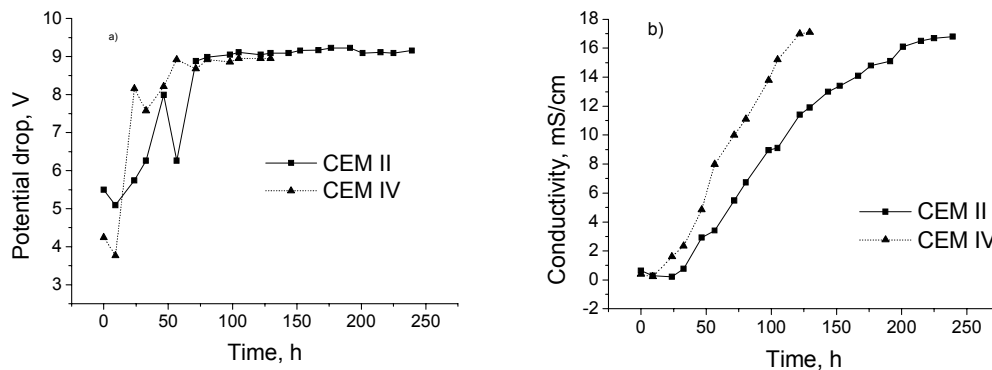
Table 1 shows the average values of the stationary chloride diffusion coefficients,  $D_s$ , obtained for both mortars by migration tests performed at different hydration times, from 14 days to 45 days. As expected, the  $D_s$  values show a decreasing tendency with the hardening age of the mortars, due to the progress of the clinker component hydration and pozzolanic reactions, but the evolution is different for each cement type. At 14 days of hydration the CEM IV mortar shows a double value for  $D_s$ , as compared with the CEM II mortar at the same age. For longer hydration times this difference is progressively decreased, and for an hydration time of 45 days the  $D_s$  values are practically equal for both cement types. These observations can be interpreted in terms of the different

composition of the cements. CEM IV has a higher content of fly ash, and hence a lower clinker content, than CEM II. Taking into account the slowness of the pozzolanic reaction it is reasonable that at 14 days the CEM IV would have produced a considerably lower amount of hydrated calcium silicates and aluminates than the CEM II at the same age. This would imply a less refined and more permeable porous network at short hydration times for the CEM IV mortar, as compared to CEM II mortar. The further progress of the pozzolanic reactions at longer hydration times, which are expected to be more important for the CEM IV mortar, would tend to diminish the differences in the porous networks characteristics and in the permeability properties. This situation seems to have been reached after 45 days of hydration, when  $D_s$  values are practically equal for both mortars.

	CEM II BV	CEM IV B(V)
	$D_s, m^2/s$	$D_s, m^2/s$
14 days	$2.03 \cdot 10^{-11}$	$4.09 \cdot 10^{-11}$
28 days	$3.25 \cdot 10^{-12}$	$4.62 \cdot 10^{-12}$
45 days	$2.32 \cdot 10^{-12}$	$2.40 \cdot 10^{-12}$

**Table 1:** Values for the diffusion coefficient in the stationary state at different hardening ages.

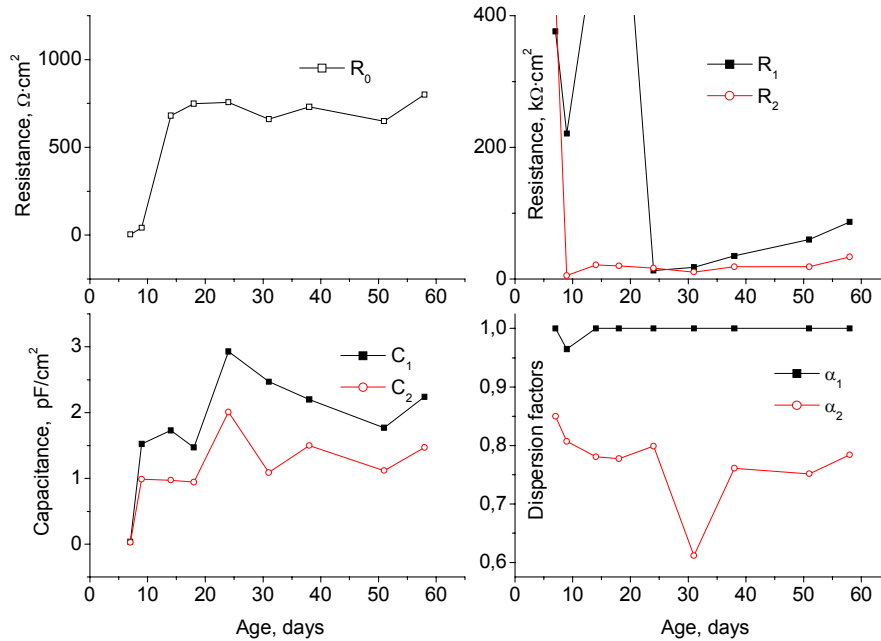
Figure 4 depicts data obtained during the migration testing of both mortars after 28 days of hydration in the 95% RH chamber. The variations of the potential drop within the mortar specimens show a similar pattern for both cement types. The evolution of the anolyte conductivity shows a higher slope for CEM IV than that corresponding to CEM II, indicating clearly a higher chloride flux for the former cement, and a higher value for the stationary diffusion coefficient.



**Figure 4:** Different evolution of the potential and anolyte conductivity, during migration testing, for mortars made with different cement type.

### 3.2.- Impedance spectroscopy results

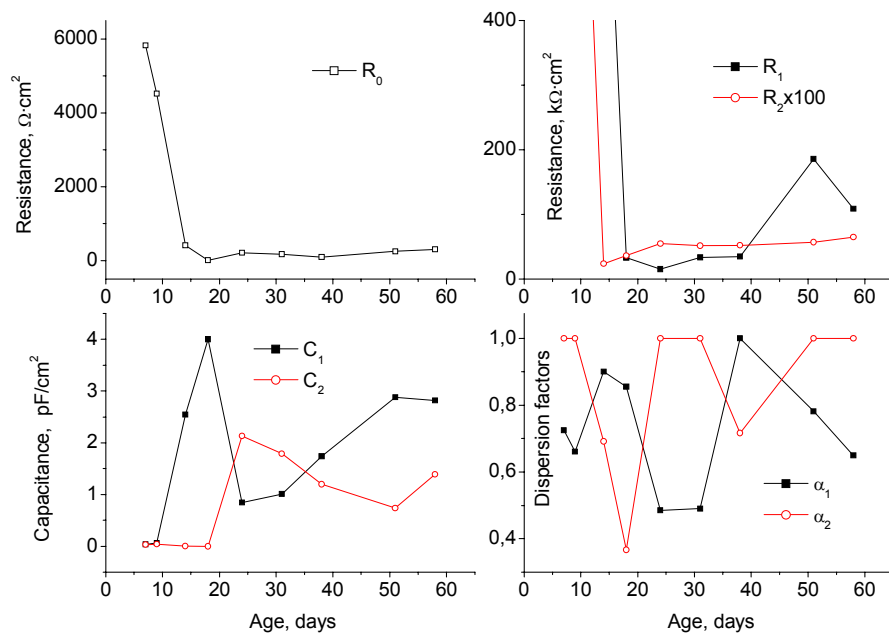
As it was explained in section 2.3 impedance spectra were obtained using a contacting method, and fitted to a model already proposed [18]. The evolution of the dielectric parameters is shown in figures 5 (for CEM II) and 6 (for CEM IV).



**Figure 5:** Evolution with the hardening age of the different elements of the equivalent circuit used to modelize the dielectrical behaviour of the mortars used, for a mortar made with CEM II and a sample thickness of 0,77 cm.

The meaning of all these parameters was clearly explained [15, 18].  $R_0$  corresponds to the resistance of the contact, and has a value almost constant, at least after 14 days for both types of cements used.  $C_1$  is the capacitance associated to the solid phase portion in the sample. It shows a slightly growing tendency for both types of cements, but the changes are more important for mortars containing a greater quantity of fly ash (CEM IV). This result coincides with the results obtained in the forced migration tests. The evolution shown by the CEM IV mortar is differed in time from the evolution of cement type II. The same result is obtained looking at the behavior of the resistance  $R_1$ . This resistance has been associated to the pores that connect both sides of the sample. After the day 24 for both types of cement, but for the CEM IV it seems to become more important after the day 38. The evolution of  $C_2$  and  $R_2$  does not have much significance in this work. Everywhere, these two parameters have been associated to the “occluded pores”, those who do not connect both sides of the sample, and the great differences in the value for the resistance denote differences in the pore network nature. Finally the dispersion factors also denote differences in the development of the final microstructure but do not give important information for this work.

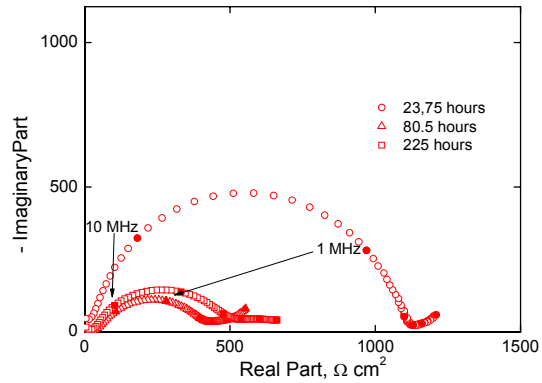




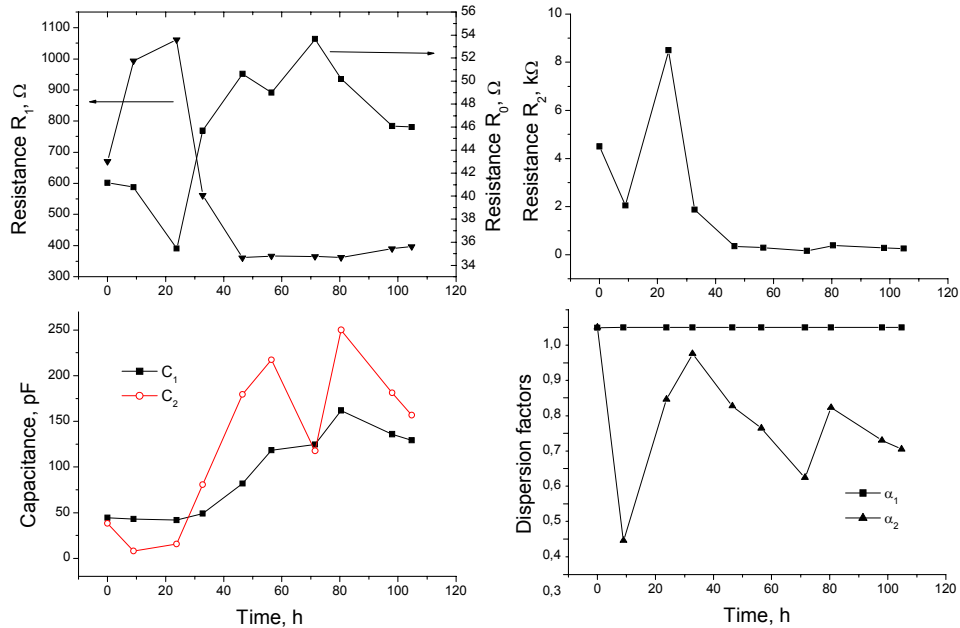
**Figure 6:** Evolution with the hardening age of the different elements, for a mortar made with CEM IV and a sample thickness of 0,8 cm.

During the forced migration experiments the impedance of the system electrolyte-sample was also measured. The model used for the fitting was already described in section 2.3, and the meaning of the parameters studied is the same as described previously, except for the resistance  $R_0$ . This resistance takes into account the contribution of the electrolyte (both anolyte and catholyte) to the impedance spectra. The impedance spectra changes with the time of forced migration experiment. Figure 7 depicts 3 different impedance spectra, corresponding to a CEM II mortar sample tested after 28 hydration days. The three impedance spectra correspond to the different zones found in the evolution of the conductivity of the anolyte (see Fig. 4.b) The first one, about 24 hours after the beginning of the experiment, while the chlorides are still filling the sample, the second one, about 80 hours when the conductivity increases in a linear way, and the third one close to the end of the experiment. The value of the resistance of the arc changes during the experiment, but it is not the only factor that changes. As it can be appreciated, also the relative position of the frequencies changes denotes changes in the microstructure.

The fitting of these impedance spectra to the model proposed in [26] gives the values for the parameters shown in figure 8 (only the first 105 hours are shown, because the most interesting phenomena can be explained with this time fraction).



**Figure 7:** Evolution with time of forced migration experiments of the impedance spectrum of the system mortar sample + electrolyte. The sample is a mortar containing cement type CEM II, tested at 28 hydration days.



**Figure 8:** Evolution with time of forced migration experiments of the dielectrical parameters for a sample of mortar containing cement type CEM II, tested at 28 hydration days.

The evolution of the resistance  $R_1$  corresponds to the expected one. The value of the resistance has high values until the sample is saturated with chlorides. The evolution is the same for the resistance associated to the occluded pores  $R_2$ . The pores are initially filled with water and while the sample gets saturated the conductivity of the electrolyte increases, and the resistance decreases. After 80 hours of forced migration the resistance  $R_1$  starts an increasing tendency. This result is directly related to the behavior of the capacitance  $C_1$ . This capacitance, that is proportional to the solid phase fraction, remains constant

while the sample is saturated with chlorides, but after this time it starts to increase. Chlorides forced to pass through the sample may react and create new solid products, increasing the capacitance, and making more difficult the movement of ions, reflected in an increase of resistance. This fact is also reflected in the high values shown by the capacitance  $C_2$ . This capacitance is associated to the interface solid-electrolyte, and the increasing tendency in this capacitance reflects the creation of new solid products in the pore walls, due to the forced migration of chlorides.

#### **4.- Conclusions**

In this work several aspects of the microstructure and permeability to chlorides of two mortars containing different amount of fly ash have been studied. The main conclusions may be summarized as follows:

- 1.- A high enough quantity of fly ash retards the development of the final microstructure of mortars.
- 2- Mortars with high percentage of fly ash have greater diffusion coefficients for chlorides at short hydration times, and the evolution of these coefficients with time is also slower. At hydration times of 45 days the chloride diffusion coefficients are quite similar, irrespective of the fly ash content.
- 3.- Impedance spectroscopy shows the direct relation between resistivity of the samples ( $R_1$ ) and diffusion coefficients.
- 4.- Impedance spectroscopy also can be used to study the changes induced in the microstructure of samples during the forced migration test.
- 5.- These changes may be interpreted in terms of the reaction and formation of new solid structures on the wall of the pores during the forced migration tests.

#### **5.- Acknowledgements**

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