Electronic and Electrolytic Conduction of Cement Pastes with Additions of Carbonaceous Materials

C. Andrade, P. Garcés, F.J. Baeza, Ó. Galao, and E. Zornoza

Abstract Additions to concrete may change some of its basic properties in several ways depending on the nature of these additions. The addition of fibers, in particular, has enabled new concrete characteristics, making standard concrete a very modern composite material. If the fibers are electrical conductors, the properties that change in addition to the mechanical ones, are the thermal and electrical conductivities. The results indicate that the arrangement of the electrodes and the electrode-material interface are relevant, because the use of sponges between electrode and concrete prevents the contact between the metallic electrode and the carbon material which ends in different values of electrical resistance with and without sponges. Moisture conditions, that critically influence the electrical resistance of concrete without additions, resulted, also very relevant when conductive substances are present in the matrix. If the proportion of the carbonaceous addition, that lowers significantly the resistivity, is to be quantified, the best procedure seems to measure in dry concrete (0 % relative humidity) with sponges or, alternatively, wet concrete (100 % relative humidity) with silver painted electrodes (without sponges).

Keywords Cement composites • Electronic conduction • Electrolytic conduction • Carbon fiber • Graphite powder • Conductivity

1 Introduction

Concrete is a very versatile material because its properties can be enhanced by the addition of other materials such as admixtures, minerals, fibers, etc., leading to a more modern composite material. These new mixes enable multiple applications of

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concrete. The fibers, in particular, collaborate to increase its tensile strength and its ductility, for example. Various types of fibers have been used to accomplish these improvements, polypropylene, stainless steel and carbon fibers (ACI report #544.1R-96 2002). With respect to the latter as well as graphite powder (GP), their addition to a concrete mix will also influence its electrical resistance, thermal conductivity, ability to shield electrical fields, etc, which has resulted in concrete being considered as a multifunctional material (Chung 2003).

This paper is focused on the changes in electrical resistance due to the presence of carbon powder and fibers and the manner in which this resistance is measured. The electrical resistance of concrete was studied already in 1955 (Hammond and Robson 1955) as the electrical insulating properties of concrete were of interest to demonstrate its adequate performance in fabricating rail sleepers. It was well identified then that concrete behaves as a dielectric when it is almost completely dry and presents resistances in the range of a semiconductor when it is wet or water saturated. The conduction was identified to proceed through the migration of ions in the porous network (Monfore 1968). That is, it can behave as an electrolytic conductor. Further to the initial studies, resistivity levels in concrete have been identified to be closely related to setting occurrence, progression of hydration (Li et al. 2007) and to be the controlling parameter of reinforcement corrosion (Alonso et al. 1988) precisely due the resistivity is directly proportional to the degree of water saturation.

The addition of carbon fibers, while not contributing to the ionic concentration in the pore water, is expected to influence the electrical resistivity in other ways. Being the carbonaceous materials electronic conductors themselves, they may change the concrete total resistivity, particularly when the amount of addition surpasses the percolation threshold. This percolation threshold refers to the minimum quantity of carbonaceous material needed to create a continuous electronic conductive path. At this threshold the conductivity of the material experiments a significant decrease. This change may help to quantify the amount of addition present in the material. This phenomenon will occur with metallic fibers as well. Therefore, in the presence of these kinds of electrically conductive fibers there will be two types of electrical conduction in the concrete: the electrolytic one due to the ions in the pore network, and a here called “electronic” one due to the carbonaceous additions. The object of this article is to study the differences in the electrical resistance introduced by the addition of different proportions of these carbonaceous materials, to mortar samples exposed to various levels of humidity and to find the best experimental procedure to identify the percolation threshold, or at least the starting of the percolation phenomenon, due to the presence of an increasing amount of electrical conductive material.

2 Experimental Procedure

2.1 Materials and Specimen Preparation

Portland cement type CEM I 52.5 R (OPC) according to European standard (UNE-EN 2000) was used, and mixed with distilled water in all instances. Prismatic

Table 1 Chemical composition of carbon additions

	C	H	N	$(S+O)_{dif}$
GP	99.00 %	–	–	1.00 %
SCF	87.46 %	0.68 %	1.04 %	10.57 %
LCF	92.91 %	0.18 %	5.15 %	1.76 %

cement paste samples of $40 \times 40 \times 160$ mm dimension were prepared with a 0.5 water-cement ratio. Carbonaceous materials were added in the following amounts with respect to cement mass: 0 % (control), 0.5 %, 1 %, 2 %, 5 % of graphite powder (GP), short carbon fibers (SCF) and long carbon fibers (LCF). Besides, partial cement substitution of 25 and 50 % of graphite powder was used.

Commercially available coal tar pitch milled carbon fibers (SCF) provided by Donacarbo, were used for this study (general purpose carbon fiber type). The diameter and the length of this fiber are 13 μm and 130 μm, respectively. In addition, PAN based carbon fiber (LCF) provided by Hexcell was used. The diameter and the length of this fiber are 7.1 μm and 10 mm, respectively. Table 1 contains the chemical composition of carbon additions: GP, SCF and LCF.

The samples were stored in different environments corresponding to relative humidities (RH) of 0, 60, 80, and 100 % which were provided by salt solutions placed in the bottom of the chambers until constant weight of samples was achieved. The 0 % RH was obtained by drying in an oven at 105 °C until constant weight, and using silica gel in the bottom of the desiccator instead of a conditioning salt solution.

2.2 Techniques

To measure the electrical resistance, a distinction is made on whether or not sponges are introduced between the electrodes and the cement paste. The sponges prevent the direct contact of the metallic electrodes to the carbonaceous materials and then this arrangement (with sponges) is expected to provide the electrolytic resistance of the paste modified by the fact that part of the matrix is substituted with an electrically conductive material that may or not be percolated in function of the proportion added, (an induction phenomenon in the carbon materials will also occur that is not relevant for present research). Then, in the disposition "with sponges", two identically-dimensioned 4×4 cm copper plates were placed at either end of the sample (Fig. 1 down). Between each plate and the sample, wet sponges moistened with tap water were introduced to ensure electronic insulation of the metallic electrodes with the carbonaceous materials. The contact pressure between metallic electrodes-sponges-cement pastes was controlled applying a constant load of 100 N between the plates.

In the disposition "without sponges" the electrodes will be in direct contact to the electrically conductive material and then, the resistance will be much lower than with sponges and will depend on whether or not the electrical conductive material is

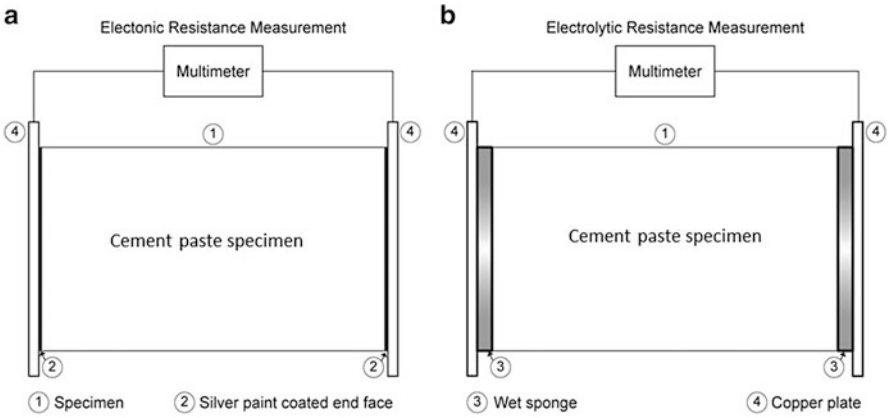


Fig. 1 Measurement arrangement "without sponges" (**a**: electronic resistance measurement) and "with sponges" (**b**: electrolytic resistance measurement) in order to measure the electrical resistance

percolated, depending on the proportion by volume added. To measure the resistance (Fig. 1 up), the two end faces of the electrodes were painted with silver conductive paint to ensure good contact between the paste having the carbonaceous materials and the mains of the resistivimeter.

Resistance measurements were made with a Keithley 2002 multimeter. To calculate the resistance, Ohm's law was used ($R = V/I$) and $\rho = RA/L$, where R = measured electrical resistance, V = applied voltage, I = current circulating due to the applied voltage, ρ = resistivity, A = cross section area (16 cm^2), L = length of the specimen (16 cm).

3 Results

3.1 Measurement of the Electrical Resistance

Figure 2 up shows the electrical resistance in the arrangement with sponges corresponding to cement samples with addition of GP in proportions of 0.5, 1, 2, and 5 %, and substitution in proportions of 25 and 50 %, in environments of RH of 0, 60, 80, and 100 %.

As may be observed in Fig. 2 up, the measured electrolytic resistance is much higher with sponges than without them and depends on the RH, as expected. At RH of 100 %, the resistance with sponges is very low, between 4.3 and 0.6 kΩ, for the control sample and substitution of 50 % GP, respectively. For the RH of 60 and 80 %, the resistance is higher but very similar to that at 100 % RH. The specimen at 80 % RH shows a slight, but negligible, increase in the resistivity with the smallest additions of GP. Apart from that, which may be within the measurement error,

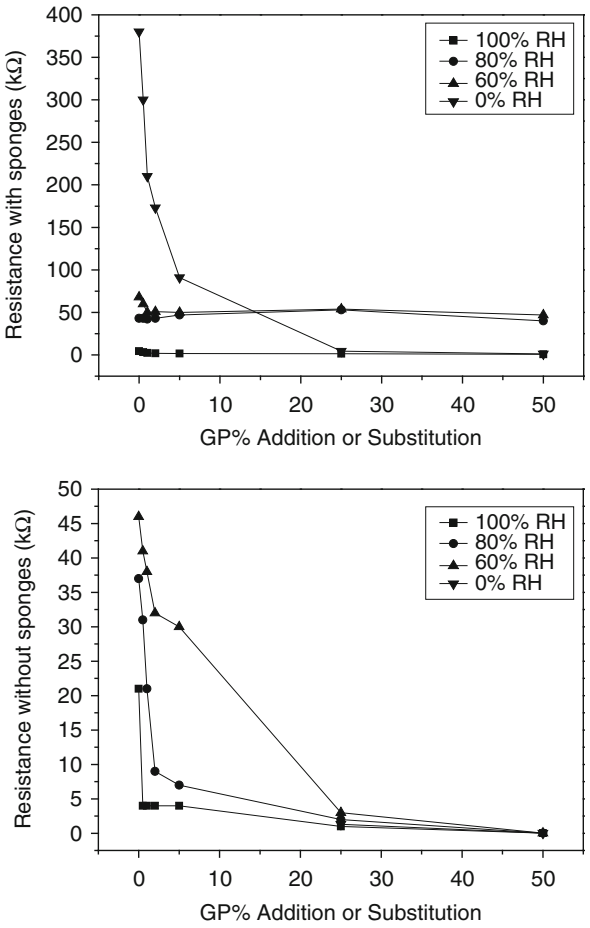


Fig. 2 Electrical resistance measurements with sponges (*up*). Electrical resistance measurements without sponges (*down*). Cement samples with addition of graphite powder in proportions of 0.5, 1, 2, and 5 %, and cement substitution in proportions of 25 and 50 % at different RH. All carbon material percentages are referred to cement mass

similar to the case of 100 % RH, it seems that the additions at 60 and 80 % RH do not influence the electrolytic resistance. For the dry specimen (0 % RH) however, the effect of additions of GP is very notorious, with dramatically decreasing values of the electrolytic resistance with small additions and a very significant decrease for the 25 % substitution, reaching values similar to 100 % RH and smaller than 60 and 80 % RH. At this addition of 25 %, it seems that almost full percolation in electronic conduction has been reached.

Figure 2 down shows the values of the resistance without sponges corresponding to cement paste samples with GP, added also in increasing proportions of 0.5, 1, 2 and 5 % with respect to cement mass and substituted in proportions of 25 and 50 %. It is worth noting that the change in the scale of resistances due to their value is now much smaller. For the 0 % RH, results are plotted only for values >25 % of addition because those with smaller amounts are out of the chosen axis scale of resistance. For other RH values, in which the resistance significantly lowers, the decrease in

resistance value is dramatic at the lower GP proportion and is gradual for higher amount of graphite powder. Then, without sponges in the low part of the figure, percolation seems to appear for very low amounts of carbonaceous powder at 100 % RH. The percolation initiation is detected at increasing amounts when the RH lowers, being at 25 % substitution at 60 % RH. That is, each disposition of electrodes shows different significant lowering of the resistance for different RH's and then, the percolation concept (decrease in resistance) needs to be defined for each arrangement and humidity level, as this last one can mask or influence significantly the detection of the decrease in electronic conduction.

Figure 3 up shows the resistance with sponges corresponding to cement paste samples with SCF additions (0.5, 1, 2 and 5 %), measured in the same environments of RH at 0, 60, 80 and 100 %.

In the arrangement with sponges (Fig. 3 up), the behavior with the SCF is very similar to that of the GP, but with a different proportion where dramatic resistance lowering is noticed. The specimens held at 60, 80 and 100 % almost do not exhibit

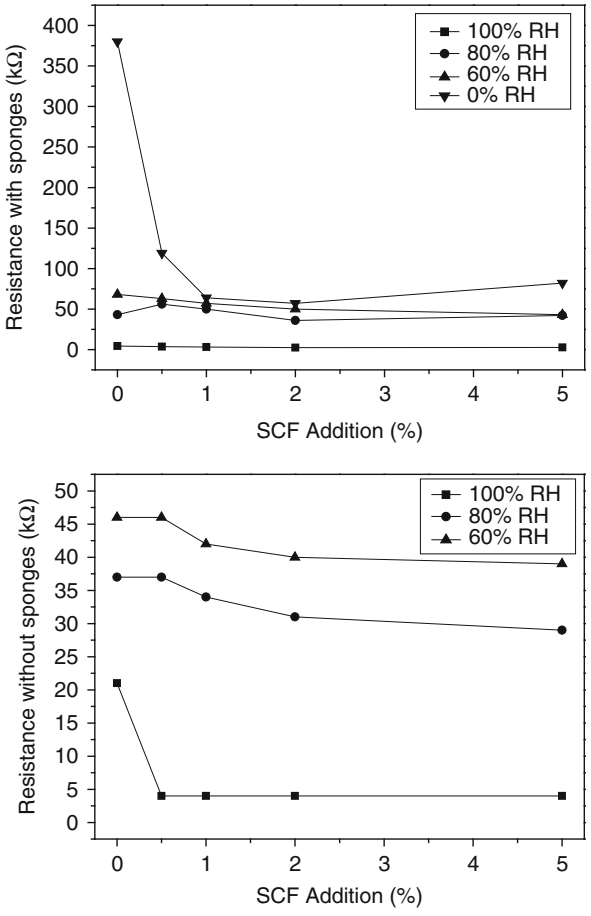


Fig. 3 Electrical resistance measurements with sponges (*up*). Electrical resistance measurements without sponges (*down*). Cement samples with addition of short carbon fibers in increasing proportions of 0.5, 1, 2 and 5 % at different RH. All carbon fiber percentages are referred to cement mass

changes due to the additions, whereas the specimen in dry conditions (0 % RH) presents an indication of the percolation at 1 % of addition. Therefore, the presence of an electronic conductor influences the resistance measured with sponges only for very dry conditions, when there is almost no water in the capillary pores. At 60, 80 and 100 % RH, where water fills the small and large capillaries, the ionic conduction is more significant, masking the measurement of electronic conduction percolation.

The arrangement without sponges is shown in Fig. 3 down. Again the scale of resistances is very different. Specimens at 0 % RH were not tested due to the high values of resistance presented. In the case of 60 and 80 % RH, additions up to 5 % did not introduce significant decreases in the resistance. However, for 100 % RH, the effect of the addition is relevant from the smallest proportion of 0.5 % and the initiation of the percolation can be noticed from 0.5 % addition.

Figure 4 shows the electrical resistance measurements with and without sponges of cement pastes with addition of LCF, 1 cm length, in increasing proportions of

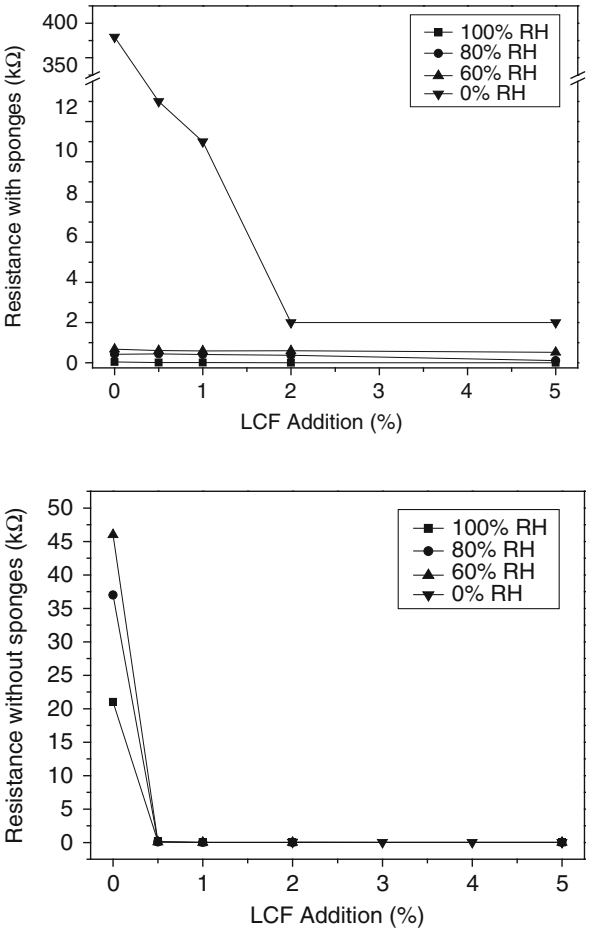


Fig. 4 Electrical resistance measurements with sponges (*up*). Electrical resistance measurements without sponges (*down*). Cement samples with addition of the long carbon fibers in increasing proportions of 0.5, 1, 2 and 5 % at different RH. All carbon fiber percentages are referred to cement mass

0.5, 1, 2 and 5 % at RH of 0, 60, 80 and 100 %. In Fig. 4 up, the data again show that only in the dry specimen the additions or substitution has a relevant effect and that the initiation of the percolation is achieved for additions of only 0.5 % of the long fibers. Figure 4 down shows the data on the electrical resistance without sponges. In this case, the effect of the presence of long fibers, which in theory have greater ability to percolate at lower proportions of additions, is clearly detected by the important decrease recorded at 0.5 % of LCF addition for all the RH tested.

As a summary it can be said that for the case without sponges the electronic conduction percolation is better detected at 100 % RH while 0 % RH was the best condition for the measurement with sponges. Thus, not only the amount and type of addition are important factors in the measured value of the electrical resistance but the RH also plays an important role in the detection of the percolation threshold beyond which the resistance decreases to a minimum.

4 Discussion

To better observe the percolation phenomenon at the different RH, Fig. 5 presents the resistance values without sponges of specimens with the three carbonaceous materials at RH of 80 and 100 %, respectively. At 100 % RH (Fig. 5 up), the initiation of the electronic percolation is produced for all types of addition at 0.5 %, whereas for 80 % (Fig. 5 down), this addition indicates initiation of percolation only for the LCF, whose size and shape favor the electrical contacts. Then the humidity may mask the detection of electronic conduction in the case of the painted electrodes without sponges.

Figure 6 shows all the results of resistance without sponges for 0.5 and 2 % additions. This figure shows that the percolation initiation can be detected by a dramatic decrease in resistance values compared to control specimen, this effect is better shown at 100 % RH for all kinds of carbonaceous additions.

Finally, Fig. 7 shows a summary of the resistances measured with sponges in all the conditions tested. It reveals more comprehensibly that the effect of the proportion and shape of the addition is best detected in the 0 % RH specimen. According to this figure, only the dry specimen (0 % RH) enables good detection of the influence of the addition/substitution in the electronic conduction. Additionally, at 0 % RH, the resistance drastically decreases as the length of the fibers increase. However, when capillary water is starting to be present (HR around and higher than 60 %), the ionic conduction through the pore network masks the conduction through the carbonaceous materials and the percolation initiation is not well observed.

4.1 Types of Measurement and Conduction Mechanisms

As mentioned, the two electrode arrangement, with and without sponges, have led to very different values of the resistance, being much lower when no sponges are

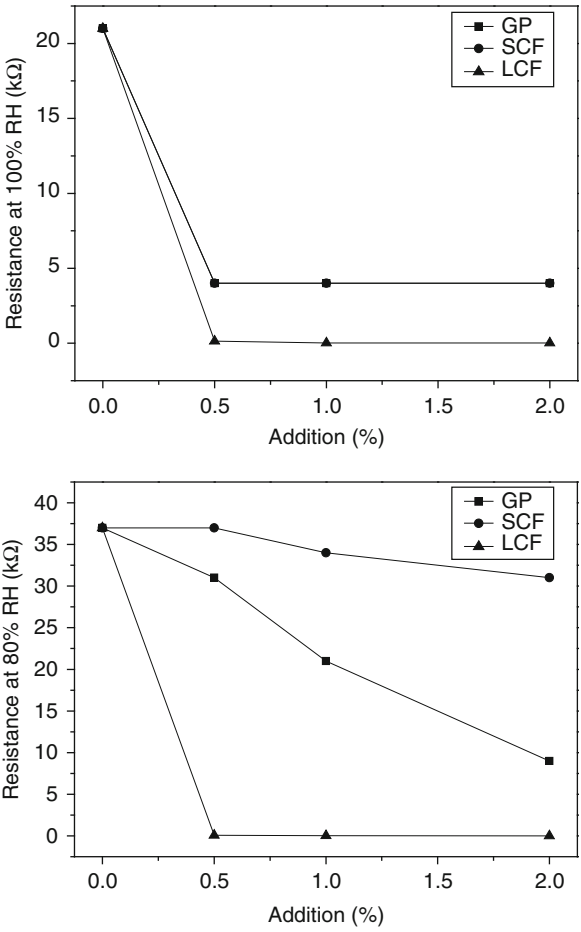


Fig. 5 Resistance without sponges of specimens with the addition of three carbonaceous materials held in a chamber at 100 % RH (*up*) and 80 % RH (*down*)

used, that is when the electrodes can touch directly the electrical conductive material. This fact indicates the existence of two types of conduction mechanisms. When electrical conductive fibers are added to the mix, the resistance changes due to at least two factors: (1) the type of interfacial contact between electrodes and concrete and (2) the decrease of volume fraction of the cement phase (cement gel and capillary porosity) and the increase of that of the electrical conductor (the carbonaceous material).

When the electrodes are in direct contact with the conductive fibers or powder (as shown in Fig. 8), they will modify the measured value of the electrical resistance while they will not if sponges are placed between electrodes and cement paste. Sponges are electronic insulators that prevent the electronic conduction between the metallic electrodes and the electronic conductive materials.

Then, in the case of painted electrodes (without sponges), due to the interfacial contact of the electrodes and the carbonaceous material (Fig. 8), the measured

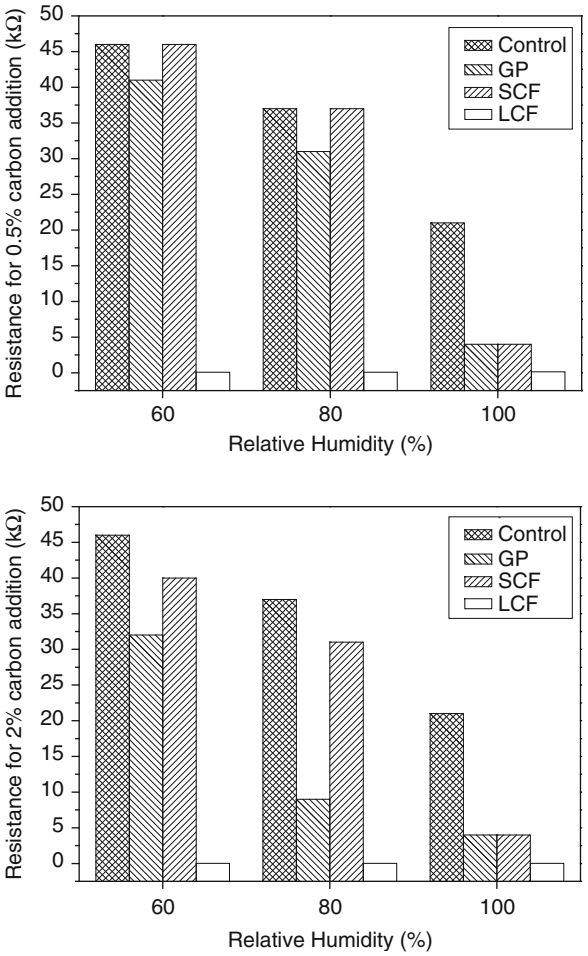


Fig. 6 Resistance without sponges of specimens in different relative humidity atmospheres. Samples with 0.5 % of carbon material addition (*up*); samples with 2 % of carbon material addition (*down*)

resistivity will be much lower than in the case with sponges were this contact electrode/carbon is not produced. Regarding the detection of the percolation due to the increase in the volume fraction of the carbonaceous material the better detection at the highest RH can be attributed to the fact that at in drier concrete the amount of conductive addition to compensate the higher resistances needs to be higher. That is the higher resistances mask the effect of the conduction of the carbon material.

In cement paste without conductive fibers, the conduction of electrical charges is made by the ions present in the pore solution, mainly that of capillary pores (Fig. 9). If the material is dry, then there is not ionic conduction and any decrease in resistivity due to the addition of fibers can be detected without any masking.

This lowering in resistance, although is not the main aim of present study to clarify it, is attributed to an electrostatic polarization, the same produced when measuring the resistivity by the four points method which recommends to avoid the

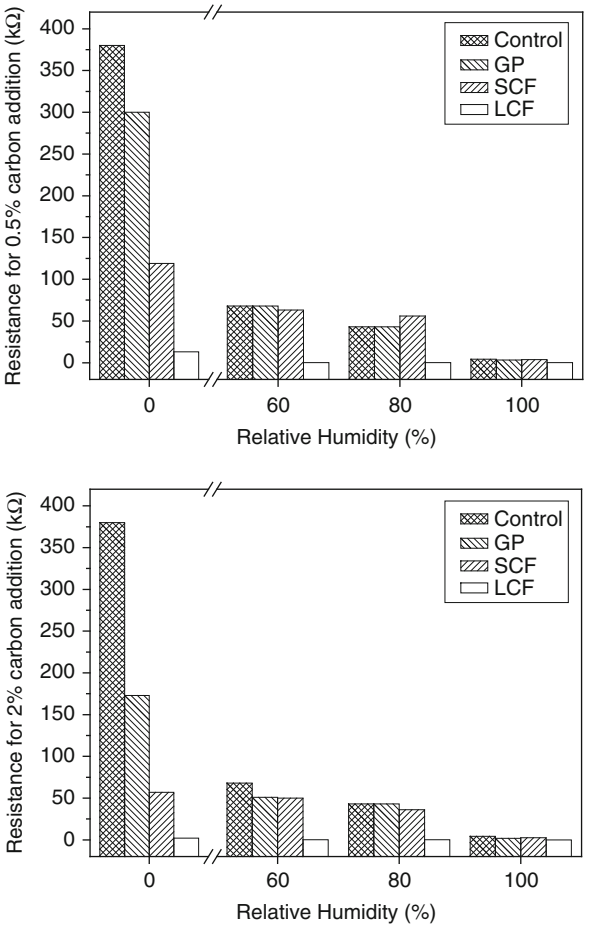


Fig. 7 Resistance with sponges of specimens in different relative humidity atmospheres: Samples with 0.5 % of carbon material addition (*up*); samples with 2 % of carbon material addition (*down*)

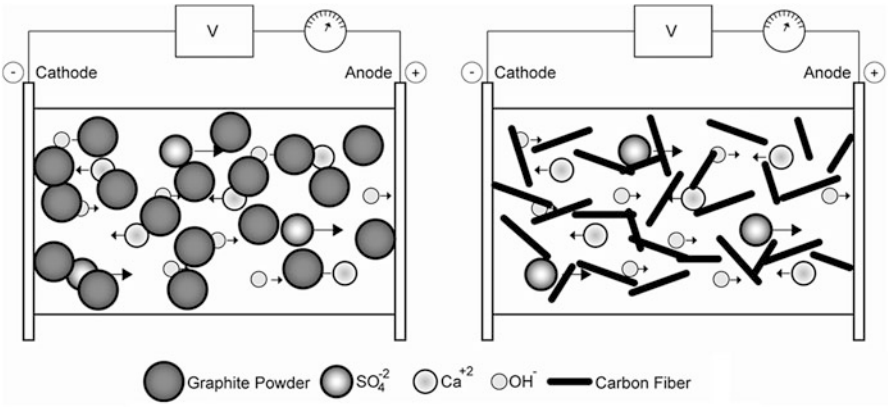


Fig. 8 Representation of electrolytic and electronic conduction due to the direct contact of electrodes with the carbonaceous materials

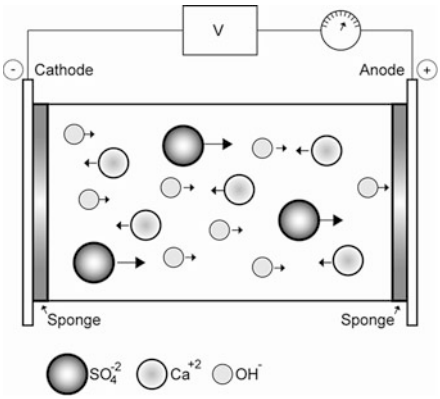


Fig. 9 Representation of the movement of ions due to the application of a continuous current: electrolytic conduction

presence of rebars below. In this method, four electrodes are placed in the concrete surface to measure the resistivity and a lowering in the value is detected when placed just on reinforcements (Castellote et al. 1999, 2002; Feliú et al. 1996). The phenomenon of the lower resistivity values with respect when no bars are below is assumed to be the same than here makes possible to detect the addition of the fibers in a dry concrete.

4.2 Effect of the Amount of Addition: Percolation Initiation for Electrical Conduction

Percolation has been considered to initiate when beyond a value where almost no decrease in electrical resistance is observed. For smaller additions, there might be "cluster" or "aggregations" of electronic conductive paths (see Fig. 8), which explain the progressive lowering of measured values of resistance. In order to analyze the effect of the volume addition, Figs. 10 and 11 represent the resistance decrease with respect to the value with 0 % addition (100 %) and the volumetric fraction added. As mentioned, the lowest threshold amount is best detected at 0 % RH for resistance measurements with sponges and at 100 % RH for measurements without sponges (painted electrodes).

4.3 Effect of the RH in the Measurements

In spite of smallest amount of carbonaceous material is detected at the lowest and highest humidities depending upon the electrode arrangement, it may be of interest

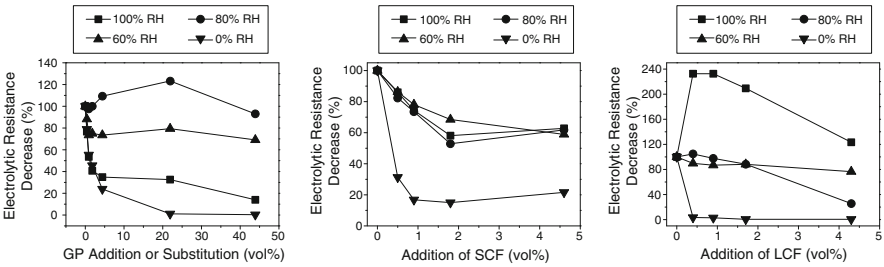


Fig. 10 Dependence of the relative decrease (% with respect to the value with 0 % addition) of measurements with sponges in function of the volume of addition of GP (*left*), of SCF (*middle*) and of LCF (*right*)

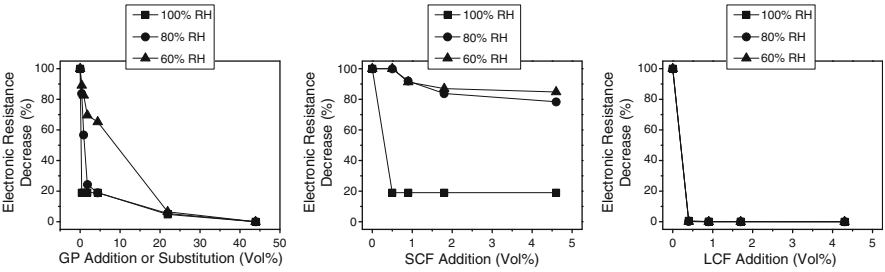


Fig. 11 Dependence of the relative decrease (% with respect to the value with 0 % addition) of measurements without sponges in function of the volume of addition of GP (*left*), of SCF (*middle*) and of LCF (*right*)

to know if the addition of these materials significantly affects the values of the resistances at the normal humidities found in concrete structures. Present tests have shown the effect of moisture on the resistance values and how the percolation threshold varies with the moisture conditions (Figs. 10 and 11) and therefore, the humidity has to be specified when defining a threshold amount (Wen and Chung 2006; Ozyurt et al. 2006; Cheng et al. 2004).

4.4 Effect of the Fiber Aspect Ratio the Measurements

There is a significant difference in the levels of resistance of the samples containing GP, SCF and LCF. This can be interpreted as due to the difference in the size and shape of the carbonaceous materials, because the longer length of the fibers permits more continuous conduction paths (see Fig. 8), leading to the greater probability of fiber-fiber contact along the sample length. Therefore, as a general trend, lower amounts leading to percolation can be expected for longitudinal than for spherical particles, as well as larger ones.

5 Conclusions

The following conclusions can be drawn:

1. The electrical resistance of a cement-based material depends on the: (a) the volumetric fraction of solid cement phases (acting as an insulator) and porosity (acting as ionic conductor if water is present) and (b) the degree of water saturation in the pores equivalent to RH if equilibrium exists in controlled chambers.
2. If electronic conductive materials are added in the mix, the electrical resistance decreases in a proportion depending on the: (a) the type of carbonaceous material, (b) the size and shape of the material (longitudinal fibers induce a lower percolation threshold) and (c) the amount added (volumetric fraction in the mix)
3. Electrolytic and electronic conductions are produced beyond noticing the lowering of the resistance. For higher amounts of addition than those of the percolation initiation, the electronic conduction prevails and then the resistance decreases dramatically.
4. The interfacial contact between the material and the electrodes is very relevant if conductive materials are added, because the traditional use of a sponge between the electrodes and the specimen surface does not allow accounting for the complete electronic conduction.
5. For detecting the minimum threshold amount of conductive material the best is to measure with sponges in fully dry specimens (0 % RH). Alternatively if the electrodes are painted in the surface, the specimens should be conditioned at 100 % RH.
6. The proportion of conductive addition has different effects, depending not only on the shape but also on the humidity content of concrete. Therefore, care should be taken to identify the moisture content of the specimens when trying to account for the amount of fibers added by comparing the resistances of mixes with conductive materials, because the different degrees of saturation modify the absolute scale of resistance value.

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