

Influence of Environmental Conditions on Durability of Slag Cement Mortars

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ABSTRACT

In recent years the use of active additions on cement, like ground granulated blast-furnace slag, has become very popular because they have many environmental benefits. In this work, the behaviour of mortars made with two different cement types, an ordinary Portland cement and an slag cement, was tested. These mortars were exposed to two different environmental conditions during their hardening, an optimum laboratory condition and a Mediterranean climate environment with lower relative humidity. The development of the microstructure of mortars and the changes of their durability properties related with resistance to chlorides ingress, were studied at different hardening ages until 180 days. The mortars made with slag cement showed a good behaviour, even better than Portland cement mortars. The influence of environmental conditions in microstructure and durability properties of slag cement mortars was more important at early hardening times.

INTRODUCTION

The use of mineral admixtures, like fly ash or ground granulated blast-furnace slag, in the cement manufacture has many environmental benefits. The main advantages are the reduction of CO₂ emissions and the lower energy consumption during the cement production, as well as the use of an industrial waste. The use of these wastes also means an economical benefit for the cement industry.

The particular case of ground granulated blast-furnace slag, and their effect on the properties of the cementitious materials is a topic of study. Many studies show that in laboratory conditions this kind of materials has a good service properties, even better than Portland cement [Bijen 1996]. This fact is due to the development of the pozzolanic reactions with the portlandite produced in the hydration of clinker, as well as to the hydration of the slag. These reactions densificate the pore structure of concrete due to the formation of additional CSH phases [Schiessl and Wiens 1995], so the pore size distribution is shifted toward finer pores (pore refinement) [Manmohan and Mehta 1981].

Durability properties of cementitious materials are known to be directly related to the microstructure of these materials [Sánchez et al. 2007]. Then, the use of slag cements also reduces the permeability of concrete and improves their resistance to aggressive ions ingress, even under non optimal laboratory conditions at early hardening ages [Hooton and Titherington 2004].

Real structures are usually hardened in different environmental conditions depending on their geographical location. The different temperature [Schindler 2004] and specially the different relative humidity [Ortega et al. 2009] present in the environment may influence the development of pozzolanic reactions and the service properties of concretes and mortars made with slag cements. This influence may cause a different microstructure [Escalante-García and Sharp 2001] and, as a consequence, different durability properties of these concretes and mortars, such as the diffusion coefficient of chlorides [Ramezani-pour and Malhotra 1995]. Although, it has been studied that under conditions with lower RH, shrinkage cracks can be formed in cementitious materials, specially in concretes with a high content of slag [Kanna et al. 1998].

In this work, mortars made with two different cement types, an ordinary Portland cement and a ground granulated blast-furnace slag cement, were tested in laboratory conditions and at a lower relative humidity. The development of their microstructure and their changes in chloride resistance were studied at different hardening ages until 180 days, as a function of the relative humidity of the environment.

EXPERIMENTAL SETUP

Sample preparation

Mortar samples were prepared using an ordinary Portland cement (OPC), CEM I 42.5 R (CEM I from now on), and a ground granulated blast-furnace slag (GGBS) cement (with a content of GGBS between 66-80% of total binder), CEM III/B 42.5 N/SR (CEM III from now on), according to the Spanish standard UNE EN 197-1. Two different water to cement ratios, 0.4 and 0.5, were employed. Fine aggregate was used according to the Spanish standard UNE EN 196-1. The aggregate to cement ratio was 3:1 for all the mortars.

The specimens were cast in cylindrical moulds of 10 cm diameter and 15 cm height. Samples were kept in 95% RH chamber and 20°C for 24 hours. After that time they were demoulded and were cut into cylinders of 5 cm thick.

Environmental conditions (RH and temperature) were managed with glycerol solutions introduced in hermetically sealed containers. Solutions were prepared according to the German standard DIN 50 008 part 1. Containers were introduced into a chamber with controlled temperature. The environmental conditions were two: condition A (100% RH and 20°C, optimum laboratory condition) and condition B (65% RH and 20°C). Condition B is very similar to environmental conditions of Alicante, in Southeast of Spain, with a Mediterranean climate. The tests were performed at 7, 28, 90 and 180 days of age.

Mercury intrusion porosimetry

In order to study the microstructure of mortar samples, a classical and well-known technique, such as mercury intrusion porosimetry (MIP), was used. Samples were oven dried for 24 hours at 105°C, even though this fact could change the contact angle between mercury and cement [Gallé 2001]. Two measurements were made on each sample. 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, that as reported by Diamond 1999 and 2000, only the dimensions of the pore superficial structure can be detected by MIP, and the irregularities in pore shape

cannot be determined. However, information on the possible tortuosity of pore network can be obtained from the mercury retained in the sample after the end of the experiment. The analysis of the curve plotting the logarithmic differential intrusion volumen vs. pore size, or applied pressure, shows the size where pores appear. The numerical analysis will be done calculating the volume of pores at different pore diameter intervals.

Steady-state diffusion coefficient obtained from saturated sample's resistivity

Electrical resistivity measurement of mortars or concretes is an indirect method to study their pores connectivity and to determine their ionic steady-state diffusion coefficient (D_s). Resistivity was determined from electrical resistance of saturated sample, according to the expression:

$$\rho = R \cdot \frac{S}{l} \quad (1)$$

where: ρ is the electrical resistivity of specimen, $\Omega \cdot m$. R is the electrical resistance of sample, Ω . l is the sample's thickness, m, and S is the electrode's area, m^2 .

Electrical resistance of saturated sample was obtained from the parameter R_1 (resistance associated to pores which cross the sample), determined through impedance spectroscopy. Fig. 1 shows an example of impedance spectrum and its value of the parameter R_1 . Samples were saturated for 24 hours according to ASTM standard C1202-97. These saturated specimens were later used for the forced migration tests.

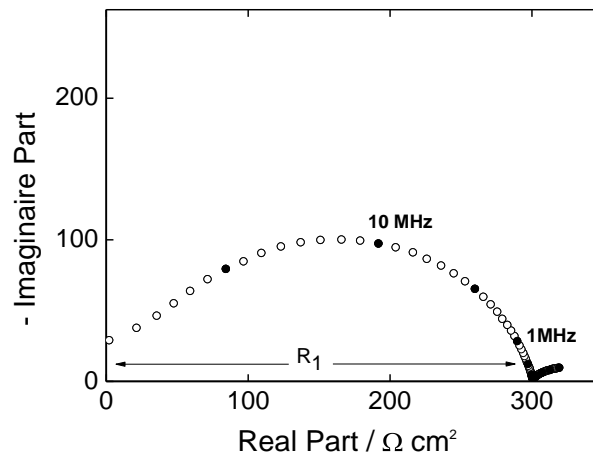


Fig. 1. Impedance Spectrum (Nyquist Diagram) obtained for a CEM I Saturated Sample with w:c Ratio 0.4, hardened under Condition A at 28 Days of Age. Resistance associated to Pores which cross the Sample (R_1) is depicted in the Figure and their Value is 284 Ω .

The steady-state diffusion coefficient was calculated according to the expression [Andrade et al. 2000]:

$$D_s = \frac{2 \cdot 10^{-10}}{\rho} \quad (2)$$

where: D_s is the sample's steady-state diffusion coefficient, m^2/s , and ρ is the electrical resistivity of specimen, $\Omega \cdot m$, calculated according to the expression (1).

For each cement type, environmental condition and w:c ratio, three different samples were tested.

Forced migration test

The forced migration test was performed according to Finnish standard NT Build 492 [Nordtest 1999]. The result of the test is the non-steady-state chloride migration coefficient. Samples were saturated for 24 hours according to ASTM standard C1202-97. The specimens, introduced in rubber sleeves, were placed in the catholyte reservoir, filled with a 10% NaCl solution. The reservoir above the specimen was filled with a 0.3 N NaOH solution. The anode was immersed in the anodic solution.

An external electrical potential was applied across the specimens to force the chlorides to migrate into the specimen. The electrical potential and test duration was chosen according to the measured current applying an initial voltage of 30 V. The value of the initial and final currents and temperatures were noted.

After the test, the specimen is axially split and sprayed with a silver nitrate solution (0.1 N). Chloride penetration depth was measured from the visible white silver chloride precipitate. The migration coefficient (D_{NTB}) can be calculated from this average penetration depth (x_d) according to the expression:

$$D_{NTB} = \frac{0,0239 \cdot (73 + T) \cdot L}{(U - 2) \cdot t} \cdot \left(x_d - 0,0238 \cdot \sqrt{\frac{(73 + T) \cdot L \cdot x_d}{U - 2}} \right) \quad (3)$$

where: D_{NTB} is the non-steady-state migration coefficient, $\times 10^{-12} m^2/s$, U is the absolute value of the applied voltage, V. T is the average value of the initial and final temperatures in the anodic solution, °C. L is the thickness of the specimen, mm, and t is the test duration, hours.

For each cement type, environmental condition and w:c ratio three different samples were tested.

RESULTS AND DISCUSSION

Mercury intrusion porosimetry results

Total porosity, Hg retained and pore size distribution of samples were studied. The results of total porosity are depicted in Fig. 2. Samples with w:c ratio 0.5 presented higher total porosity than with w:c ratio 0.4.

For environmental condition A, total porosity kept constant between 7 and 90 days in CEM I mortars prepared with w:c ratio 0.5, and decreased since then until 180 days. Samples with w:c ratio 0.4 had an important porosity decrease between 28 and 90 hardening days. Total

porosity of samples of CEM III showed a high decrease between 7 and 28 days. This decrease continued between 28 and 90 days for w:c ratio 0.5 specimens. These results could mean that a higher RH accelerates the development of the hydration and pozzolanic reactions. With these reactions, new solids appear and total porosity decreases at early ages.

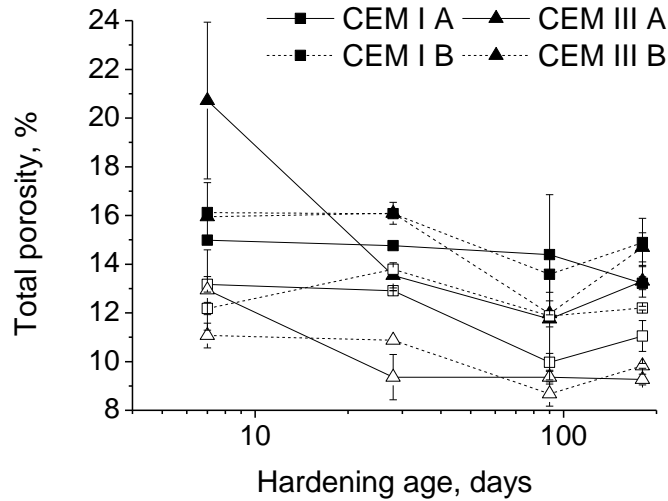


Fig. 2. Evolution with Time of Total Porosity for Both Cement Types and Hardening Conditions. Full Symbols are for w:c Ratio=0.5 while Open Symbols are for w:c Ratio=0.4.

For environmental condition B, total porosity of CEM I samples and w:c ratio 0.5 kept constant until 28 days and decreased between 28 and 90 days. At 180 days, total porosity increased for this samples. Total porosity in CEM III samples remained constant between 7 and 28 days, decreased between 28 and 90 days, and increased until 180 days. These results may be interpreted as that the lower RH slows down hydration and pozzolanic reactions, and the decrease of total porosity happens later. The increase of total porosity between 90 and 180 days for the majority of the samples, could be due to the formation of shrinkage microcracks as a consequence of lower RH in the environment.

The study of the mercury retained in the sample after the end of the experiment enables to obtain information of the possible tortuosity of pore network. The results of percentages of Hg retained are depicted in Fig. 3. The percentage of mercury retained increased in most of the samples studied. For both environmental conditions, mercury retained was higher for CEM III samples. The increase of mercury retained with time is also higher for specimens prepared with CEM III. This increase is faster for samples hardened under condition A. These results could mean that a higher RH helps the hydration and pozzolanic reactions. Then new solids are quickly made and tortuosity of pore network increases.

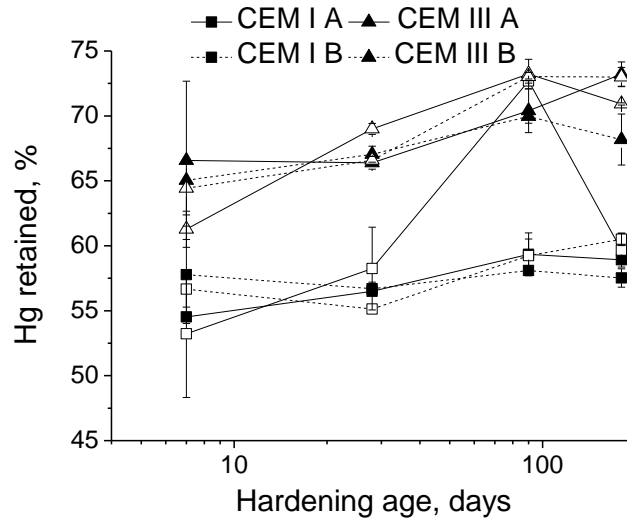


Fig. 3. Results of Mercury Retained for the Specimens studied. Full Symbols are for w:c Ratio=0.5 while Open Symbols are for w:c Ratio=0.4.

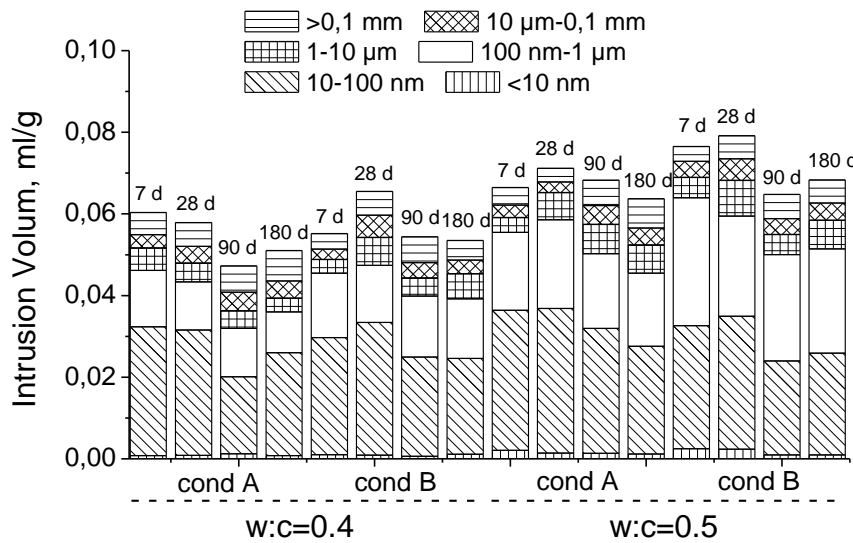


Fig. 4. Pore Size Distribution for CEM I Specimens under Environmental Conditions A and B.

The study of pore size distribution of samples was done considering the following diameter ranges: < 10nm, 10-100 nm, 100 nm-1 μm, 1-10 μm, 10 μm-0.1 mm and > 0.1 mm. For all the samples studied, the majority ranges were 10-100 nm and 100 nm-1 μm. Values of the contributions to total porosity are shown in Fig. 4 for samples prepared with CEM I. The intrusion volume decreased with age in the majority of these mortars. At 7 and 28 days of age, the intrusion volume is higher for CEM I samples under environmental condition B. However, this volume is similar for the majority of the specimens at 180 days of age, independently of environmental conditions. The pores volume of majority ranges decreases with time. From these results, it can be said that the higher RH accelerates the hydration

reactions of CEM I specimens, and then, the pores volume of majority ranges decreases mainly at early ages. For specimens with w:c ratio 0.5 hardened under condition B, the pores volume slightly increased between 90 and 180 days of age. This increase was produced in capillary pores (10-100 nm) and pores of the range 1-10 μm . The rise of range 1-10 μm pores volume, may be due to the formation of shrinkage microcracks, as a consequence of a lower RH in the environment [Kanna et al. 1998].

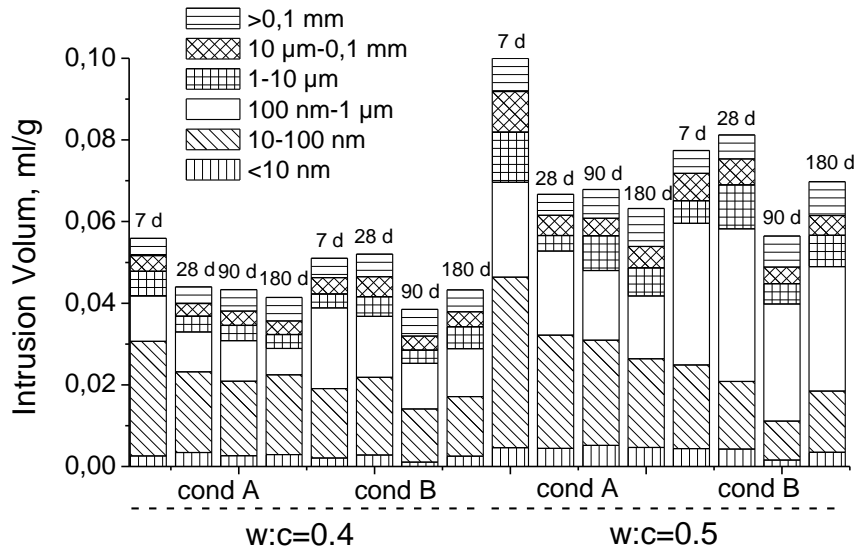


Fig. 5. Pore Size Distribution for CEM III Specimens under Environmental Conditions A and B.

For specimens prepared with CEM III, the pore size distributions are shown in Fig. 5. The intrusion volume decreased quickly for samples under hardening condition A. For environmental condition B, the intrusion volume decreased slower until 90 days of age. This results show that a higher RH in the environment, makes easier the development of pozzolanic and hydration reactions, and then, the intrusion volume decreases quickly. If RH is lower, intrusion volume decreases later in the case of cement type III. Nevertheless, for condition B, intrusion volume increased between 90 and 180 days hardening, mainly in specimens with w:c ratio 0.5. For these samples, the pore ranges with higher volume rise were 10-100 nm and 1 μm -0.1 mm. The growth of pores volume between 1 μm and 0.1 mm could be related with the formation of shrinkage microcracks [Kanna et al. 1998], due to the lower RH present in the environment. The increase of pores volume range 1 μm -0.1 mm (for condition B and w:c ratio 0.5) at ages higher than 90 days, was greater in CEM III than CEM I samples. Then, the replacement of a high percentage of clinker by slag, can produce a higher shrinkage microcracking in mortars, if they are exposed to environments with a lower RH during long periods of time.

Under environmental condition B, mainly for samples with w:c ratio 0.5, the volume of capillary pores (ranges 10 nm-1 μm) was higher for CEM I specimens than for CEM III ones at 180 days hardening. This difference is notably higher for the pore range 10-100 nm. The values of total porosity for these mortars were very similar, independently of the kind of cement employed. This fact may be due to the densification of the pore structure and pore refinement [Manmohan and Mehta 1981] in CEM III mortars, as a consequence of the

development of pozzolanic reactions with the portlandite produced in the hydration of clinker, as well as to the hydration of the slag, despite the lower RH in the environment.

Steady-state diffusion coefficient from resistivity results

The results of the steady-state chloride diffusion coefficient (D_S) are shown in Fig. 6. Under environmental condition A, D_S had lower values for CEM III samples than for CEM I. For specimens prepared with CEM III, D_S decreased with time. This coefficient increased until 28 days for CEM I samples, and decreased since then until 180 days.

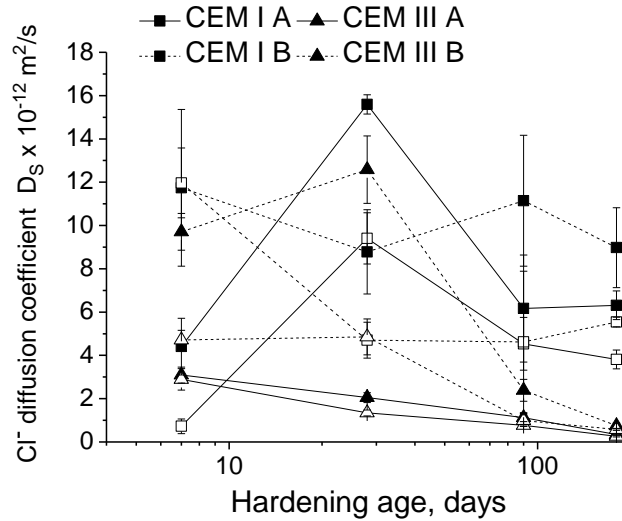


Fig. 6. Results of the Steady-State Diffusion Coefficient (D_S) for Both Type of Cements Studied. Full Symbols are for w:c Ratio=0.5 while Open Symbols are for w:c Ratio=0.4.

For hardening condition B, CEM III mortars had smaller values of chlorides diffusion coefficient at greater ages. For CEM I samples, D_S decreased between 7 and 28 days of age, and kept practically constant until 180 days hardening. This coefficient decreased from 28 days until 180 days of age for specimens made with CEM III.

As could be expected from previous results, the results of steady-state diffusion coefficient could mean that a higher RH facilitates the hydration and pozzolanic reactions, specially in the case of CEM III samples. Then new solids are produced faster and the steady-state diffusion coefficient decreases at early ages. When RH in the environment is lower, the development of hydration and pozzolanic reactions is slower, and then the steady-state diffusion coefficient decreases later.

Forced migration results

The results of the non-steady-state migration coefficient (D_{NTB}) are depicted in Fig. 7. The migration coefficient had smaller values for samples prepared using CEM III than using CEM I. This result could be expected from the results obtained for the total porosities. For mortar specimens with CEM I under environmental condition A (100% RH), the samples with w:c ratio 0.4 had the highest migration coefficient at 7 days age. The chloride migration

coefficient obtained with these samples decreased with the hardening age, and at the age of 180 days their migration coefficient is the lower of all the CEM I samples.

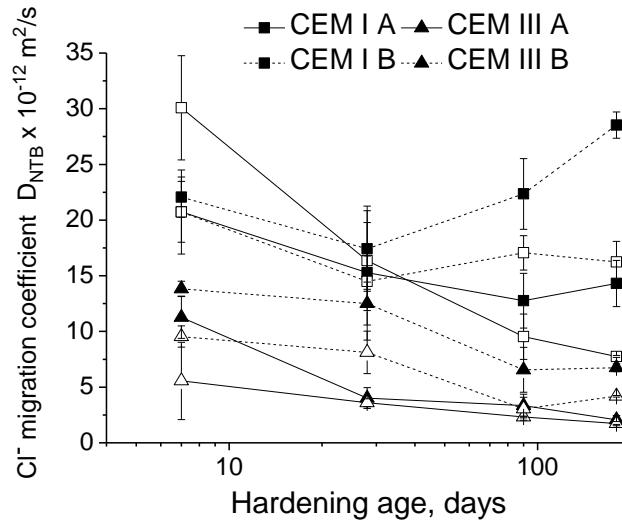


Fig. 7. Results of the Non-Steady-State Migration Coefficient (D_{NTB}) for Both Type of Cements Studied. Full Symbols are for w:c Ratio=0.5 while Open Symbols are for w:c Ratio=0.4.

For environmental condition B (65% RH), CEM I samples and w:c ratio 0.5 had higher D_{NTB} than samples with w:c ratio 0.4, and both presented a similar decreasing tendency of this coefficient between 7 and 28 days of age. For CEM I specimens with w:c ratio 0.5, the coefficient D_{NTB} increased between 28 and 180 days. This rise was not observed for CEM III samples with the same w:c ratio hardened under condition B. As could be expected from the results obtained with mercury intrusion porosimetry, this could be due to the higher volume of capillary pores in CEM I samples than in CEM III ones at ages higher than 90 days. The higher volume of capillary pores makes easier the ingress of chlorides into these CEM I mortars with w:c ratio 0.5. Besides, the development of shrinkage microcracks in that samples, as a consequence of lower RH in the environment, also could facilitate the ingress of chlorides. These microcracks could facilitate that a higher volume of capillary pores are accessible to aggressives. This effect of microcracking could also be produced in CEM III mortars with w:c ratio 0.5, but their smaller volume of capillary pores makes more difficult the ingress of chlorides, as indicated by their lower D_{NTB} at 180 days of age.

As should be expected from previous results, samples prepared with CEM III in environmental condition A had an important decrease of D_{NTB} with special importance between 7 and 28 days. In hardening condition B, the biggest decrease of migration coefficient happened between 28 and 90 days. At the age of 90 days, D_{NTB} was very similar for all the CEM III mortars, independently of environmental condition. At 180 days of age, D_{NTB} continued decreasing for samples under condition A, and kept practically constant for specimens under condition B.

Again, it is shown that a high RH in the environment makes easier the development of hydration and pozzolanic reactions, and then, the non-steady-state migration coefficient decreases quickly. Nevertheless, if RH is lower, pozzolanic reactions develop slower and the

non-steady-state migration coefficient decreases later, but also reaches good values for CEM III. At greater ages (more than 90 days), the influence of lower RH has more effect in CEM I samples, specially for those with w:c ratio 0.5, and their D_{NTB} increases. This fact is a consequence of combination between shrinkage effects and higher volume of capillary pores, which show the direct relation between microstructure and non-steady-state chloride migration coefficient.

CONCLUSIONS

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

- Relative humidity has an influence on materials properties. This influence is higher in cements containing ground granulated blast furnace slag (CEM III).
- Hg retained is greater in CEM III mortar samples. This show that the tortuosity of pore network increases due to the formation of new solids, by the hydration and also the pozzolanic reactions.
- In general, CEM III samples show better properties of durability at 180 days of age.
- High relative humidity improves slightly the durability properties of CEM I mortars. The presence of water favours hydration reactions of CEM I components.
- The development of pozzolanic reactions and the formation of new solids, cause an important improvement of durability properties of CEM III mortars.
- The improvement of the durability is delayed in environments with relative humidity lower than 100%, but after 180 days hardening these properties have reasonable good values in the majority of the cases studied.
- Relative humidity lower than 100% can produce shrinkage microcracking in mortars at greater hardening ages, as indicated by the increase of total porosity for most of the samples studied.
- The replacement of high percentage of clinker by ground granulated blast-furnace slag produces a densification of pore structure and a pore refinement. This fact causes a decrease of the volume of capillary pores and an improvement of the resistance to chloride ingress for CEM III mortars, specially under non optimal laboratory conditions.
- Cements with ground granulated blast-furnace slag, hardened under environmental conditions of Mediterranean climate, can have good service properties in the long term.

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