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Influence of Environmental Conditions on Durability Properties of Fly Ash Cement Mortars

I. Sánchez, T.S. Albertos, J.M. Ortega, M.A. Climent.

Departament d'Enginyeria de la Construcció, Obres Públiques i Infraestructura Urbana. Universitat d'Alacant. P.O. Box 99. 03080 Alacant (Spain). E-mail: <isidro.sanchez@ua.es>, <taliasefarad@hotmail.com>, <jm.ortega@ua.es>, <ma.climent@ua.es>.

ABSTRACT

It is a well known fact that the use of active additions to clinker provides both economical and ecological benefits. The fly ashes have been proved to be materials with pozzolanic activity that improve concrete service properties.

The Spanish cement industry produces cements that have different percentage of substitution of clinker by fly ash.

Chloride diffusion coefficients have been measured for mortars prepared with cements with different content in fly ash. Those coefficients were determined in saturated samples.

Two factors that can have the most severe effect on the behavior of these materials are the moisture and temperature where samples are cured. Most of the experiments are performed in an optimum laboratory environment, close to 100% relative humidity and controlled temperature. In real structures the environment is very different.

These conditions can affect the development of the hydration and pozzolanic reactions. The effect of the temperature on the hydration reactions has already been observed.

INTRODUCTION

The use of active additions is quite popular since many years ago. It is an efficient way to treat wastes, and to improve the properties of concrete. These additions react with the $Ca(OH)_2$ that is formed during the hydration of the calcium silicates of the clinker, and forms new hydrated products that improve the properties of concrete. For these pozzolanic reactions it is necessary the presence of water, that can be the water for the mixture, or water present in the environment.

For these materials the tests in the laboratory provide very good results, from several points of view, such as mechanical properties [Wang et al. 2003, 2004], or chloride ingress [Sanchez et al. 2007]. In the laboratory the samples are kept in humidity chambers, which usually keep the relative humidity (RH) over 95%.

Many structures are not hardened in environments rich in water, they are cast in situ, and the hardening occurs at a RH lower than the optimum laboratory environment (100% RH), and under those conditions the development of the microstructure can vary, and cause differences in the service properties. It has been shown in a laboratory environment that the chloride diffusion coefficient at 75 days is not dependent on the degree of replacement of clinker by fly ash [Sanchez et al. 2007]. In that work the microstructure was studied using a non destructive technique of impedance spectroscopy and it was observed that the changes started later in the cement with higher replacement of clinker, but the final point was similar to a cement with a minor quantity of fly ash.

The objective of this work is to study the influence of the relative humidity in the environment on the development of the pozzolanic reactions, and the service properties of the materials. This study has been made for cements with different content in fly ash, to check if the curing conditions also has different effects when the degree of substitution of clinker by fly ash changes. If, in spite of the curing conditions, both cements have a reasonably good behaviour, the cement with a higher degree of replacement of clinker will be much better from the point of view of the sustainability as well as from an economic point of view.

EXPERIMENTAL SETUP

Sample preparation

Mortar samples were prepared using two different types of commercial cement, with a different degree of replacement of clinker by fly ash. The study has been made using two commercial Spanish cements. A Portland cement with fly ash (CEM II B-V 42.5 R according to the Spanish standard UNE EN 196-1) was supplied by Cementos Lafarge, and this cement has a content of fly ash from 21 to 35%. Cementos Portland Valderrivas provided the second cement type, a pozzolanic cement (CEM IV B(V) 32.5 N, according to the Spanish standard UNE EN 196-1) that has a degree of replacement from 36 to 55%. Mortars were prepared according to the UNE EN 196-1 standard, with ratio sand: cement 3:1 and water: cement 0.4 and 0.5.

Both cement types contain fly ash. The chemical composition of the fly ash employed is not available, but both can be classified as type V (according to the Spanish standard). This classification means that their reactive CaO content is less than 10% in mass and the SiO_2 reactive is more than 25% in mass.

The samples were cast in cylindrical moulds, of 10 cm radius, and 15 cm height, and after 24 hours in the moisture chamber, at 20ºC and 95% RH they were demoulded. Two slices of 5 cm thickness were obtained from each cylinder.

These cylinders were kept in RH controlled chambers at 20ºC until the testing time. The RH controlled chambers contained distilled water for a RH of 100%, and a solution of glycerol to achieve a RH of 65%. This solution was prepared according to the standard DIN 50 008 part 1.

Tests were run at 7, 28 and 90 days hardening, for each cement type and each w:c ratio. Three samples were tested at each hardening age.

Microstructural characterisation

The microstructure of the mortars hardened under different environmental conditions was determined using mercury intrusion porosimetry. This is a well known technique, and has been widely reported elsewhere [Cabeza et al. 2002, Sánchez et al. 2008], as well as the main problems of using this technique [Diamond 2000, Galle 2001].

The measurements were made using an Autopore IV 9500 from Micromeritics. This porosimeter allows pore diameter determination in the range from 5 nm to 0.9 mm.

The main analysis made, on the obtained results, were the total porosity, the volume of pores with pore diameter on each decade, and also the total porosity. This result, as published by Cabeza et al [Cabeza et al. 2002], can be related to the tortuosity of the pore network and can be used to study the degree of development of the pozzolanic reactions in this type of materials [Sanchez 2007].

Service properties

The properties of the materials were measured to know both the mechanical resistance, as well as their durability properties at different ages, and also as a function of the curing conditions.

Mechanical properties

The mechanical properties of the mortars were measured according to the Spanish standard UNE EN 196-1 standard. The compressive strength was measured on each of the six samples for condition.

Durability: capillary sorption test.

It is a fact well known that aggresives in concrete can arrive where water arrives [Baroghel-Bouny 2007]. This is why the RILEM has established the capillary sorption test as one of the main tests to estimate the durability of concrete.

Due to the special characteristics of the samples tested, and the objective of this work, the samples were not conditioned to a 70% of saturation degree. As it was established the objective of the work is to study the influence of the relative humidity in the development of the microstructure and in the service properties. As the testing times were 7, 28 and 90 days it seemed necessary to remove all the water possible to start the test with the sample with the microstructure influenced by the environment at the testing age.

Samples were dried in an oven at 105ºC for 12 hours and then kept in an hermetic recipient with silica gel for another 12 hours, to have the samples at room temperature at the beginning of the experiment.

The test was made using the standard PrUNE 83.932 and sample mass was measured at the beginning of the experiment and at the times suggested by the standard. The results obtained are the capillary suction coefficient and the water porosity, which are calculated according to the following expressions:

$$\varepsilon_e = \frac{Q_n - Q_0}{A \cdot h \cdot \delta_a} \qquad (1)$$

$$K = \frac{\delta_a \cdot \varepsilon_e}{10 \cdot \sqrt{m}} \text{ with } m = \frac{t_n}{h^2} \qquad (2)$$

where: ε_e is the effective porosity. Q_n is the weight of the sample at the end of the test, g. Q_0 is the weight of the sample before starting the test, g. A is the surface of the sample in contact with water, cm^2. h is the thickness of the sample, cm. δ_a is the density of water, 1 g/cm^3. K is the capillary suction coefficient, $kg/m^2min^{0,5}$. m is the resistance to water penetration by capillar suction, min/cm^2. t_n is the time necessary to reach the saturation, minutes.

Three samples of each cement type were tested at each age.

Durability: forced migration test.

Other factor that can cause deterioration of concrete structures is the pitting corrosion of reinforcing steel bars due to chloride ingress. This is a common problem of maritime structures. The determination of the chloride migration coefficient was made using a forced migration technique. Due to the objective of the work a very fast migration experiment was chosen. The method chosen is described in the standard NT Build 492 [Nordtest 1999] and it takes about 24 hours. Previous to the migration test the mortar samples need to be water saturated according to the standard ASTM C1202-97 [ASTM 1997].

Fig. 1: Sample Prepared with CEM II after 90 Days Hardening at 100% RH, and After the Chloride Forced Migration Test. The White part Corresponds to the Region where Chlorides have Penetrated Due to the Electric Field Applied, while the Rest of the Sample has not Suffered Chloride Ingress.

Once the samples are saturated they are placed inside a rubber tube, and fixed. The upper part of the tube is filled with a NaOH 1M solution, according to the standard, while the recipient where the set sample-tube is introduced is filled with a solution 10% NaCl in mass. The absence of liquid leaks is checked and the experiment starts. Depending on the current across the sample at a fixed potential of 30 V, they are chosen both the applied voltage during the experiment and the duration of the test. Once the test has finished the samples are axially broken and both halves are sprayed with a silver nitrate solution. The part of the sample where chlorides have penetrated becomes white. It permits the determination of the penetration profile. According to the standard, the penetration depth on 7 points is measured inside the sample, and with the average penetration depth, the applied potential, and the test time the chloride migration coefficient is calculated according to the expression (3):

$$D_{nssm} = \frac{0{,}0239 \cdot (273 + T) \cdot L}{(U - 2) \cdot t} \cdot \left(x_d - 0{,}0238 \cdot \sqrt{\frac{(273 + T) \cdot L \cdot x_d}{U - 2}} \right) \tag{3}$$

Where x_d is the average penetration depth, in cm, L is the sample thickness, in cm. U is the applied potential in volts. T is the average temperature measured in ºC at the beginning and the end of the experiment, and finally t is the time of the experiment in hours. Tests were made on three samples of each cement type at 7, 28 and 90 days of hardening.

RESULTS

The results will be presented following the same structure used for the experimental section.

Microstructural characterisation

The total porosity, as well as the mercury retained after the experiment are shown in Fig. 2, and the pore size distribution is shown in Fig. 3. The values for the total porosity are among 10 and 18 % of the volume. The total porosity decreases for all the samples with the hardening age, except for the samples made with CEM IV with w:c ratio 0.4 that were hardened at 65% RH. The value of the porosity for a given cement type and environment is always greater for samples with w:c=0.5. The relative humidity seems not to have much influence on the total porosity of the samples.

Taking a look at Fig. 2.c and Fig. 2.d it can be seen that the retention of mercury also is increased with the hardening age, with independence of the cement type and curing conditions. Most of the samples kept at 65% RH show higher mercury retention than their twins kept at 100% RH. The distribution of the total porosity by diameter is shown in Fig. 3. As it can be seen there are some differences depending on the relative humidity of the environment where they are hardened.

For samples hardened at 100% RH there is a clear decrease, with the age, in the percentage of pores with diameters in the range from 100 nm to 1 µm. This result is general for both cement types and w:c ratios. As it can also be seen in Fig. 3.a, the total volume of pores with diameter minor than 1 µm also decreases with the age of the samples.

For samples kept at 65% of RH there are some differences. The pores with diameter among 100 nm and 1 µm do not show a decreasing tendency with time. In most of the cases there is an increasing tendency in the volume of pores with diameter between these two values. Only for samples made with CEM IV and w:c=0.5 at the age of 90 days the volume of these pores decreases. The volume of pores with diameter lower than 1 µm remains approximately constant, or decreases slowly for samples with w:c=0.5, under the condition of 65% RH in the environment.

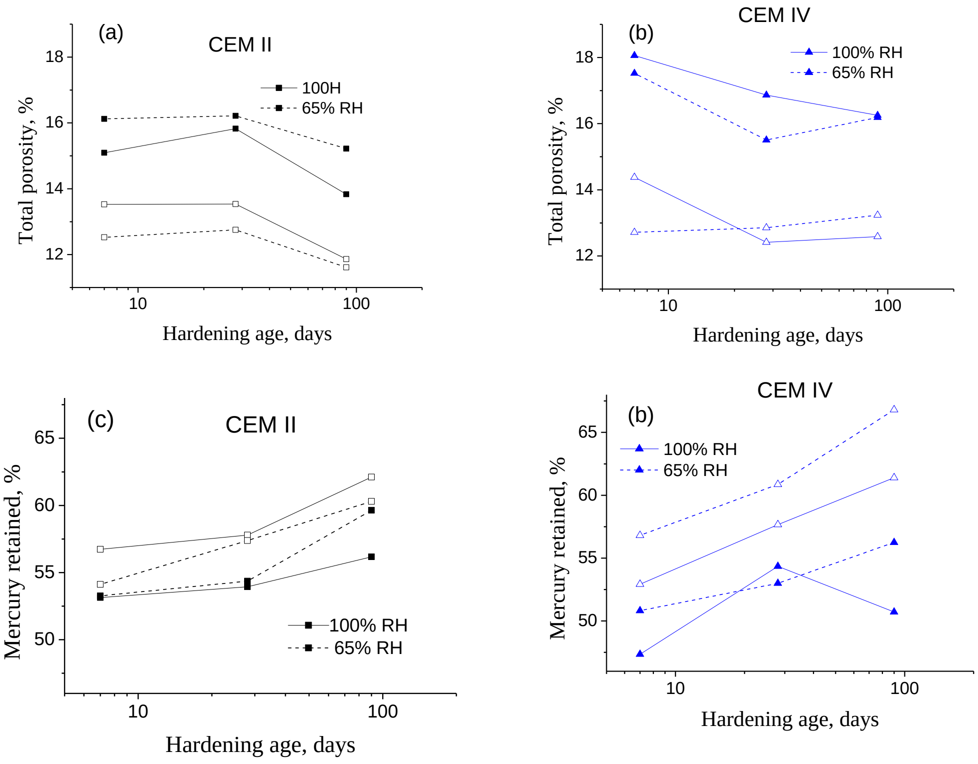

Fig. 2: Total Porosity (a,b) and Mercury Retention at the End of the Experiment (c,d) for Both Cement Types. Filled Symbols Correspond to w:c Ratio 0.5, and Open Symbols to w:c=0.4.

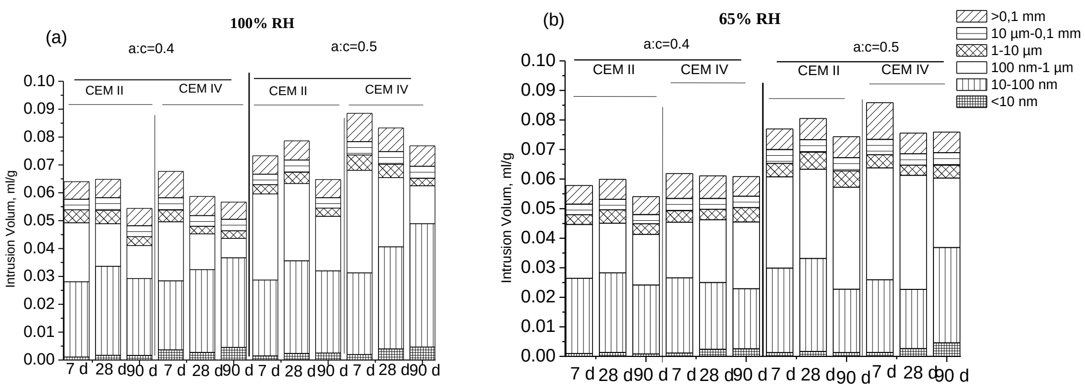

Fig. 3: Distribution by Diameter Ranges of the Total Porosity, for All Samples Studied.

Mechanical properties

As expected the compressive strength increased with time. The value of the strength was greater for samples with lower w:c ratio. The value obtained with CEM IV is always lower than the value obtained with CEM II, according to the differences in strength classes.

In the first days, for some of the samples, the mechanical strength of the samples kept at 65% RH is higher than for those kept at 100% RH. After 90 days hardening a sample hardened at 100% RH always shows greater strength than the same sample at 65% RH.

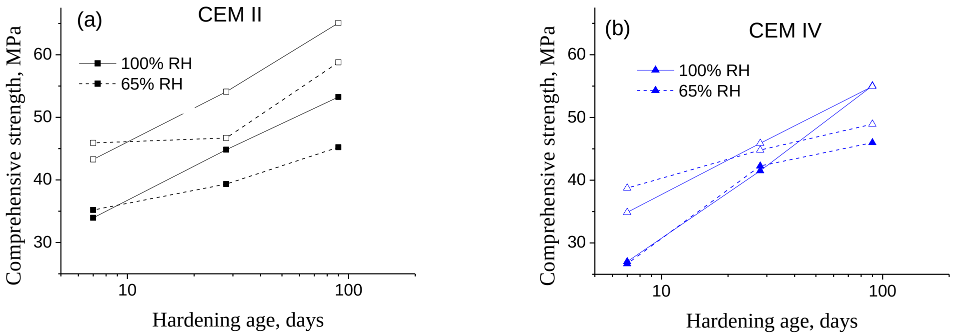

Fig. 4: Evolution with Time of the Compressive Strength for the Studied Samples. CEM II Results are Shown in Fig. 4 (a) while for CEM IV in (b). Filled Symbols are for w:c Ratio 0.5 and Open Symbols for w:c=0.4.

Durability: capillary sorption test

The capillary sorption coefficient determines the rate of penetration of water inside the sample in terms of absorbed water per time and per surface exposed.

Water penetrates inside empty and accessible pores. The result obtained is in agreement with the fact that total porosity of the sample decreases with time, and the capillary suction coefficient also decreases. This general result is especially clear in the case of CEM II hardened in the environment with 100% RH.

CEM IV does not show a significant variation, and with low w:c ratio, and hardened at 65% RH the value of the suction coefficient does not change with the hardening time.

From this experiment the water porosity can also be obtained. It measures the total volume of pores that can be acceded by water, and with the single mechanism of capillarity. This result is depicted in Figs. 5c and 5d.

The value of the water porosity is in general lower for samples hardened in a high moisture environment. The value of the water porosity decreases drastically form 28 to 90 days for samples prepared with CEM II and hardened at 100% RH.

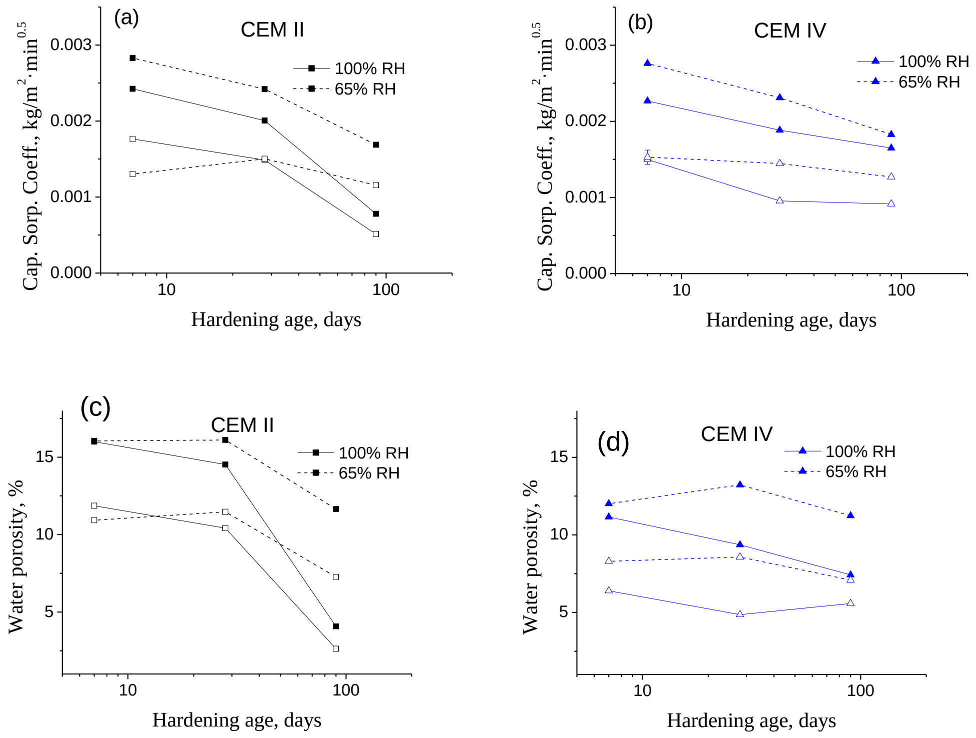

Fig. 5: Evolution with Time of the Capillary Suction Coefficient (a, b) and Water Porosity (c,d). Both Parameters are Obtained from the Capillary Sorption Experiment. Full Symbols Correspond to w:c=0.5 and w:c=0.4 is Represented with Open Symbols.

Durability: chloride forced migration test.

As it was explained before, chlorides are very aggressive ions for reinforced concrete in marine environment.

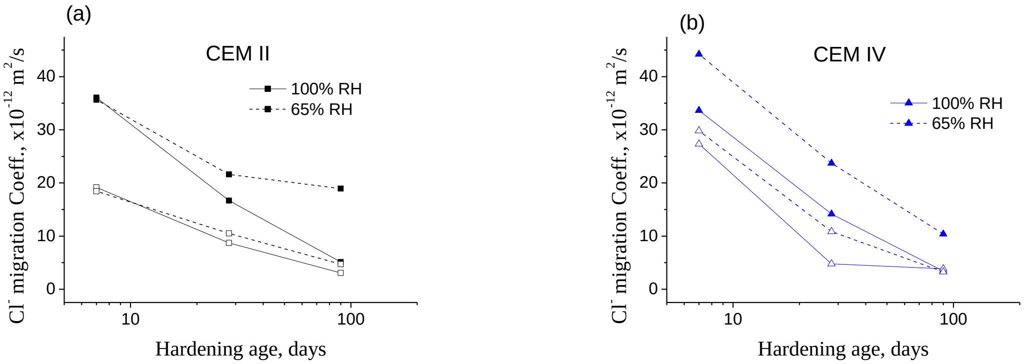

Fig. 6: Evolution with Time of the Chloride Migration Coefficient, Obtained from the Forced Migration Test, for Samples of CEM II (a) and CEM IV (B). Open Symbols Represent w:c ratio 0.4 and Full Symbols w:c=0.5

The rate of diffusion of these ions can be estimated by measuring the migration coefficient through a material.

The results obtained using the accelerated migration technique described in the experimental section can be seen on Fig. 6.

The value of the migration coefficient decreases with the hardening time as a general result. The lower is this coefficient the slower chlorides can ingress in the structure. The obtained migration coefficients are greater for samples with higher w:c ratio. It also can be seen that in general samples hardened at 65% RH show higher values for the diffusion coefficient than their twins kept at 100% RH.

DISCUSSION

The analysis of the pore network for each sample type reveals a refinement of the microstructure especially in the samples made with CEM IV, hardened under 100% RH. The total porosity also decreases and the evolution of pore dimensions suggests that inside the pores with diameter greater than 100 nm appear new solids, which form a finer pore network. This decrease is less important for CEM II, with lower content of fly ash, and it can confirm that the new solids are products of the pozzolanic reaction.

In the case of samples hardened at 65% RH the results are quite different. For these samples the volume of pores of diameter minor than 100 nm does not vary much for CEM II samples. Only for CEM type IV there is a decrease of the amount of pores with diameter among 10 and 100 nm after 90 days hardening, and it only happens for samples that were prepared with w:c ratio 0.5. However there is also a refinement of the pore network of all these materials. As it can be seen there is an increase in the amount of pores with diameter below 10 nm. This increase in the amount of pores with small diameter is confirmed by the increase in the retention of mercury after the experiment, bigger for samples with CEM IV.

The differences in the evolution of the microstructure could be explained taking into account the RH in the environment where samples are hardened. Both cements have the same type of fly ash in their composition, with different quantity. It is a fact well known that they need water for the pozzolanic reaction. The lower RH in the environment means the less water available for these reactions. If the pozzolanic reactions can not progress there will be less changes in the microstructure, and that may be the reason why samples hardened at 65% RH show almost no changes in their microstructure.

The results obtained from mercury porosimetry confirm the results of the mechanical resistance of the materials. The decrease in the total porosity, as well as the increase of the pores of small dimension is in coincidence with the increase of the mechanical resistance. These small dimension pores are more related to the durability properties.

The strength of CEM IV increases faster than it does for CEM II, when samples are hardened at 100% RH. In these samples, the amount of pores with diameter over 100 nm decreases very fast. For samples hardened at 65% RH the evolution of the compressive strength is different. Samples of CEM II show an increase of resistance after 28 days hardening, while samples made with CEM IV have an increase of resistance between 7 and 28 days. This result can be explained in terms of the differences of the microstructural evolution, where CEM IV shows a constant amount of pores over 1 μm after 28 days.

The water porosity, calculated from the capillary sorption test essentially is coincident with the result of total porosity for both cement types. The main difference can be seen in CEM II. The value of total porosity decreases drastically at the age of 90 days. This decrease is less important for samples hardened at 65% RH. As it has already been explained, this fact could be due to the minor evolution of the hydration and pozzolanic reactions. The limited presence of water in the environment could be the cause of this result. This result is in agreement with the decrease of the total porosity, and the decreasing tendency.

The capillary sorption coefficient, also calculated from these experiments has the meaning of the velocity of ingress of water by capillarity inside the materials. As the total porosity decreases, this parameter should decrease also, because there are less pores than can be filled with water and the ingress of water will be slower. The second cause that can make this coefficient decrease is the presence of smaller pores in the material. Water penetrates easily in big pores than it does in the small ones. The presence of more pores with small diameter in a material means a decrease in the capillary suction coefficient. The combination of both factors, observed in the studied materials, causes a decrease in the capillary sorption coefficient as observed in Figure 5. For samples hardened at 100% RH the decrease of the coefficient is more important for CEM type II. This result agrees with the fact that the CEM type IV had a bigger refinement of the pore network, with a big increase of pores of small diameter. For samples hardened at 65% RH the behaviour is coincident also with the microstructural evolution. Under this condition the value of the suction coefficient is equivalent for both cement types.

The chloride migration test shows a decreasing tendency in the value of the migration coefficient for all samples. This result is in agreement with the decreasing tendency observed in the porosity.

For most of the conditions the migration coefficient decreases faster for CEM type IV than for type II. This result had already been shown for samples kept at 95% RH and using another testing procedure [Sanchez 2007]. In that case the result was also explained in terms of a refinement of the microstructure. The same argument can be used here. The smaller are the pores the slower chlorides can penetrate. In our case, samples hardened at 100% RH show a big increase of the pores with dimensions below 100 nm, with hardening age. As it was said the pore network changes less when samples are kept at 65% RH, possibly due to the absence of water for the pozzolanic reactions, and this result is in coincidence with the result obtained from the forced migration experiment.

However, independent from the RH the values obtained for CEM IV samples reach values equivalent or even lower than samples prepared with CEM type II.

CONCLUSIONS

The relative humidity of the hardening environment, or the curing conditions, has influence on both the microstructure and the service properties of mortars prepared with fly ash cements.

The microstructure does not change much when samples are hardened at 65% RH, while samples hardened at 100% RH show a big increase in the volume of pores with diameter minor than 100 nm, and a decrease of the fraction of pores bigger than 100 nm.

This fact causes an increase in the compressive strength, bigger for samples hardened in a moisture rich environment. Samples kept at 65% RH during the hardening also show an increasing strength, but with a minor slope.

The durability properties, both capillary sorption, and chloride ingress improve with the hardening time.

The properties studied at 90 days have bigger dependence on the relative humidity than in the degree of replacement of clinker by fly ash. This means that both cement types can be used without losing service properties in real conditions. It will imply an important step for the sustainability of the construction industry due to the less consumption of clinker.

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REFERENCES

ASTM C1202-97. “Standard test method for electrical indication of concrete’s ability to resist chloride ion penetration.” ASTM International, West Conshohocken, PA, 6 pages.

Baroghel-Bouny, V. (2007). “Water vapour sorption experiments on hardened cementitious materials: Part I: Essential tool for analysis of hygral behaviour and its relation to pore structure” Cem Concr. Res. 37(3) 414-437.

Baroghel-Bouny, V. (2007). “Water vapour sorption experiments on hardened cementitious materials. Part II: Essential tool for assessment of transport properties and for durability prediction” Cem Concr. Res. 37(3), 438-454.

Cabeza M., Merino P., Miranda A., Nóvoa X.R., Sanchez I. (2002). “Impedance spectroscopy study of hardened Portland cement paste”. Cem Concr. Res., 32 881-891

Diamond, S. (2000). “Mercury porosimetry. An inappropriate method for the measurement of pore size distributions in cement-based materials.” Cement and Concrete Research, 30, 1517-1525.

Gallé, C. (2001). “Effect of drying on cement-based materials pore structure as identified by mercury intrusion porosimetry. A comparative study between oven, vacuum and freeze-drying.” Cement and Concrete Research, 31, 1467-1477.

NT Build 492. “Concrete, mortar and cement-based repair materials: Chloride migration coefficient from non-steady-state migration experiments.” Nordtest. (1999) Espoo (Finland).

Sánchez, I., López, M.P., Climent, M.A. (2007); Effect of Fly Ash on Chloride Transport through Concrete: Study by Impedance Spectroscopy.; Proceedings of the 12th International Congress on the Chemistry of Cement; edited by J.J. Beaudoin, J.M. Makar and L. Raki; Durability and Degradation of Cement Systems: Corrosion and Chloride Transport ; T4.04-4; published by the National Research Council of Canada; Montreal Canada; (2007). ISBN: 978-0-660-19695-4

Wang, A., Zhang, C., Sun. W. Fly ash effects: The morphological effect of fly ash. Cem Concr. Res. 33, (2003). pp 2023-2029

Wang, A., Zhang, C., Sun. W. Fly ash effects: The active effect of fly ash. Cem Concr. Res. 34, (2004). pp 2057-2060