

Article

Effects of Environment in the Microstructure and Properties of Sustainable Mortars with Fly Ash and Slag after a 5-Year Exposure Period

José Marcos Ortega , Rosa María Tremiño, Isidro Sánchez  and Miguel Ángel Climent * 

Departamento de Ingeniería Civil, Universidad de Alicante, Ap. Correos 99, 03080 Alicante, Spain; jm.ortega@ua.es (J.M.O.); rmta2@alu.ua.es (R.M.T.); isidro.sanchez@ua.es (I.S.)

* Correspondence: ma.climent@ua.es; Tel.: +34-96-5903-400 (ext. 2468)

Received: 30 January 2018; Accepted: 27 February 2018; Published: 1 March 2018

Abstract: Nowadays, getting a more environmentally sustainable cement production is one of the main goals of the cement industry. In this regard, the use of active additions, like fly ash and ground granulated blast-furnace slag, has become very popular. The behaviour, in the short-term, of cement-based materials with those additions is well-known when their hardening is produced under optimum conditions. However, real structures are exposed to different environments during long periods, which could affect the development of microstructures and the service properties of cementitious materials. The objective of this work is to analyse the effects in the long-term (up to 5 years approximately) produced by the exposure to different non-optimum laboratory conditions in the microstructure, mechanical and durability properties of mortars made with slag and fly ash commercial cements. Their performance was compared to that observed for ordinary Portland cement (OPC) mortars. The microstructure has been analysed using mercury intrusion porosimetry. The effective porosity, the capillary suction coefficient, the chloride migration coefficient and mechanical strengths were analysed too. According to the results, mortars prepared using slag and fly ash sustainable commercial cements, exposed to non-optimum conditions, show a good performance after 5-years hardening period, similar or even better than OPC mortars.

Keywords: ground granulated blast-furnace slag; fly ash; long-term exposure; environment; temperature; relative humidity

1. Introduction

Nowadays, getting a more environmentally sustainable cement production is one of the main goals of the cement industry. Among the different ways to reach this aim, the use of additions as clinker replacement has lastly become increasingly common [1–6], providing benefits such as the lessening of CO₂ emissions and the reduction of energy consumption throughout the cement manufacture, as well as the reuse of wastes coming from other industrial sectors, which would also help to solve their storage problem.

The most popular active additions are ground granulated blast-furnace slag and fly ash and consequently their effects on the pore structure and cementitious materials properties have been well-studied, mainly when their hardening was produced in optimum laboratory conditions [7–9]. Under those conditions, they showed a better behaviour compared to cement-based materials prepared using ordinary Portland cement (OPC) without any addition [7]. On one hand, for slag this result is related to the hydration reactions of this addition, which form new CSH phases, entailing a more refined pore network [7,8,10]. On the other hand, the fly ash has pozzolanic activity, which means that it reacts with portlandite produced along the clinker hydration, giving rise to the formation of additional hydrated products, thus increasing the refinement of the pore network of mortars and

concretes [9–11]. The abovementioned pore refinement produced by both additions improves the performance of cementitious materials, for example their chloride ingress resistance [12–17] and their permeability [18].

However, real structures are hardened in different environmental temperature and relative humidity conditions than optimum laboratory one and this could affect the development of the pore network and service properties of cementitious materials, especially when active additions are used. In this regard, there are not too many experimental works where slag and fly ash cement-based materials had been hardened under real in-situ environments [12,13,19–26] and considering their results, those materials showed different behaviour as a function of the climate characteristics of the place in which the specimens were located, although the majority of them coincide in the fact that the use of both additions is particularly adequate for marine structures [13,23,27,28].

For studying the effects of the different environmental parameters which are involved in the development of microstructure and properties of cement-based materials, the main problem of exposing the materials to a real in-situ hardening conditions is the higher variability of the environmental temperature and relative humidity (among other parameters) during the exposure period, which make difficult to determine the effects of each one of them, especially when active additions are used. Then, it could also be appropriate to analyse the influence of exposure of those materials to non-optimum laboratory conditions, with a combination of constant temperature and relative humidity, as a complement and a good approach to real in-situ environment studies.

Regarding those non-optimum laboratory hardening conditions, there are several researches where slag and fly ash cementitious materials were kept under different constant temperature and relative humidity [29–37] and most of them concluded that overall the performance of those materials was adequate [30,31,33–35,38], mainly when the condition presented relatively high values of those environmental parameters [30,31]. Nevertheless, the above-mentioned research has only studied the influence of those parameters over a relatively short time (in general less than 1 exposure year) and their effects would probably be more noticeable after very long exposure times. Furthermore, the analysis of the performance in the very long-term of cementitious materials with fly ash and slag kept under non-optimum laboratory hardening conditions could be also interesting in relation to the fact that the real structures should be designed for long service life periods, generally up to 50 years or even longer [39].

Then, the main purpose of this work is to observe the very long-term effects (until 5 years approximately) produced by the exposure to different non-optimum laboratory conditions, in which different constant relative humidity and temperature values were combined, in the microstructure, mechanical and durability behaviour of mortars prepared with fly ash and ground granulated blast-furnace slag commercial cements. Their performance has been compared to that noted for ordinary Portland cement (OPC) mortars. With respect to the experimental methodology of this research, the microstructure has been characterised through mercury intrusion porosimetry. Moreover, the studied parameters related to durability were the non-steady state chloride migration coefficient, the capillary suction coefficient and the effective porosity. Lastly, the mechanical behaviour of the mortars was checked determining their compressive and flexural strength.

2. Materials and Methods

2.1. Sample Preparation

In this work, mortar samples were tested, which were made using four commercial cements. The first one was an ordinary Portland cement, CEM I 42.5 R (CEM I hereafter) according to the Spanish and European standard UNE-EN 197-1 [40]. The others were sustainable cements. On one hand, a slag cement type III/B 42.5 L/SR [40] (CEM III from now on), with a content of ground granulated blast-furnace slag between 66% and 80% of total binder, was studied. On the other hand, two commercial fly ash cements were also analysed, a Portland cement with fly ash, CEM

II/B-V 42.5 R [40] (CEM II hereafter), with fly ash content from 21% to 35% and a pozzolanic cement, CEM IV/B(V) 32.5 N [40] (CEM IV from now on), whose percentage of fly ash was between 36% and 55% of total binder. The different components of each one of the commercial cements and their percentage of the total binder are detailed in Table 1. It is important to emphasize here that the four studied cements were commercial ones, for reproducing more accurately the conditions of in-situ construction, when it commonly is difficult to mix OPC and additions in the field. The mortars were made using water to cement (w:c) ratios 0.4 and 0.5. Fine aggregate was used according to the standard UNE-EN 196-1 [41] and the aggregate-to-cement ratio was 3:1 for all the mortars.

Cylindrical specimens, with dimensions 10 cm diameter and 15 cm height, have been prepared, as well as 4 cm × 4 cm × 16 cm prismatic specimens [41]. After setting, all specimens were kept in a chamber with 20 °C and 95% RH along 24 h. Previously to the exposure to the different environmental conditions, the cylindrical specimens were cut in order to obtain cylinders of 1 cm and 5 cm thickness. Finally, the tests were performed at 28, 365 and 1900 days (5 years approximately) of age.

2.2. Environmental Conditions

As it has been explained in the introduction section, the main objective of this work is to analyse the very long-term effects (up to about 5 years) in different types of sustainable cement mortars, produced by the exposure to different non-optimum laboratory conditions, in which temperature and relative humidity values were combined.

In order to reach this aim, four different laboratory environments were analysed (see Table 2). The first one (environment A) consisted of an optimum laboratory condition with 20 °C and 100% relative humidity (RH), which was considered as a reference for comparing the effects of the rest of non-optimum environments in the pore structure and properties of the mortars. The environments B (15 °C and 85% RH) and C (20 °C and 65% RH) represented the Atlantic and Mediterranean climates. Those climates are present in different areas of Iberian Peninsula (Spain and Portugal) and their RH and temperature values were selected according to the annual average values of both parameters for each climate. Lastly, an extreme environmental condition was analysed, named as environment D, with 30 °C and 40% RH.

The climatic conditions corresponding to environments A to D were achieved putting the mortar specimens into hermetically sealed recipients containing distilled water or glycerol aqueous solutions of the appropriate concentration, following the standard DIN 50,008 part 1 [42], to get the desired RH value. The contact between the mortar samples and the liquid was avoided. Then, the containers were stored in chambers of controlled temperature.

Table 1. Components of the commercial cements used.

Component	CEM I		CEM II		CEM III		CEM IV	
	UNE-EN 197-1 [40]	Manufacturer Data ¹						
Portland cement clinker	95–100%	95%	65–79%	75%	20–34%	31%	45–64%	50%
Limestone	-	5%	-	-	-	-	-	-
Blast-furnace slag	-	-	-	-	66–80%	69%	-	-
Fly ash	-	-	21–35%	25%	-	-	36–55%	50%

¹ Specific percentage of each component usually used according to the manufacturer.

Table 2. Overview of studied environments.

Environment	Temperature	Relative Humidity	Represented Climate
Environment A	20 °C	100%	Optimum condition
Environment B	15 °C	85%	Atlantic climate
Environment C	20 °C	65%	Mediterranean climate
Environment D	30 °C	40%	Extreme condition

2.3. Mercury Intrusion Porosimetry

The mortars pore network has been analysed with mercury intrusion porosimetry technique. The equipment used was a porosimeter model Autopore IV 9500 from Micromeritics, which allows a maximum pressure of 225 MPa. Prior to the experiment, samples were dried in an oven throughout 24 h at 105 °C. Two measurements were performed at all testing ages. The tested samples were taken from cylinders with 1-cm thickness. Pore size distribution, total porosity and percentage of Hg retained at the end of the experiment were studied.

2.4. Capillary Absorption Test

This test was performed in accordance with the standard UNE 83982 [43] and it is based on the Fagerlund method for obtaining the concrete capillarity. Before the test, the specimens were subjected to a pre-conditioning procedure, which firstly consisted of a complete drying in oven at 105 °C for 12 h. After that and up to starting the test (minimum 12 h), the specimens were maintained in a hermetic desiccator containing silica gel [14,44,45]. This pre-conditioning procedure was used, instead of other recommended protocols [46], in order to avoid too long pre-conditioning periods and the eventual need of contact of some of the mortar samples with liquid water. The results of this test are the effective porosity and the capillary suction coefficient. For each environment and cement type, three cylindrical specimens of 10 cm diameter and 5 cm thickness were tested at each age.

2.5. Forced Migration Test

Water-saturated mortar samples were tested according to NT Build 492 standard [47]. The obtained result of this test was the non-steady-state chloride migration coefficient D_{NTB} . For each condition and cement type, three 10 cm diameter and 5 cm height cylindrical specimens were tested at each studied age.

2.6. Mechanical Strength Test

Both compressive and flexural strengths were determined in accordance with the standard UNE-EN 196-1 [41]. Three 4 cm × 4 cm × 16 cm prismatic specimens were tested for each cement type and environment at the studied hardening ages.

3. Results and Discussion

3.1. Mercury Intrusion Porosimetry

The total porosity results obtained for the analysed mortars are shown in Figure 1. For environment A, generally this parameter decreased with time for all of them. This result could be related to the high relative humidity (100%) combined with a high enough temperature (20 °C) of this optimum environment, which allows an adequate development of clinker and slag hydration [30,44] and fly ash pozzolanic reactions [44,48], whose products would entail a rise of samples solid fraction and consequently a porosity reduction. The lowest total porosities for environment A corresponded to CEM III mortars, while this parameter was very similar for CEM I and II mortars and a little higher for CEM IV ones, which would be in keeping with other authors [7]. In relation to environment B, after approximately 5-years period, the values of total porosity were slightly higher compared to those observed for environment A for each cement type, although in general terms there was not so much total porosity difference between both conditions. However, the reduction rate with time of this parameter was lower for mortars exposed to environment B. The slightly higher total porosities and their slower decrease observed for environment B could be due to its lower temperature (15 °C), which would slow down the development of clinker and slag hydration [29,30], as well as the fly ash pozzolanic reactions [36,49], producing a slower formation of new solid phases. Furthermore, the lower relative humidity (85%) of this environment B in comparison with environment A would entail that less

water would be available in the long-term to carry on the development of abovementioned reactions, which would hinder them [44], as suggested that total porosity kept practically constant at very high ages, especially for CEM I and III mortars. Despite that, the slag and fly ash cement mortars again showed lower or similar total porosities compared to CEM I ones after more than 5-years exposure to condition B.

The total porosity values for mortars kept in the environment C hardly changed during the studied period, except for CEM II and III specimens prepared with w:c ratio 0.5, for which this parameter notably decreased with time. The fact that this parameter showed slight modifications could be related to the low environmental relative humidity (65%), although it is combined with an optimum temperature (20 °C). This optimum temperature would permit a suitable development of hydration and pozzolanic reactions [30,36] but the relatively low environmental relative humidity would make it difficult [44,48,50], causing a smaller new solid phases formation. Once again, the mortars prepared using sustainable cements with slag and fly ash hardened in the environment C, also showed lower or similar total porosities in the very long-term compared to CEM I mortars. Regarding environment D, the total porosity increased with hardening age for many of the studied samples and it slightly changed for the rest. This behaviour could be explained as a consequence of the extreme conditions of this environment, with a high temperature (30 °C) and very low relative humidity (40%). On one hand, the high temperature would accelerate the development of hydration and pozzolanic reactions [35,36,49], entailing a fast formation of solids in the short-term, as would corroborate the relatively low total porosities noted at 28 days. Nevertheless, the very low relative humidity would not permit the further progression of this process [30,31,33]. Moreover, this dryness of the environment could produce the appearance of shrinkage microcracking in the samples [51], which could justify the rise of the total porosity in the long-term, which has been noted in many studied mortars. In spite of that, after about 5-year exposure period, the CEM II and III mortars exposed to environment D showed lower or similar total porosities compared to those prepared using CEM I. On the other hand, the greatest values of this parameter in the long-term were observed for CEM IV mortars, which could mean that the porosity of this cement type would be more affected by the extreme conditions of environment D than the others analysed, probably by the more severe effects of the previously explained shrinkage microcracking phenomenon.

The pore size distributions obtained for specimens kept in environment A can be observed in Figure 2. Overall, it has been noted a progressive pore refinement with age for all the studied mortars. This result agrees with the total porosity results already discussed. The high water availability in this environment, combined with a high enough temperature, would facilitate the development of clinker and slag hydration, as well as the fly ash pozzolanic reactions, producing a fast new solid formation, which would reduce the size of the pores of the sample [30,44,48]. In addition to this, it is important to indicate that mortars with fly ash and slag showed a more refined microstructure than CEM I ones. This could be due to the formation of additional CSH phases as products of slag hydration and fly ash pozzolanic reactions [7–9].

The changes with time of pore size distribution for mortars kept under environment B are depicted in Figure 3. As happened in environment A, a continuous pore network refinement with hardening age has also been observed for environment B. Nevertheless, this microstructure refinement was produced in a slower way in this environment and in general terms, for all studied cement types the pore network was less refined at 1900 days compared to environment A. This result would be in keeping with those noted for total porosity and it would confirm the slowing down of hydration and pozzolanic reactions [29,30,36,49] in an environment with a temperature lower than the optimum one. In spite of that, the relatively high relative humidity would allow that these reactions continued developing [33,44], as would suggest the ongoing increase of volume of smaller pores, although without reaching the refinement degree observed for environment A.

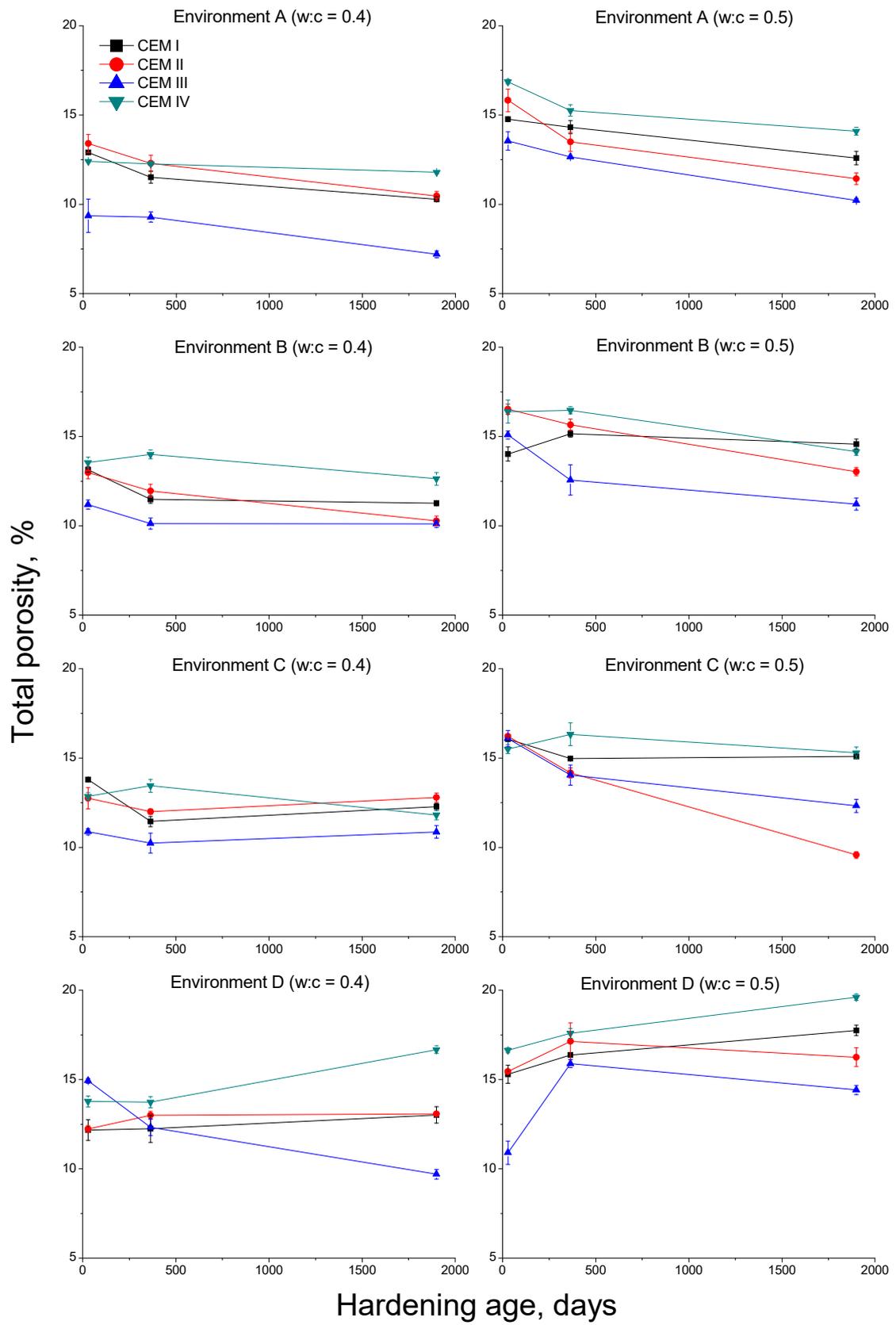


Figure 1. Results of total porosity for the studied mortars.

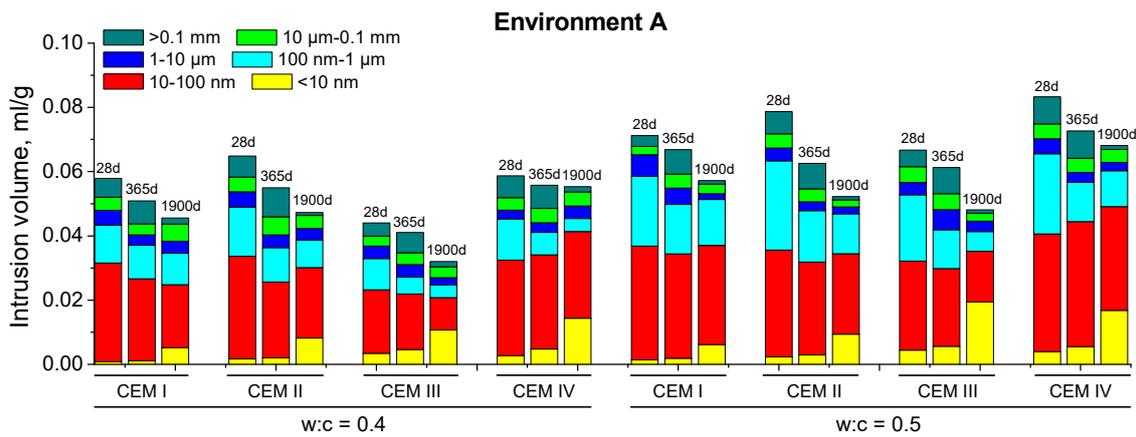


Figure 2. Pore size distributions obtained for environment A.

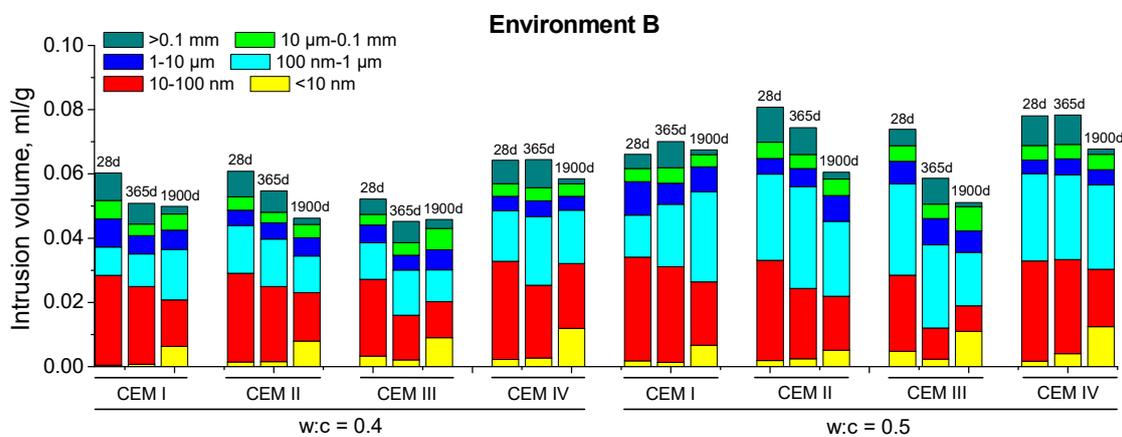


Figure 3. Pore size distributions obtained for environment B.

The development of pore size distributions for samples hardened in environment C can be observed in Figure 4. Generally, the microstructure of the samples kept under this environment was less refined than that obtained for environment A. Furthermore, at 365 days the pore size distributions of the majority of the mortars noted for environment C, were similar to those observed for environment B. However, between 365 and 1900 days, most of the samples hardened under environment C did not experience a rise of volume of fine pores (sizes less than 100 nm) and even many of them showed a loss of microstructure refinement. This would reveal the fact that an optimum temperature would favour the development of hydration and pozzolanic reactions [30,35,49] but a relative low relative humidity in the environment would prevent them in the long-term, reducing the formation of new solids [31,44] and consequently avoiding the pore refinement process.

Regarding the pore sizes distributions for mortars hardened in environment D, they are depicted in Figure 5. At 28 days, they did not differ too much compared to those observed for the rest of non-optimum conditions. In spite of that, since then until 1900 days, the majority of the mortars showed a progressive reduction of microstructure refinement, as suggested the increase of pores volume with sizes greater than 100 nm, with the exception of CEM III mortars, which were hardly affected by this extreme condition. The microstructure evolution of samples exposed to environment D generally coincided with total porosity results. The pore size distributions noted in the very-short term in environment D could be a result of its high temperature, which would accelerate the solid fraction formation by the hydration and pozzolanic reactions [30,33,35,36], increasing the volume of finer pores. Nevertheless, in the middle- and long-term the lack of enough water in the environment would prevent that this process continues [31,44]. In addition to this, as has already been explained, the very

low environmental relative humidity could produce the appearance of shrinkage cracking [31,51], which would open the pore network, reducing its refinement, as has been registered for several of the studied samples.

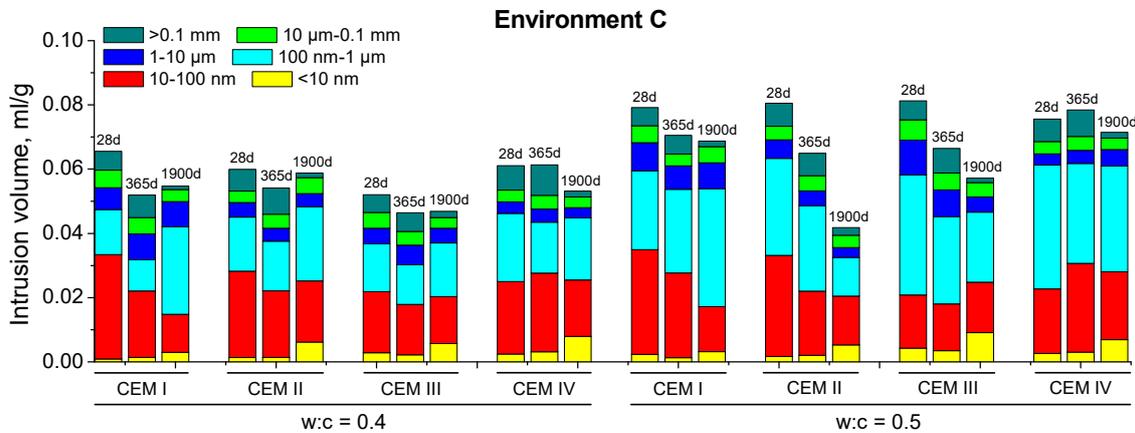


Figure 4. Pore size distributions obtained for environment C.

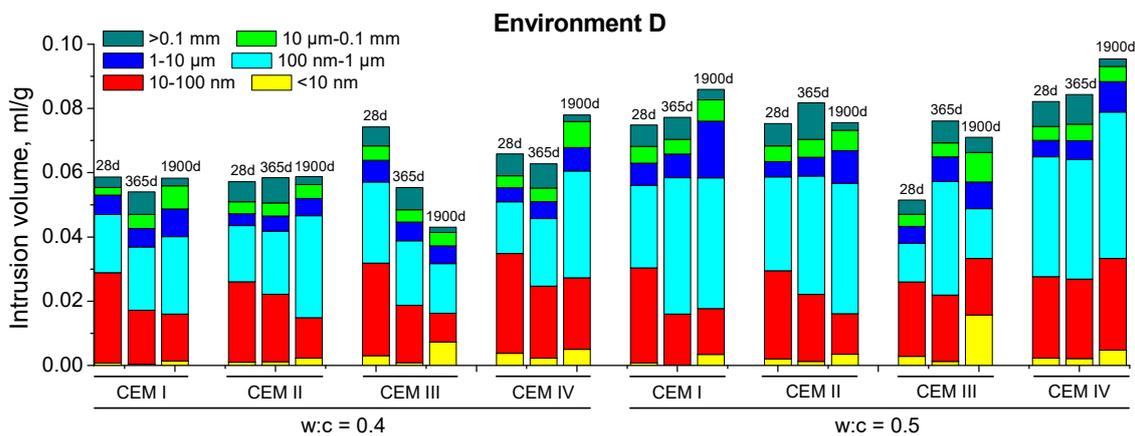


Figure 5. Pore size distributions obtained for environment D.

The results of percentages of Hg retained in the samples at the end of the experiment are shown in Figure 6. This parameter gives information about the pore structure tortuosity [52]. Overall, the highest Hg retained values were observed for mortars hardened in environment A, which would mean that the microstructure of these samples had a higher tortuosity. This agrees with the pore size distribution results obtained for this environment, which revealed a greater pore network refinement, favoured by its optimum temperature and relative humidity. In relation to environment B, the Hg retained values were similar to those noted for environment A or even slightly lower in the very long-term, which would also be in keeping with other mercury intrusion porosimetry results, previously explained. For environment C, the Hg retained also showed similar or higher values compared to those observed for environment B in the middle-term, which would indicate that the samples pore network had a similar tortuosity. However, at 1900 days this parameter was lower for mortars hardened in environment C, especially for those prepared with w:c ratio 0.4. These results would be coinciding with the loss of pore refinement in the very long-term observed for these samples, which was already discussed in relation to the relative low humidity present in this environment. Finally, in spite of its relative high values at 28 days, the Hg retained decreased or kept constant with time for the studied mortars kept in environment D. This could mean that no increase or even a fall of pore network tortuosity was produced, which would again agree with the loss of microstructure refinement observed

for most of the mortars kept under this environment. This result could be related to the formation of shrinkage microcracks due to its very low humidity [51], which would open the microstructure and would reduce its tortuosity. For all the environments, the higher Hg retained values corresponded to CEM III mortars, which would agree with their most refined pore network and would reveal the beneficial effects of slag hydration in the pore network development of cementitious materials [7,8,12], even in the very long-term.

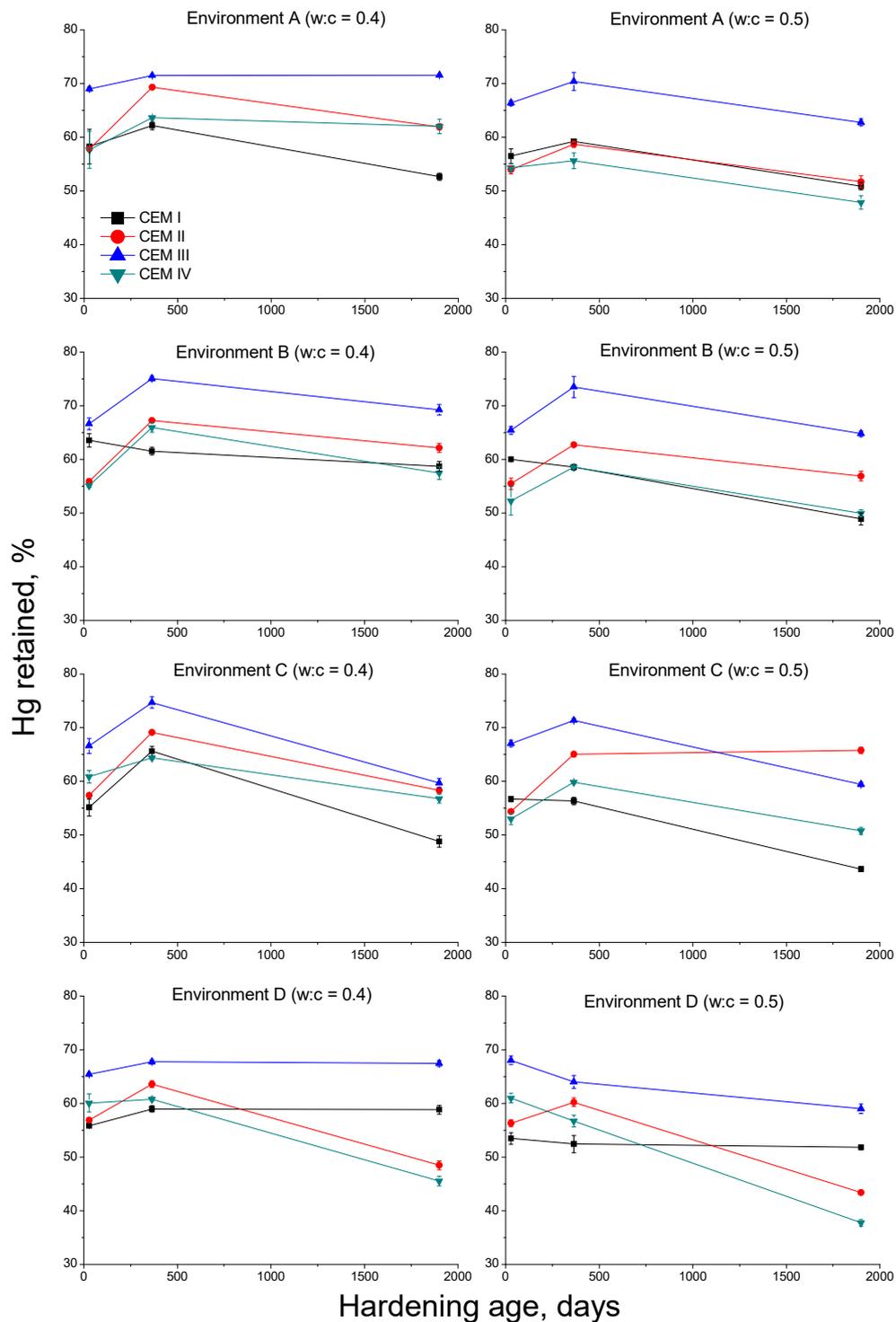


Figure 6. Results of mercury retained at the end of MIP tests for the studied mortars.

3.2. Capillary Absorption Results

The results of the capillary suction coefficient K can be observed in Figure 7. Overall, there were no high differences of the coefficient K between the studied environments. For environments A and B, its values were higher for CEM II and IV and it showed a global decreasing tendency with age, mainly in the middle-term, for all the studied mortars. This result could be related to the high humidity present in both environments, which would favour the pozzolanic and hydration reactions development [30,44], as has been explained for microstructure results. The coefficient K increased over 365 days for most of the studied mortars that were hardened in environment C, and for the majority of those exposed to environment D, the rise of this parameter started earlier (at 28 days). This also agrees with mercury intrusion porosimetry results, which would indicate the deleterious effect in the very-long term as a consequence of the low availability of water in the environment, hindering the hydration and pozzolanic reactions [31,44] and causing the possible formation of shrinkage microcracks [51]. Lastly, it is important to indicate that for environments C and D, the mortars prepared using sustainable cements with slag and fly ash generally showed similar or lower values of coefficient K in the very long-term compared to CEM I ones.

The effective porosity results are depicted in Figure 8. They showed similarities with those observed for coefficient K . The lower effective porosities were noted for condition A, especially for CEM I and III mortars, which would coincide with the majority of results of this work, showing the influence of a condition with an optimum relative humidity [30,44,48]. The results of effective porosity noted for environment B did not differ too much compared to environment A, probably due to its relative high humidity [44], as has been already explained. For both environments A and B, the effective porosity showed greater values for CEM II and IV mortars than for CEM I and III ones. In relation to environment C, the very long-term effective porosities were similar to those obtained for environment B, especially for fly ash mortars, while they were slightly higher for CEM I and III ones. The greatest values of effective porosity at longer ages corresponded to environment D and they increased with time. This is also in keeping with mercury intrusion porosimetry results and it would indicate the negative effect in the long-term caused by an environment with very low relative humidity [31,33,51], previously discussed. Finally, for environments C and D, the effective porosity at greater ages for mortars with active additions was not too much different than that noted for CEM I ones.

3.3. Forced Chloride Migration Results

The non-steady-state chloride migration coefficient D_{NTB} results are represented in Figure 9. Generally, the migration coefficients showed by mortars with additions were lower for all studied conditions in comparison with those noted for CEM I mortars. This would agree with several studies [12,15,23,24], which have pointed out that using slag and fly ash cements brings a noticeable improvement in chloride ingress resistance. Firstly, this could be explained in relation to the higher refinement of pore network provided by fly ash and slag in comparison with pure clinker [7–9,14,15]. On the other hand, this good resistance of fly ash and slag mortars to chloride ingress since very early ages and its maintenance when the hardening was produced under non-optimum environments, which produced a lower microstructure refinement in the long-term compared to an optimum condition, could also be justified as a consequence of the higher chloride binding capacity of slag and fly ash cements, compared to OPC. The high content of calcium aluminates provided by fly ash and slag explains this improved binding capacity [10].

Regarding the influence of the environmental conditions, it is important to emphasize the increase with time of the migration coefficient for CEM I mortars exposed to environments C and D. This rise was also observed for CEM II specimens but only hardened in environment D. Both environments had a relatively low relative humidity, so it seems that this circumstance would have deleterious effects in the resistance against chloride ingress of both mortar types, especially for CEM I ones,

possibly related to the abovementioned shrinkage microcracks formation combined with a less refined microstructure [50,51].

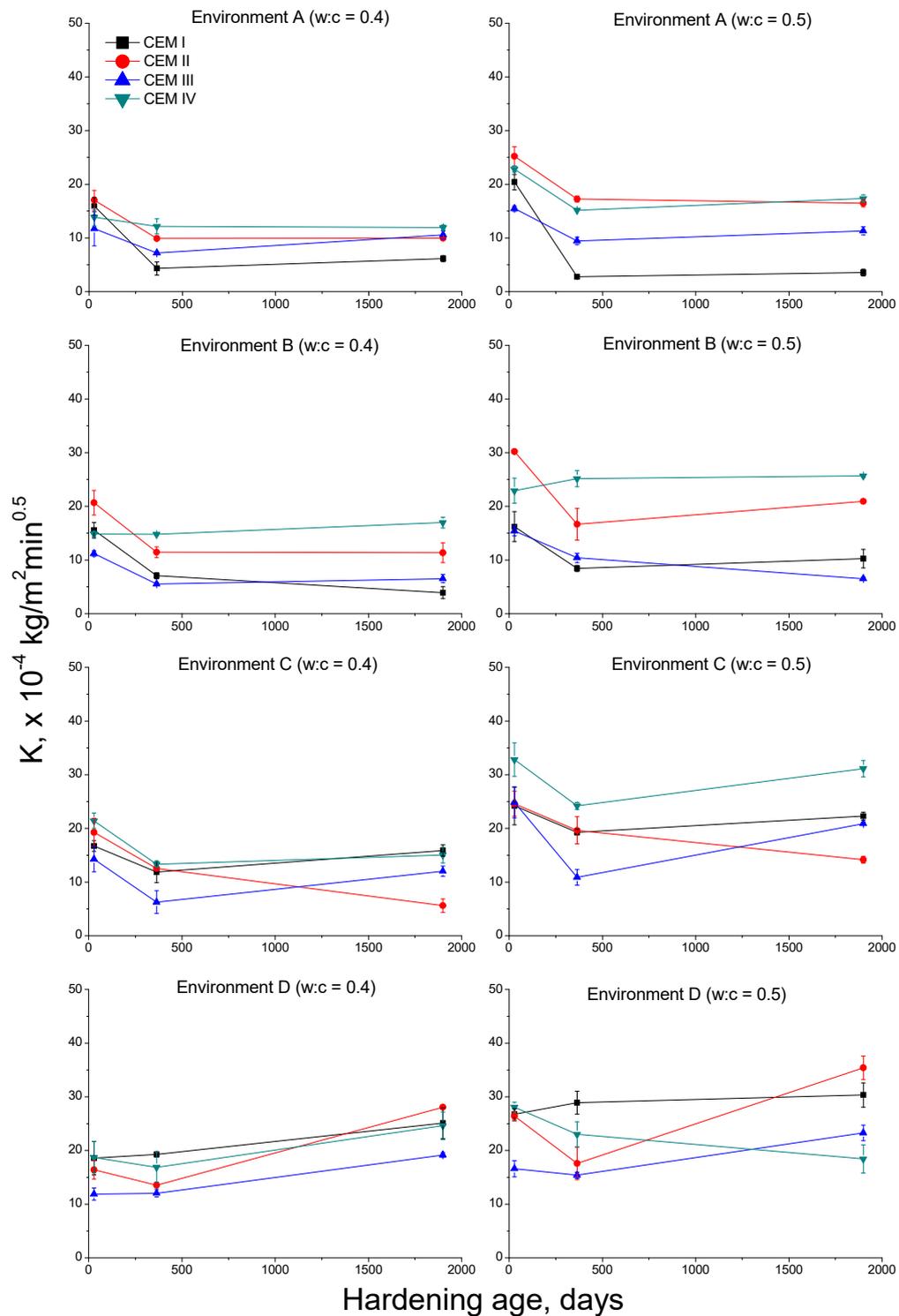


Figure 7. Results of capillary suction coefficient (K) for the studied mortars.

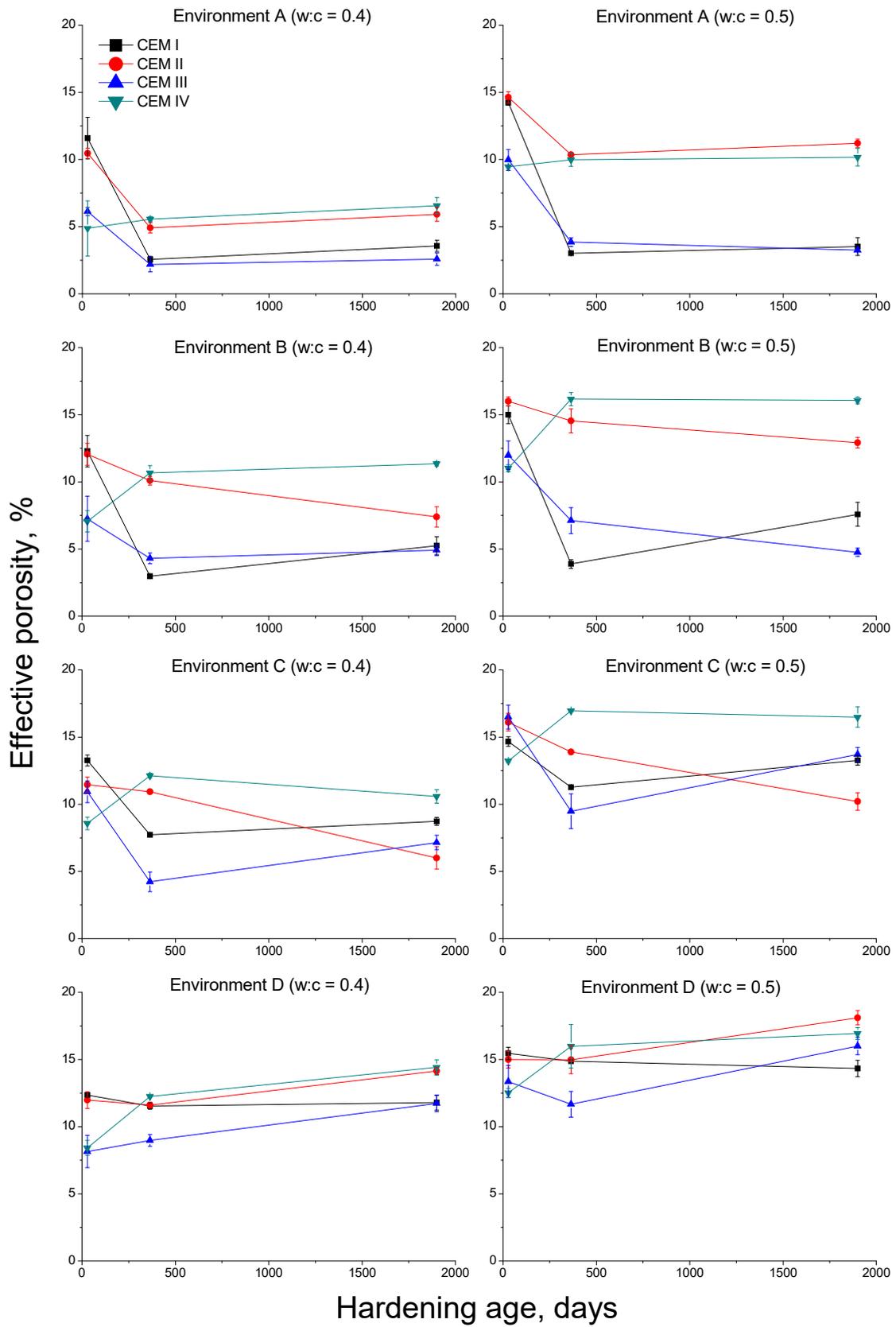


Figure 8. Effective porosity results for the studied mortars.

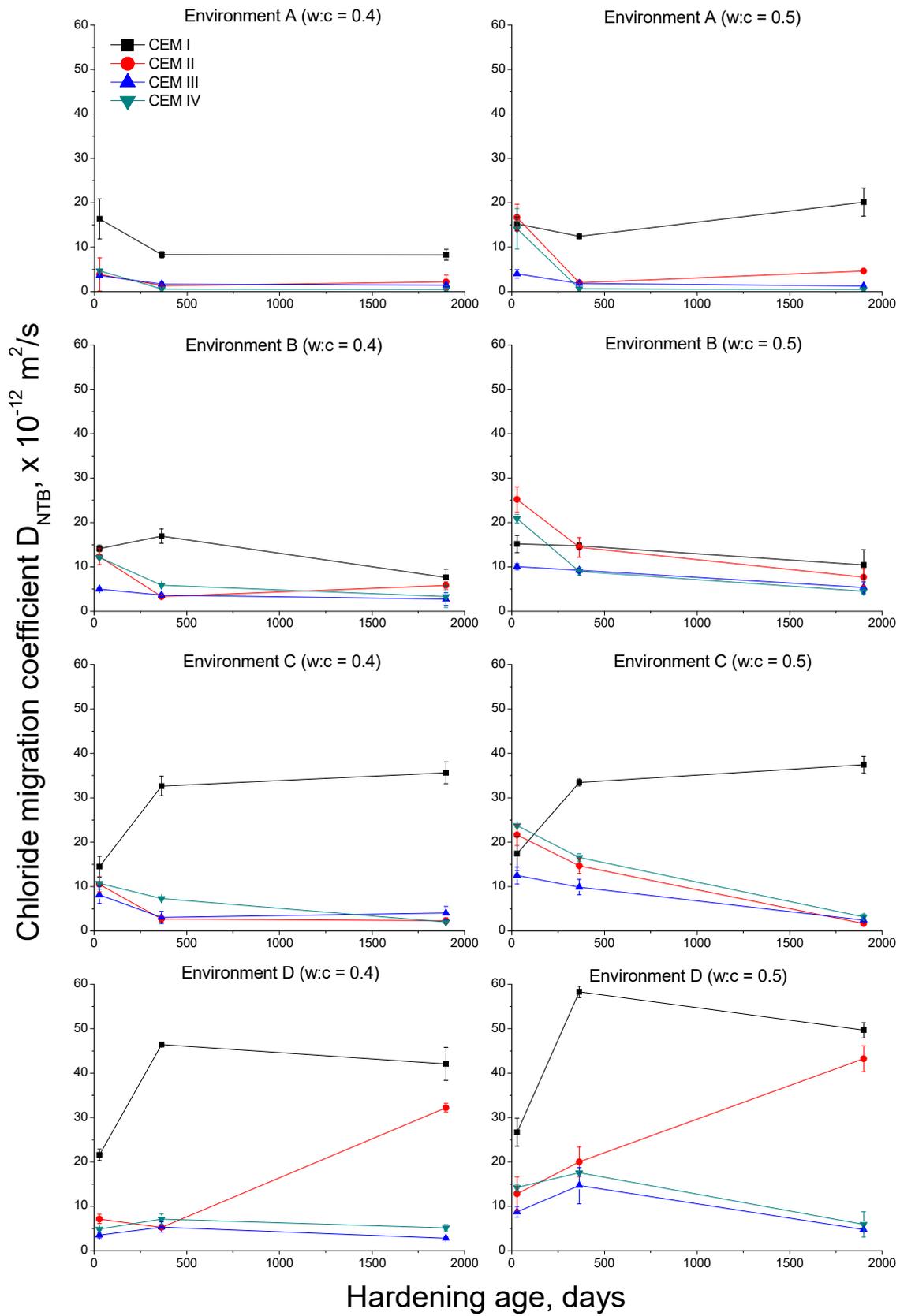


Figure 9. Non-steady-state chloride migration coefficient evolution for the studied mortars.

3.4. Mechanical Strength Results

The results of compressive and flexural strengths obtained for the studied mortars are depicted in Figures 10 and 11, respectively. First of all, it is important to emphasize that after more than 5-years exposure period, the mortars made with fly ash and slag cements generally showed similar or higher compressive and flexural strengths compared to CEM I ones. This would agree with several studies [9,12,53], which have pointed out that slag and fly ash cements provide an important increase of mechanical strength in the long-term.

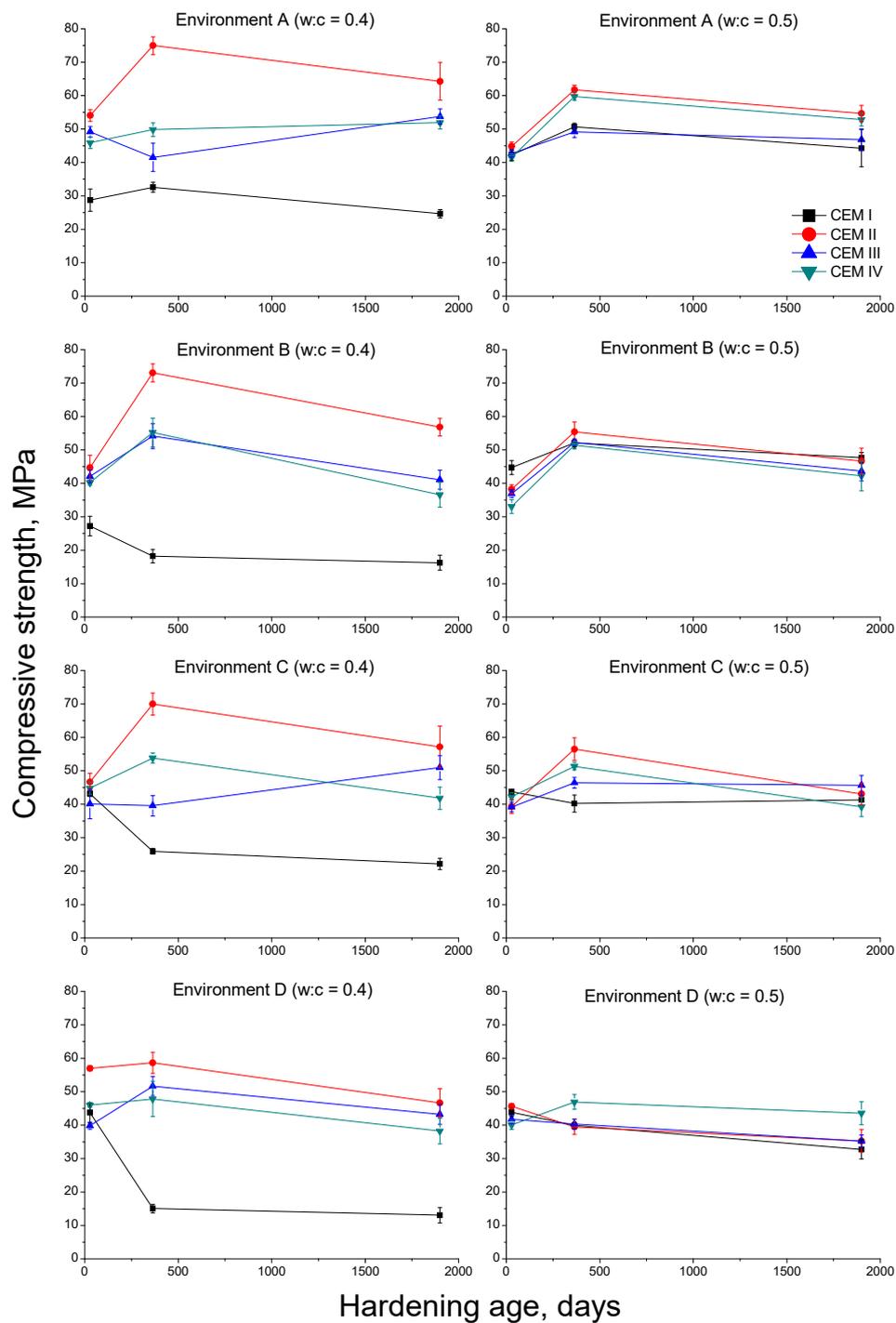


Figure 10. Results of compressive strength for the studied mortars.

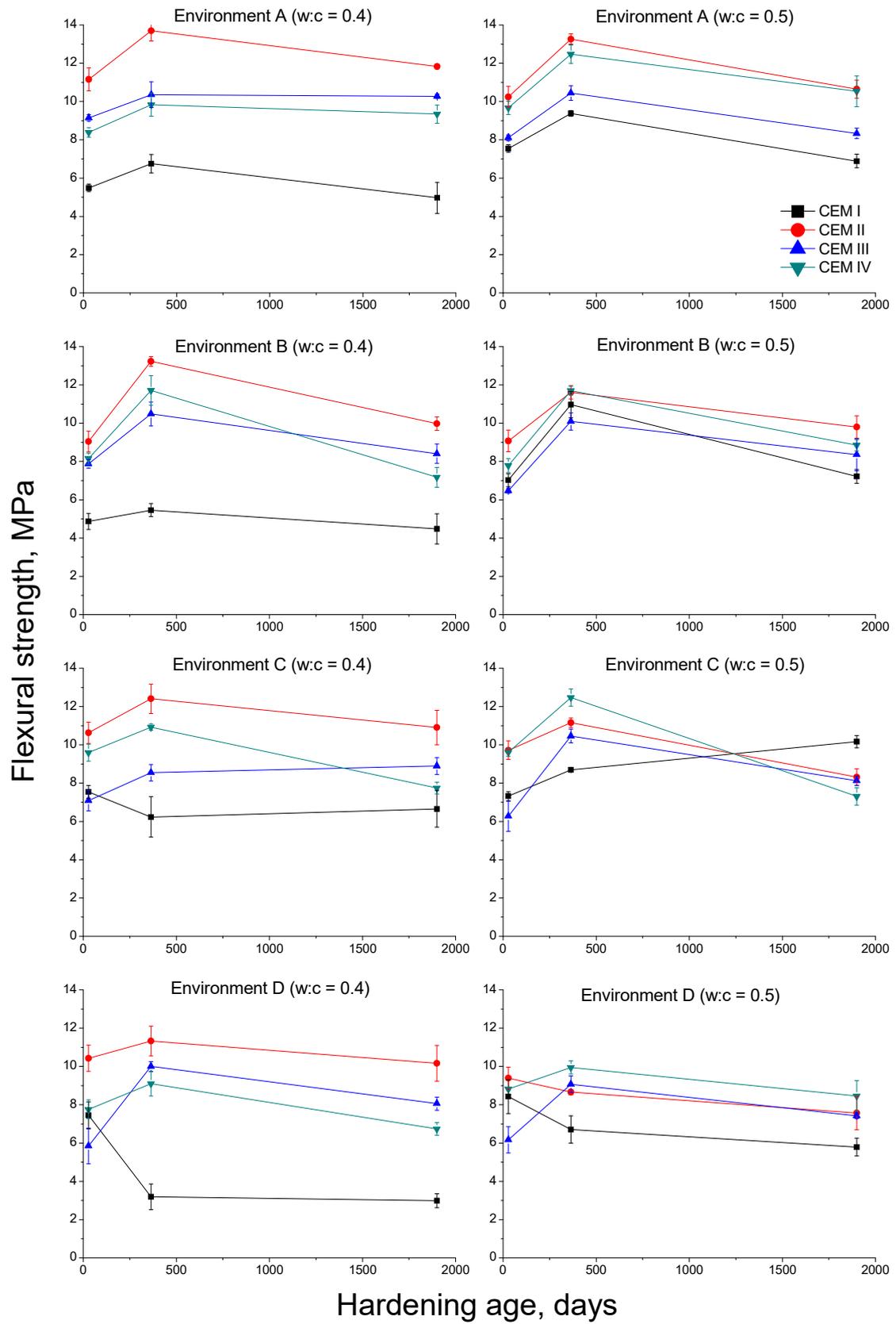


Figure 11. Results of flexural strength for the studied mortars.

With respect to the influence of hardening conditions, the compressive and flexural strengths results at greater ages did not differ too much between the analysed environments. Only, a slightly higher strengths were observed for environment A and scarcely lower for environment D, which would suggest the influence of the water availability in the environment [51], as has been previously explained. Despite that, it seems that the environmental temperature and relative humidity would not have a high influence in the mechanical performance of the studied mortars. Finally, the very low compressive and flexural strengths obtained for CEM I mortars prepared using w:c ratio 0.4 may be influenced by the compaction problems noted during the setting of prismatic samples of those mortars, which showed very low fluidity. In spite of that, no plasticiser was included in the mix, for keeping the same mixing conditions for all the analysed mortars. This problem was not observed for fly ash and slag cement mortars made with the same w:c ratio.

The present results give further evidence that it is possible to use cementitious materials for concrete elements and structures with a high level of replacement of Portland cement clinker by active additions, such as fly ash and ground granulated blast furnace slag [54]. In this study commercial cements containing the active additions have been used, since the structural concrete codes of certain countries restrict the possibility to incorporate some active additions when mixing the concrete and/or limit the replacement level of clinker by these materials [55]. These more sustainable binders can be used without reductions of the mechanical strength, at least in the long term and sometimes with improvements of the durability properties of the hardened cementitious materials, in agreement with previous results [54]. In this work, the focus has been put on studying the influence of the climatic conditions (mild Mediterranean and Atlantic climates) on the development of mechanical strength and on properties related with the durability of reinforced concrete elements exposed to a marine environment, where the corrosion of steel reinforcement is triggered by chloride ions which mainly penetrate the concrete cover on steel through capillary absorption or diffusion mechanisms. Nevertheless, when going to engineering design practice caution must be taken to fully consider all the degradation mechanisms and all the performance requirements of the construction under study [56]. For instance, it has been demonstrated that concrete with high levels of supplementary cementitious materials, like fly ash and slag, may not be suitable for exposure to a marine environment with multiple cycles of freezing and thawing, since these materials may suffer increased surface material loss in the long term [56].

4. Conclusions

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

- (1) An environment with high relative humidity would produce a more refined microstructure and would improve the mechanical performance and the durability-related properties of fly ash, slag and OPC mortars in the very long-term (5-years period approximately).
- (2) The environmental temperature has an influence in the development of pore structure and service properties of fly ash, slag and OPC mortars. A high temperature would accelerate the pore network refinement and the improvement of properties in the short-term, while a lower environmental temperature would slow down them. This is due to the effects of the temperature in the progress of clinker and slag hydration and fly ash pozzolanic reactions.
- (3) A low environmental relative humidity would entail a reduction of pore network refinement in the very long-term for all the studied mortars.
- (4) Generally, the pore structure of fly ash and slag cement mortars was more refined for all the analysed environments than that observed for CEM I ones. This may be due to the additional solid phases formed as products of fly ash pozzolanic reactions, as well as slag hydration.
- (5) The effective porosity and the capillary suction coefficient for all the studied mortars in the very long-term were hardly influenced by the environmental conditions.

- (6) The mortars prepared using sustainable cements with slag and fly ash generally showed in the very long-term similar or lower values of both effective porosity and capillary suction coefficient, as compared to OPC mortars, when they are exposed to low relative humidity environments.
- (7) The lowest non-steady state chloride migration coefficients were observed for the mortars made with fly ash and slag cements, regardless of the environmental condition. This may be related to the pore structure refinement provided by fly ash and slag compared to clinker and by the greater binding capacity of cements with those additions.
- (8) The CEM I mortars exposed to the environments with 40% and 65% relative humidity showed an important increase of the non-steady state chloride migration coefficient in the long-term. This was also noted for CEM II mortars but only for 40% relative humidity condition. Then, it seems that an environment with low relative humidity would have deleterious effects in the long-term resistance against chloride ingress of mortars in which the abovementioned cement types were used.
- (9) After a 5-years exposure period, the mortars prepared using sustainable slag and fly ash cements overall showed similar or higher compressive and flexural strengths compared to CEM I ones.
- (10) The mechanical strengths of all the studied mortars in the very long-term were slightly affected by the environmental conditions.
- (11) In view of the results obtained, mortars made with sustainable commercial cements with ground granulated blast-furnace slag and fly ash, exposed to non-optimum environments, show a good performance in the very long-term (after a 5-years hardening period) with respect to their microstructure, mechanical and durability-related properties, being similar or even better compared to OPC mortars.

Acknowledgments: This research has been financially supported by the “Ministerio de Economía y Competitividad” (formerly “Ministerio de Ciencia e Innovación”) and AEI of Spain and FEDER (EU) with projects BIA2006-05961, BIA2010-20548, BIA2011-25721 and BIA2016-80982-R. The authors wish to thank Cementos Portland Valderrivas S.A. for providing the cements used in this study.

Author Contributions: The results included in this paper related to the short- and middle-term effects of the environment in the studied mortars were obtained in the Ph.D. thesis carried out by José Marcos Ortega at University of Alicante (Spain), under the supervision of Isidro Sánchez and Miguel Ángel Climent. The results included in this paper regarding the long-term effects of the environment in the studied mortars were obtained in the master’s final project carried out by Rosa María Tremiño, under the supervision of José Marcos Ortega and Isidro Sánchez, to obtain the Civil Engineering Master’s degree at University of Alicante (Spain). José Marcos Ortega wrote the paper with contributions from the other co-authors. José Marcos Ortega, Rosa María Tremiño and Isidro Sánchez performed the experiments. Isidro Sánchez and Miguel Ángel Climent supervised the research work and revised the paper. All the authors contributed to conceive and design the experiments and to analyse and discuss the results.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Ponikiewski, T.; Gołaszewski, J. The effect of high-calcium fly ash on selected properties of self-compacting concrete. *Arch. Civ. Mech. Eng.* **2014**, *14*, 455–465. [[CrossRef](#)]
2. Glinicki, M.; Józwiak-Niedźwiedzka, D.; Gibas, K.; Dąbrowski, M. Influence of Blended Cements with Calcareous Fly Ash on Chloride Ion Migration and Carbonation Resistance of Concrete for Durable Structures. *Materials* **2016**, *9*, 18. [[CrossRef](#)] [[PubMed](#)]
3. Ortega, J.M.; Esteban, M.D.; Rodríguez, R.R.; Pastor, J.L.; Sánchez, I. Microstructural Effects of Sulphate Attack in Sustainable Grouts for Micropiles. *Materials* **2016**, *9*, 905. [[CrossRef](#)] [[PubMed](#)]
4. Ortega, J.M.; Esteban, M.D.; Rodríguez, R.R.; Pastor, J.L.; Ibanco, F.J.; Sánchez, I.; Climent, M.A. Long-Term Behaviour of Fly Ash and Slag Cement Grouts for Micropiles Exposed to a Sulphate Aggressive Medium. *Materials* **2017**, *10*, 598. [[CrossRef](#)] [[PubMed](#)]

5. Williams, M.; Ortega, J.M.; Sánchez, I.; Cabeza, M.; Climent, M.A. Non-Destructive Study of the Microstructural Effects of Sodium and Magnesium Sulphate Attack on Mortars Containing Silica Fume Using Impedance Spectroscopy. *Appl. Sci.* **2017**, *7*, 648. [[CrossRef](#)]
6. Ortega, J.M.; Esteban, M.D.; Rodríguez, R.R.; Pastor, J.L.; Ibanco, F.J.; Sánchez, I.; Climent, M.A. Influence of Silica Fume Addition in the Long-Term Performance of Sustainable Cement Grouts for Micropiles Exposed to a Sulphate Aggressive Medium. *Materials* **2017**, *10*, 890. [[CrossRef](#)] [[PubMed](#)]
7. Bijen, J. Benefits of slag and fly ash. *Constr. Build. Mater.* **1996**, *10*, 309–314. [[CrossRef](#)]
8. Wedding, P.; Manmohan, D.; Mehta, P. Influence of Pozzolanic, Slag and Chemical Admixtures on Pore Size Distribution and Permeability of Hardened Cement Pastes. *Cem. Concr. Aggreg.* **1981**, *3*, 63–67. [[CrossRef](#)]
9. Papadakis, V.G. Effect of fly ash on Portland cement systems. *Cem. Concr. Res.* **1999**, *29*, 1727–1736. [[CrossRef](#)]
10. Leng, F.; Feng, N.; Lu, X. An experimental study on the properties of resistance to diffusion of chloride ions of fly ash and blast furnace slag concrete. *Cem. Concr. Res.* **2000**, *30*, 989–992. [[CrossRef](#)]
11. Nochaiya, T.; Wongkeo, W.; Chaipanich, A. Utilization of fly ash with silica fume and properties of Portland cement–fly ash–silica fume concrete. *Fuel* **2010**, *89*, 768–774. [[CrossRef](#)]
12. Geiseler, J.; Kollo, H.; Lang, E. Influence of blast furnace cements on durability of concrete structures. *ACI Mater. J.* **1995**, *92*, 252–257.
13. Thomas, M.D.A.; Scott, A.; Bremner, T.; Bilodeau, A.; Day, D. Performance of slag concrete in marine environment. *ACI Mater. J.* **2008**, *105*, 628–634.
14. Ortega, J.M.; Albaladejo, A.; Pastor, J.L.; Sánchez, I.; Climent, M.A. Influence of using slag cement on the microstructure and durability related properties of cement grouts for micropiles. *Constr. Build. Mater.* **2013**, *38*, 84–93. [[CrossRef](#)]
15. Pastor, J.L.; Ortega, J.M.; Flor, M.; López, M.P.; Sánchez, I.; Climent, M.A. Microstructure and durability of fly ash cement grouts for micropiles. *Constr. Build. Mater.* **2016**, *117*, 47–57. [[CrossRef](#)]
16. Jain, J.A.; Neithalath, N. Chloride transport in fly ash and glass powder modified concretes—Influence of test methods on microstructure. *Cem. Concr. Compos.* **2010**, *32*, 148–156. [[CrossRef](#)]
17. Kamali, M.; Ghahremaninezhad, A. An investigation into the hydration and microstructure of cement pastes modified with glass powders. *Constr. Build. Mater.* **2016**, *112*, 915–924. [[CrossRef](#)]
18. Ortega, J.M.; Pastor, J.L.; Albaladejo, A.; Sánchez, I.; Climent, M.A. Durability and compressive strength of blast furnace slag-based cement grout for special geotechnical applications. *Mater. Constr.* **2014**, *64*. [[CrossRef](#)]
19. Scott, A.N.; Thomas, M.D.A.; Bremner, T.W. Marine performance of concrete containing fly ash and slag. In Proceedings of the Annual Conference—Canadian Society for Civil Engineering, St. Johns, NL, Canada, 30 May 2009; Volume 3, pp. 1559–1568.
20. Shattaf, N.R.; Alshamsi, A.M.; Swamy, R.N. Curing/environment effect on pore structure of blended cement concrete. *J. Mater. Civ. Eng.* **2001**, *13*, 380–388. [[CrossRef](#)]
21. Pasupathy, K.; Berndt, M.; Castel, A.; Sanjayan, J.; Pathmanathan, R. Carbonation of a blended slag-fly ash geopolymer concrete in field conditions after 8 years. *Constr. Build. Mater.* **2016**, *125*, 661–669. [[CrossRef](#)]
22. Polder, R.B.; De Rooij, M.R. Durability of marine concrete structures—Field investigations and modelling. *Heron* **2005**, *50*, 133–154.
23. Thomas, M.D.A.; Matthews, J. Performance of pfa concrete in a marine environment—10-year results. *Cem. Concr. Compos.* **2004**, *26*, 5–20. [[CrossRef](#)]
24. Chalee, W.; Jaturapitakkul, C.; Chindapasirt, P. Predicting the chloride penetration of fly ash concrete in seawater. *Mar. Struct.* **2009**, *22*, 341–353. [[CrossRef](#)]
25. Ortega, J.M.; Sánchez, I.; Cabeza, M.; Climent, M.A. Short-Term Behavior of Slag Concretes Exposed to a Real In Situ Mediterranean Climate Environment. *Materials* **2017**, *10*, 915. [[CrossRef](#)] [[PubMed](#)]
26. Ortega, J.M.; Esteban, M.D.; Sánchez, I.; Climent, M.A. Performance of sustainable fly ash and slag cement mortars exposed to simulated and real in situ Mediterranean conditions along 90 warm season days. *Materials* **2017**, *10*, 1254. [[CrossRef](#)] [[PubMed](#)]
27. Chalee, W.; Ausapanit, P.; Jaturapitakkul, C. Utilization of fly ash concrete in marine environment for long term design life analysis. *Mater. Des.* **2010**, *31*, 1242–1249. [[CrossRef](#)]
28. Ganjian, E.; Pouya, H.S. The effect of Persian Gulf tidal zone exposure on durability of mixes containing silica fume and blast furnace slag. *Constr. Build. Mater.* **2009**, *23*, 644–652. [[CrossRef](#)]

29. Detwiler, R.J.; Kjellsen, K.O.; Gjør, O.E. Resistance to chloride intrusion of concrete cured at different temperatures. *ACI Mater. J.* **1991**, *88*, 19–24.
30. Çakır, Ö.; Aköz, F. Effect of curing conditions on the mortars with and without GGBFS. *Constr. Build. Mater.* **2008**, *22*, 308–314. [[CrossRef](#)]
31. Ramezani-pour, A.A.; Malhotra, V.M. Effect of curing on the compressive strength, resistance to chloride-ion penetration and porosity of concretes incorporating slag, fly ash or silica fume. *Cem. Concr. Compos.* **1995**, *17*, 125–133. [[CrossRef](#)]
32. Ortega, J.M.; Sánchez, I.; Climent, M.A. Durability related transport properties of OPC and slag cement mortars hardened under different environmental conditions. *Constr. Build. Mater.* **2012**, *27*, 176–183. [[CrossRef](#)]
33. Ortega, J.M.; Sánchez, I.; Climent, M.A. Impedance spectroscopy study of the effect of environmental conditions in the microstructure development of OPC and slag cement mortars. *Arch. Civ. Mech. Eng.* **2015**, *15*, 569–583. [[CrossRef](#)]
34. Ortega, J.M.; Sánchez, I.; Antón, C.; De Vera, G.; Climent, M.A. Influence of environment on durability of fly ash cement mortars. *ACI Mater. J.* **2012**, *109*, 647–656.
35. Maltais, Y.; Marchand, J. Influence of curing temperature on cement hydration and mechanical strength development of fly ash mortars. *Cem. Concr. Res.* **1997**, *27*, 1009–1020. [[CrossRef](#)]
36. Hanehara, S.; Tomosawa, F.; Kobayakawa, M.; Hwang, K. Effects of water/powder ratio, mixing ratio of fly ash and curing temperature on pozzolanic reaction of fly ash in cement paste. *Cem. Concr. Res.* **2001**, *31*, 31–39. [[CrossRef](#)]
37. Climent, M.A.; Ortega, J.M.; Sánchez, I. Cement mortars with fly ash and slag—Study of their microstructure and resistance to salt ingress in different environmental conditions. In *Concrete Repair, Rehabilitation and Retrofitting III, Proceedings of the 3rd International Conference on Concrete Repair, Rehabilitation and Retrofitting (ICRRR 2012), Cape Town, South Africa, 3–5 September 2012*; Taylor & Francis Group: London, UK, 2012; pp. 345–350.
38. Ortega, J.M.; Sánchez, I.; Climent, M.A. Impedance spectroscopy study of the effect of environmental conditions on the microstructure development of sustainable fly ash cement mortars. *Materials* **2017**, *10*, 1130. [[CrossRef](#)] [[PubMed](#)]
39. European Committee for Standardization. *EN 1992-1-1 Eurocode 2: Design of Concrete Structures—Part 1-1: General Rules and Rules for Buildings*; Committee European Normalization (CEN): Brussels, Belgium, 2004.
40. Asociación Española de Normalización y Certificación (AENOR). *UNE-EN 197-1:2011. Composición, Especificaciones y Criterios de Conformidad de Los Cementos Comunes*; AENOR: Madrid, Spain, 2011; p. 30. (In Spanish)
41. Asociación Española de Normalización y Certificación (AENOR). *UNE-EN 196-1:2005. Métodos de Ensayo de Cementos. Parte 1: Determinación de Resistencias Mecánicas*; AENOR: Madrid, Spain, 2005; p. 36. (In Spanish)
42. Deutsches Institut für Normung, e.V. *Deutsche Norm DIN 50008 Part 1*; DIN: Berlin, Germany, 1981. (In German)
43. Asociación Española de Normalización y Certificación (AENOR). *UNE 83982:2008. Durabilidad del Hormigón. Métodos de Ensayo. Determinación de La Absorción de Agua Por Capilaridad del Hormigón Endurecido. Método Fagerlund*; AENOR: Madrid, Spain, 2008; p. 8. (In Spanish)
44. Ortega, J.M.; Sánchez, I.; Climent, M.A. Influence of different curing conditions on the pore structure and the early age properties of mortars with fly ash and blast-furnace slag. *Mater. Constr.* **2013**, *63*. [[CrossRef](#)]
45. Ortega, J.M.; Sánchez, I.; Climent, M.A. Influence of environmental conditions on durability of slag cement mortars. In *Proceedings of the 2nd International Conference on Sustainable Construction Materials and Technologies, Ancona, Italy, 28–30 June 2010*; pp. 277–287.
46. RILEM TC 116-PCD. A. Preconditioning of concrete test specimens for the measurement of gas permeability and capillary absorption of water. *Mater. Struct.* **1999**, *32*, 174–179. Available online: <https://link.springer.com/article/10.1007%2FBF02481510> (accessed on 28 February 2018).
47. Nordtest. *NT Build 492. Concrete, Mortar and Cement-Based Repair Materials: Chloride Migration Coefficient from Non-Steady-State Migration Experiments*; Nordtest Espoo: Greater Helsinki, Finland, 1999; p. 8.

48. Ortega, J.M.; Ferrandiz, V.; Antón, C.; Climent, M.A.; Sánchez, I. Influence of curing conditions on the mechanical properties and durability of cement mortars. In *Materials Characterisation IV: Computational Methods and Experiments*; Mammoli, A.A., Brebbia, C.A., Eds.; WIT Press: Southampton, UK, 2009; pp. 381–392. [[CrossRef](#)]
49. Escalante-García, J.I.; Sharp, J.H. Effect of temperature on the hydration of the main clinker phases in Portland cements: Part II, blended cements. *Cem. Concr. Res.* **1998**, *28*, 1259–1274. [[CrossRef](#)]
50. Sánchez, I.; Albertos, T.S.; Ortega, J.M.; Climent, M.A. Influence of environmental conditions on durability properties of fly ash cement mortars. In *Proceedings of the 2nd International Conference on Sustainable Construction Materials and Technologies*, Ancona, Italy, 28–30 June 2010; pp. 655–666.
51. Kanna, V.; Olson, R.A.; Jennings, H.M. Effect of shrinkage and moisture content on the physical characteristics of blended cement mortars. *Cem. Concr. Res.* **1998**, *28*, 1467–1477. [[CrossRef](#)]
52. Cabeza, M.; Merino, P.; Miranda, A.; Nóvoa, X.R.; Sanchez, I. Impedance spectroscopy study of hardened Portland cement paste. *Cem. Concr. Res.* **2002**, *32*, 881–891. [[CrossRef](#)]
53. Demirboğa, R. Thermal conductivity and compressive strength of concrete incorporation with mineral admixtures. *Build. Environ.* **2007**, *42*, 2467–2471. [[CrossRef](#)]
54. Malhotra, V.M.; Mehta, P.K. *High-Performance, High-Volume Fly ash Concrete: Materials, Mixture Proportioning, Properties, construction Practice and Case Histories*; Supplementary Cementing Materials for Sustainable Development, Inc.: Ottawa, ON, Canada, 2002.
55. Comisión Permanente del Hormigón. *Instrucción De Hormigón Estructural EHE-08*; Ministerio de Fomento: Madrid, Spain, 2008. (In Spanish)
56. Thomas, M.D.A.; Bremner, T.; Scott, A.C.N. Actual and modeled performance in a tidal zone. Concrete mixtures with supplementary cementitious materials evaluated after 25-year exposure at Treat Island. *Concr. Int.* **2011**, *33*, 23–28.



© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).