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Comparative effects of different real conditions in the microstructure and properties of ternary blended cement mortars for being used in rehabilitation works

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ABSTRACT

The use of ternary binders in commercial cements is very low, at least in Spain. A possible field of application of these ternary cements would be the rehabilitation of coatings of old buildings, whose performance may be affected by the external environment. The goal of this research is to analyze the comparative effects of two in-situ environments in the microstructure and several service parameters of mortars with several ternary binders. The real environments verified the requirements of classes XC3 and XC4 of Eurocode 2. The mortars were also exposed to an optimum condition. Reference mortars with ordinary Portland cement and binary mortars were also studied. Mercury intrusion porosimetry, carbonation depth measurements and mechanical strength tests were performed. The real in-situ environments produced a carbonation development, an overall lower pore refinement and worsening of mechanical properties. Mortars which incorporated at least one active addition generally presented a better performance.

1. Introduction

At present, it is common that the materials used in old structures and constructions, such as heritage buildings, require a retrofitting in order to ensure their safety (Petrovčič and Kilar, 2020; Vereecken and Roels, 2016; Abdel-Aty, 2018). The need for rehabilitation interventions could be due to the degradation of the materials (Brimblecombe and Lefèvre, 2021), caused by the attack of aggressive substances over time which would affect their durability, the exposure to fire or other accidental situation (Pauletta et al., 2018; Pazlar and Kramar, 2015), or even due to changes in the use of the ancient building (Pigliautile et al., 2019).

With respect to cement mortars, their use in plasters and coatings is very common (Vidovszky and Pintér, 2020, alvarez, 2020). The coatings of old buildings, in particular those on facades and external surfaces, generally show deterioration and need to be renovated. In addition, it is important to highlight that plasters and coatings play a major function in the conservation and durability of buildings, because they constitute the first barrier that protects the rest of the materials of the building from the aggressive agents present in the external environment, as well as from atmospheric conditions.

On the other hand, the search of solutions for reducing the energy and environmental problems caused by the manufacture of Portland cement (Benhelal et al., 2021) is a main issue to be addressed in the construction materials field, within the current context with the aim of lessening the global warming, according to the objectives of sustainable development. In this line, the development of eco-friendly cements (Restrepo-Baena et al., 2020; Andrade and Sanjuán, 2021) with additions, could be a good alternative for contributing to reach a more sustainable industry of cement.

Among the different environmental advantages for the utilization of blended cements with additions, it is noteworthy to underline the lessening of CO_2 emissions and energy consumption, because of the lower quantity of clinker required for manufacturing commercial cements. Furthermore, most of those additions consisted of wastes produced by other industrial processes (V Ribeiro et al., 2011), thus their recycling is useful for reducing their storage in dumping specific sites, avoiding other harmful effects in the environment. Additionally, these additions may have positive influence in the behavior of materials (Bijen, 1996; Wang et al., 2004), so the study of their effects for developing green cements is still an important field of investigation.

With respect to standardized additions, fly ash and blast-furnace slag and are among the most widely used. Several works (Bijen, 1996;

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Papadakis, 1999) have pointed out that these additions improve the behavior of materials, compared to ordinary Portland cement. Regarding slag, their hydration reactions entail new CSH phases formation, giving as a result a finer microstructure (Bijen, 1996; Leng et al., 2000), producing an adequate performance of materials. Regarding fly ash, its pozzolanic activity, which allows the reaction of its components with portlandite formed in clinker hydration, also results in the formation of hydrated products, rising the refinement of materials' microstructure (Wang et al., 2004; Papadakis, 1999). The beneficial effects in the microstructure produced by both fly ash and slag turn into the improvement of several properties of cement-based materials (Geiseler et al., 1995; Thomas et al., 2008; Jain and Neithalath, 2010). They are active additions, because of their reactivity already explained. Limestone is also widely used in cement production, but it lacks of hydraulic or pozzolanic activity. Therefore, it principally acts as filler, having also an influence on their properties and pore structure of materials (Dhandapani et al., 2021; Marchetti et al., 2020).

Regarding the manufacture of eco-friendly commercial cements, at present those prepared using binary binders, with clinker partially replaced by one addition, are mainly manufactured. Nevertheless, the regulations of commercial cements (AENOR and UNE-EN 197-1:2011, 2000) allow using ternary binders, for which clinker is partially substituted by two additions. Despite that, ternary binders are hardly used for producing commercial cements, at least in Spain. The incorporation of two additions in the binder could also entail an enhancement of the cement-based materials behavior, because of the synergistic effects of combining them (Dadsetan and Bai, 2017; Ban et al., 2019). According to that, the study of cementitious materials with ternary binders (Dhandapani et al., 2021; Radwan et al., 2020), focused on their application as commercial cements, would be a potential field of research for developing additional alternatives aimed to reduce the pollutant effects of cement production. Additionally, a possible field of application of these ternary commercial cements may be the renovation and rehabilitation of coatings of ancient buildings and other old constructions.

In this line, as has been previously explained, it is noteworthy to consider that the performance of cement-based coatings of buildings may be affected by the climate and weather conditions to which they are exposed, and by the existence of aggressive agents in the environment. On this subject, active additions could be more influenced by changes in environmental parameters, because their variations may affect the hydration and pozzolanic reactions development (Çakır and Aköz, 2008; Ramezanianpour and Malhotra, 1995). Regarding the research field related to the exposure of sustainable cement-based materials to in-situ conditions (Thomas et al., 2008; Thomas and Matthews, 2004; Chalee et al., 2009), in most of them binary binders were tested, generally pointing out certain variability as a function of the climate conditions and the aggressiveness of environment. Subsequently, to study the behavior of materials with ternary binders matured in real in-situ environments may be noteworthy for increasing their use in commercial cements production and for finding suitable specific applications.

Then, the goal of this work is to analyze the comparative effects of two real in-situ environments in the pore structure and several service parameters of mortars incorporating ternary binders, in which limestone, fly ash and blast furnace slag are incorporated. The real environments were selected according to the requirements of exposure classes and XC4 and XC3, respectively, indicated in Eurocode 2 (European Committee for Standardization, 2004). Additionally, a group of specimens were stored in an optimum condition, which was taken as a reference. Fly ash, blast furnace slag and limestone were selected due to the fact that they are the most used additions in Spain for blended commercial cements. Moreover, for reaching a higher applicability of the results obtained in this work, the tested ternary binders verified the requirements for commercial cement type CEM II/B-M (AENOR and UNE-EN 197-1:2011, 2000). Finally, the effects of the different analyzed environments were also studied in reference specimens prepared with ordinary Portland cement and in binary mortars, with only one of the analyzed additions. The main novelty of the research performed is focused on studying the effects of several ternary binders, compatible with the standard requirements for commercial cements, in the behaviour of mortars exposed to specific real environments, which correspond to specific exposure deleterious conditions included in the regulations of construction and building materials and structures. As has been explained, the fact of analysing mortars with standardized binders under harmful environments explicitly set out in the regulations, would mean that the results obtained would be useful for direct application in real construction and building projects and works.

2. Experimental procedures

2.1. Materials and sample preparation

Materials tested were mortars. Firstly, reference mortars were prepared using an ordinary Portland cement, CEM I 42.5 R (UNE-EN 197-1 (AENOR and UNE-EN 197-1:2011, 2000)), whose designation was REF.

Furthermore, mortars prepared using three ternary binders have been analyzed. One of them included 15% (in weight) of blast furnace slag and 15% limestone as replacement of CEM I 42.5 R, and its designation was SL. The second binder has been named as SF, and CEM I 42.5 R was in part replaced by 15% slag and 15% fly ash. Finally, FL was the designation of the last ternary binder, in which the cement CEM I 42.5 R was in part substituted by 15% limestone and 15% fly ash.

Moreover, three binary mortars have been tested too. In them, 30% (in weight) of CEM I 42.5 R has been substituted by one of previously indicated additions. They were named as L, S and F, with 30% content of limestone, slag and fly ash, respectively. In Table 1 are compiled the designations of the analyzed binders.

Slag, fly ash and limestone accomplished the requirements of the standard UNE-EN 197-1 (AENOR and UNE-EN 197-1:2011, 2000) for being incorporated in the production of commercial cements. They were facilitated by the company Cementos Portland Valderrivas (Spain) and at present they are used in the production of the blended cements manufactured by this company. Their chemical compositions are shown in Table 2.

The prepared binders verified the requirements for a commercial cement CEM II/B, according to the UNE-EN 197-1 standard (AENOR and UNE-EN 197-1:2011, 2000). The motivation for selecting that kind is because the type II cements (AENOR and UNE-EN 197-1:2011, 2000) are currently the most produced in Spain, so this could make easier a wider potential real application of the results obtained in this research.

The water/binder ratio has been 0.5 for all the analyzed series. The mortars has been prepared with an aggregate/binder ratio 3:1, and the fine aggregate used verified the requirements of UNE-EN 196-1 (AENOR and UNE-EN 196-1:2005, 2005).

Two kinds of specimens have been made. The first one was cylindrical samples with 5 cm diameter and 6 cm height. Furthermore, prisms with sizes 4 cm × 4 cm x 16 cm have been prepared.

They were stored in a chamber with 95% relative humidity (RH) and 20 °C temperature along the initial 24 h after setting. Once ended that period, they were de-moulded. Tests were performed at 250 days.

Table 1
Mortars designation and percentage (in weight) of CEM I and additions.

Designation	CEM I 42.5 R	Limestone	Blast furnace slag	Fly ash
REF	100%	–	–	–
L	70%	30%	–	–
S	70%	–	30%	–
F	70%	–	–	30%
SL	70%	15%	15%	–
SF	70%	–	15%	15%
FL	70%	15%	–	15%

Table 2
Chemical composition of blast furnace slag, fly ash and limestone.

Components	Blast furnace slag	Fly ash	Limestone
SiO_2	31.50%	54.40%	2.85%
K_2O	0.52%	3.12%	0.18%
Al_2O_3	10.10%	27.70%	1.22%
TiO_2	0.94%	1.05%	0.11%
P_2O_5	0.02%	0.46%	0.02%
CaO	46.80%	2.55%	94.40%
SO_3	1.94%	0.53%	0.10%
Fe_2O_3	0.37%	8.06%	0.54%
MnO	0.17%	0.06%	–
MgO	6.98%	1.40%	0.47%
Na_2O	0.30%	–	–
ZnO	–	0.11%	–

2.2. *Environmental conditions*

Three exposure environments have been studied (see Table 3). The first one consisted of an optimum condition (20 °C and 100% RH), named as environment A. In this condition, samples were stored in hermetic boxes with distilled water on their bottom part for reaching 100% RH. Specimens were introduced into the boxes without contact with water, for which a rack beyond the level of water was used. Moreover, these boxes were stored in a chamber with temperature 20 °C. This optimum condition has been studied as a reference for comparing the effects of the real environments.

Regarding the real in-situ environments, the samples exposed to them, after being de-moulded, were also cured under an optimum condition (100% RH and 20 °C) up to 7 days, once they were taken to the exposure stations. This curing period of 7 days was selected according to the results of several researches (Thomas et al., 2008; Ramezanianpour and Malhotra, 1995), which pointed out the relevance of curing for cement-based materials matured in low RH environments.

The first real in-situ condition was designated as environment B. The samples were exposed to an inland Mediterranean climate condition. The exposure station was placed in the town of Orxeta (38° 33′ 47″ N, 0° 15′ 43″ W, 177 m.a.s.l.) in the southeast of Spain (Alicante province). It was approximately at 10 km from the coast. The mortars were left in the roof of a house, without protection from the weather conditions. This site verified the prescriptions of exposure class XC4 (corrosion induced by carbonation, cyclic wet and dry) indicated in Eurocode 2 (European Committee for Standardization, 2004). The time of exposure started once finished the abovementioned 7-days curing, and ended at 250 days, including the period between February and October. The daily average, minimum and maximum temperature and RH recorded in the site along the time of exposure are respectively represented in Figs. 1 and 2. The temperatures were overall mild, being higher in the summer season, while the relative humidity showed great variability. Regarding the rainfall, the majority of rainy days occurred during the first 60 days of exposure, and since then scarce rainfall was registered in the site, as can be observed in Fig. 3. The weather data of environment B were measured using a “Wifi HD weather station with 7-in-1 sensor” model 7003500 manufactured by Bresser GmbH.

The second real in-situ condition was designated as environment C and specimens were left in an underground garage of a housing building with moderate circulation of vehicles. This location matched with the exposure class XC3 (corrosion induced by carbonation, moderate humidity) included in Eurocode 2 (European Committee for Standardization, 2004). The exposure time was the same than that indicated for environment B. The average CO_2 concentration registered in the site was approximately 2000 ppm, being the absolute maximum concentration scarce greater than 5000 ppm. The temperatures in this site were generally in the interval from 18 °C to 23 °C, while the average relative humidity ranged between 65% and 70%. The abovementioned environmental parameters were measured using a controller model HD46 manufactured by Delta Ohm Srl.

Table 3
Summary of environments studied.

Exposure environment	Characteristics
Environment A	Optimum condition (constant 20 °C and 100% RH)
Environment B	Outdoor real in-situ exposure to Mediterranean climate conditions in an inland location at southeast of Spain, exposure class XC4 of Eurocode 2
Environment C	Indoor real in-situ exposure condition in an underground garage of a building, exposure class XC3 of Eurocode 2

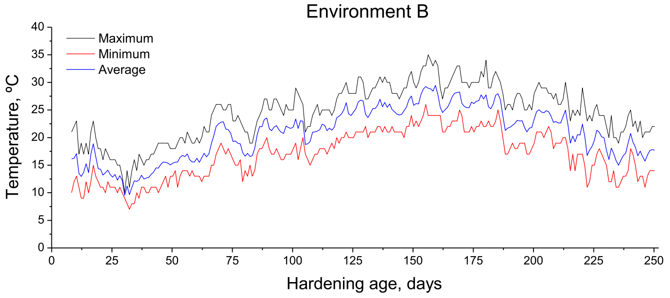

Fig. 1. Daily average, minimum and maximum temperature registered in the exposure location of environment B along the studied time period.

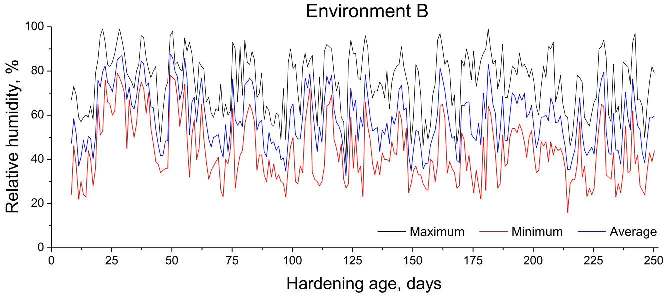

Fig. 2. Daily average, minimum and maximum RH registered in the exposure station of environment B during the studied time period.

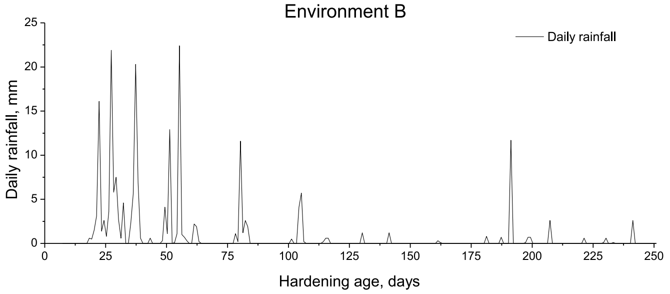

Fig. 3. Daily rainfall distribution along the exposure time period.

2.3. *Mercury intrusion porosimetry*

This technique is useful for studying the pore structure of different kinds of materials (Ouellet et al., 2007; Horpibulsuk et al., 2010; Olson et al., 1997). Here, it has been performed with a Poremaster-60 GT porosimeter commercialized by Quantachrome Instruments (Boynton Beach, Florida, USA). Before the test, the specimens were dried at 50 °C during 48 h. The pore size distributions and total porosity have been analyzed. For the pore size distributions, the next intervals of pore sizes were established: <10 nm, 10–100 nm, 100 nm-1μm, 1–10 μm, 10 μm-0.1 mm, and >0.1 mm (Pedeferri and Bertolini, 2000; Ho et al., 2018). For each series and environment, two measurements were performed at the studied age. Pieces obtained from cylindrical samples were tested.

2.4. Depth of carbonation front

The depths of carbonation have been determined according to the RILEM recommendation CPC-18 (RILEM, 1988). Fragments removed from the cylindrical samples were sprayed with a 1% phenolphthalein solution. The depth of the colorless carbonated part from the outer surface of the specimen was determined. Six fragments were tested at 250 days for each binder and environment.

2.5. Mechanical strengths

The flexural and compressive strengths have been determined following the standard UNE-EN 1015-11 (AENOR and UNE-EN 1015-11:1999, 1999). For each type of mortar and environment, three prisms have been tested at 250 days.

3. Results and discussion

3.1. Mercury intrusion porosimetry

The results of total porosity noted for the analyzed binders at 250 days are shown in Fig. 4. In the case of reference mortars, it was higher when samples were matured in environment B, while it was relatively similar for conditions A and C. This also happened with mortars with limestone addition (L series), although their porosity was greater compared to REF mortars for all the analyzed environments. Small differences depending on the exposure condition were observed for the binary binders with fly ash and slag (F and S series). The binary mortars with slag showed scarce higher total porosity values for the real in-situ conditions (environments B and C), in comparison with the optimum laboratory environment. For binary series with fly ash, the total porosity was quite similar for both conditions A and B, while it was slightly higher for environment C. These similar values of total porosity for environments A and B could be related to the rainfall registered in the exposure site of condition B during the first 60 days of exposure, including some days with heavy rain (see Fig. 3). The fly ash pozzolanic reactions are very sensitive to the environmental humidity (Ortega et al., 2017) and to the presence of portlandite (Wang et al., 2004; Meena et al., 2023; Nayak et al., 2022). These rainy days would produce a high relative humidity in the environment B, as indicated the fact that maximum values of this parameter around 100% were registered (see Fig. 2). This would favor the fly ash pozzolanic reactions in the first maturing days in condition B, being more noticeable their effects in the binary binder with this addition, compared to other series. This beneficial influence of environment B at early maturing ages is still noticeable in the long term, despite the deleterious processes which affect series F exposed to this environment. The differences in total porosity between the studied exposure conditions were more noticeable for ternary binders, for which it has been overall noted greater total porosity for conditions B and C compared to A.

The pore size distributions of the tested mortars as a function of the exposure condition are represented in Fig. 5. For all the binders, it has been observed lower percentages of finer pores (ranges <10 nm and 10–100 nm) in the real environments B and C compared to laboratory condition A. The microstructure of reference mortars were slightly more affected by real environment C than for B. For series with limestone (FL, SL and L mortars), the proportion of pores belonging to the smaller ranges were higher in condition C than in B, which also happened for slag binary series (S mortar). On the contrary, for the fly ash binary mortar (F series) and the ternary binder with both fly ash and slag additions (SF series) a greater percentage of finer pores intervals has been registered when they are exposed to environment B, in comparison with condition C. These different effects of the studied environments in the pore structure of the mortars, depending on the binder would be relevant.

As has been described in subsection 2.2, the environment A was an optimum condition, with constant temperature of 20 °C and with approximately 100% RH. Under this environment, there was enough water available for an adequate progress of slag and clinker hydration (Çakır and Aköz, 2008; Bouikni et al., 2009; Loke et al., 2022), and for the development of fly ash pozzolanic reactions (Wang et al., 2004; Papadakis, 1999; Meena et al., 2023; Nayak et al., 2022; Khankhaje et al., 2023). Their products are solid phases, which progressively filled the pores, entailing a refinement of pores with time. In addition, the optimum temperature of this environment A also contributed to an adequate development of the abovementioned reactions (Çakır and Aköz, 2008; Barnett et al., 2006; Escalante-García and Sharp, 1998; Kanavaris et al., 2023; Shumuye et al., 2021), without slowing down them. The exposure to those optimum conditions during a relatively long time period, such as 250 days, would allow a high degree of progress of hydration and pozzolanic reactions, resulting in the greater volume of finer pores and refinement of pore network noted for all the binders, compared to other real environments analyzed. In general, mortars with active additions (series S, F, SL, SF and FL) showed more pore refinement, with higher percentage of finer pores (size interval <10 nm), after 250 days compared to other studied mortars (series REF and L). This may be caused by slag hydration effects (Çakır and Aköz, 2008; Bouikni et al., 2009), as well as by those produced by pozzolanic reactions of fly ash (Wang et al., 2004; Papadakis, 1999; Nayak et al., 2022), producing additional solids formation. In addition, regarding the comparison between mortars with active additions, it is noteworthy to highlight that this pore refinement was overall higher for mortars with fly ash (series F, SF and FL) compared to mortars with only slag (series S and SF). Limestone addition mainly worked as filler (Meddah et al., 2014; Benjeddou et al., 2021), without reactivity, so its positive

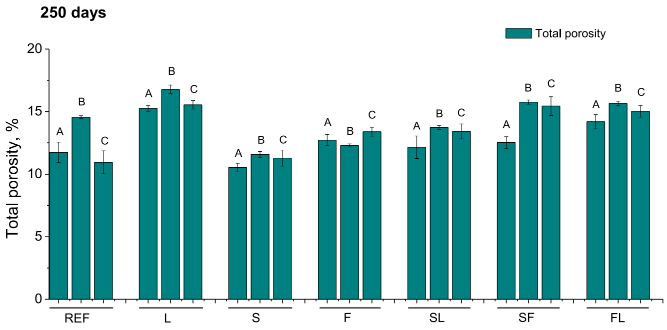

Fig. 4. Results of total porosity at 250 days of exposure to the studied environments.

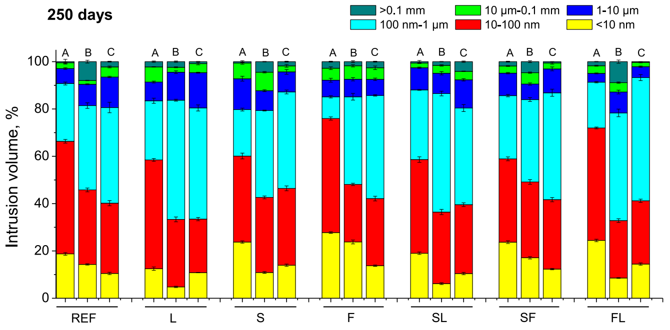

Fig. 5. Pore size distributions for the analyzed binders and environments at 250 days.

influence in the pore structure was limited, as showed the lower proportion of pores in the interval <10 nm in L series, as well as the slight less refinement of FL and SL specimens in comparison to S and F binders, respectively.

With respect to the real in-situ conditions, the environment B was an outdoor Mediterranean condition (see subsection 2.2), while in the environment C the mortars were hardened in an underground garage of a building, with moderate presence of CO_2 in the air (see subsection 2.2). In both environments, the materials were subject to more harmful conditions, compared to the optimum environment A, which would affect their microstructure, as has been observed.

In relation to the environment B (see subsection 2.2), the temperature recorded in the station was relatively mild (Fig. 1) and the relative humidity, despite its variability, was generally lower than in the optimum condition A (Fig. 2). Furthermore, most of the exposure time period corresponded to the spring and summer seasons in the location, in which scarce rain was registered and the number of daily sunshine hours were greater. These factors would contribute to a gradual material drying (Ortega et al., 2015, 2017), avoiding the progress of hydration and pozzolanic reactions, which need an enough presence of water for their development (Nayak et al., 2022; Ortega et al., 2015, 2017), so their effects in the long term would be more limited in the properties and pore network of the mortars. In addition, several authors have reported (Ortega et al., 2015; Kanna et al., 1998) that the progressive drying of the material could produce de formation of shrinkage microcracks, which may also affect the behaviour of the mortars.

On the other hand, in the environment C (see subsection 2.2), the temperatures were relatively similar to environment A (around 20 °C), although the average RH was lower (in the range between 65% and 70%). Therefore, the abovementioned drying of the material could be also produced in this environment, with the consequent effects in the progress of pozzolanic and hydration reactions, previously indicated for environment B, as well as in the pore network and performance of the mortars. Moreover, the moderate CO_2 concentration in the environment C could also lead the development of carbonation in the binders. This process could also affect the specimens exposed to the outdoor environment B, but probably to a lesser extent.

In general, the abovementioned harmful processes related to the conditions of real environments B and C, would explain the general lower pore refinement noted for all the binders in comparison with environment A. Furthermore, the smaller proportion of finer pores showed by SF, F and REF specimens exposed to condition C, compared to condition B, would suggest that the effects of an environment which combined a higher presence CO_2 with smaller RH, may affect more the development of their microstructure. According to several researches (Neville, 1995; Díaz et al., 2015), the carbonation process may produce a coarser pore structure of the material. This coarse pore structure would entail a reduction of percentage of finer pores and an increase of percentage of higher pores, that is, a loss of pore refinement, and it may be caused by the formation of additional silica produced by the C–S–H gel decomposition, due to contact with environmental CO_2. Furthermore, it has been shown that the addition of fly ash produced greater carbonation (Ngala and Page, 1997; Lu et al., 2018), due to the consumption of portlandite during the fly ash pozzolanic reactions. Then, it is interesting to highlight that the lower pore refinement for the SF, F and REF specimens would be compatible with the abovementioned effects of carbonation process, although the possible formation of shrinkage microcracks could have also contributed to this lower microstructure refinement under environment C.

For S, FL, SL and L mortars, their pore network was less refined for environment B than for environment C. This would indicate that an outdoor environment with the drying as a predominant harmful process, and probably accompanied by carbonation, would have more influence in their pore structure. In the case of slag, several works (Ortega et al., 2015; Kanna et al., 1998) have reported the tendency to develop greater shrinkage cracking in materials with this addition, when they are exposed to conditions with relatively warm temperatures and drying, being this in agreement with the results obtained. Moreover, the fact that the presence of limestone in the mortars also produced a reduction of microstructure refinement in an environment with predominance of drying phenomenon would also be in keeping with other authors (Meddah et al., 2014), which pointed out a scarce rise of the drying shrinkage strains for ternary binders with limestone (Meddah et al., 2014). Lastly, for both real environmental studied, mortars which incorporated at least one active addition in the binder generally presented similar or even greater pore refinement compared to reference mortars without additions, which could be relevant.

The total porosity differences between conditions B and C were small for most of the binders studied, so this would indicate that the real exposure environments studied probably had similar influence in this parameter. This result may be interesting. Nevertheless, it has been noted noticeable low porosity for reference series matured in condition C, even reaching smaller values of this parameter than in environment A. This has been also registered for L specimens, but to a lesser extent. According to previous works (Díaz et al., 2015; Ngala and Page, 1997), in which the effects of carbonation in cementitious materials have been studied, this result could be due to the $CaCO_3$ formation inside the microstructure. The $CaCO_3$ fills more space in the pore network compared to the original hydrated compounds from which it is formed, producing a porosity lessening (Taylor, 1997). The result obtained, suggesting that this effect of carbonation in total porosity was more noticeable for reference mortars, would agree with other authors (Díaz et al., 2015), and it may be explained in terms of the greater presence of portlandite, in these mortars without additions. Finally, the fact that simultaneously a reduction of porosity and lower pore refinement were noted in those mortars would be also in accordance with other authors (Díaz et al., 2015; Ngala and Page, 1997).

3.2. Carbonation front depths

The results of carbonation front depths are represented in Fig. 6. For environment A, there was not carbonation for all the binders. This would be due to the storage conditions of the samples in hermetically sealed containers with 100% relative humidity along the studied time period (see subsection 2.2), which would avoid the contact of the materials with possible harmful agents present in the external air. The samples matured in real environments B and C developed carbonation. In general, the carbonation front depths were more noticeable for environment C, which may be due to the higher CO_2 concentration in an indoor environment with moderate circulation of vehicles (see subsection 2.2).

The carbonation depths were overall more noticeable for binders with additions in the abovementioned real environments, compared to reference mortars, which could be an interesting outcome from a practical point of view. This result would agree with other authors (Neville, 1995; Díaz et al., 2015; Ngala and Page, 1997; Lu et al., 2018), who pointed out that it may be explained regarding the lower presence of portlandite in those mortars which incorporated additions (Neville,

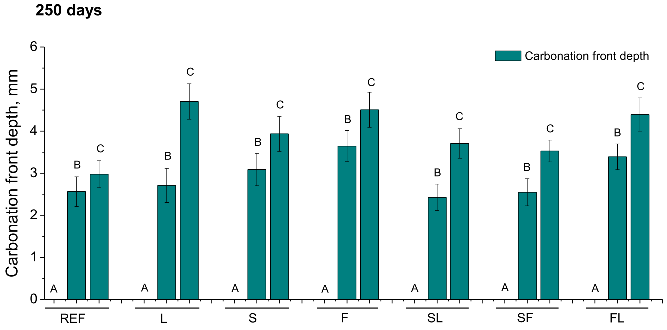

Fig. 6. Depths of carbonation front noted at 250 days.

1995; Lu et al., 2018). In addition, the higher carbonation depths noted in environments B and C compared to environment A for all the studied binders, would be compatible with the lower refinement of pores reported in both real environments, as was explained for porosimetry results in relation to progressive C–S–H gel decomposition in contact to CO_2 (Neville, 1995; Díaz et al., 2015). Furthermore, as has been also discussed for pore size distribution results, the pore network was less refined in environment B than in environment C for S, L, SL and FL binders, despite having lower carbonation depths when they were exposed to environment B. This would show that the drying shrinkage probably produced in real environments with lower RH may also influence the microstructure development, simultaneously with carbonation process.

3.3. Mechanical strengths

The compressive and flexural strengths observed are respectively shown in Figs. 7 and 8. Both mechanical strengths were generally lower in environments B and C for all the studied binders, in comparison with environment A.

The higher values of compressive and flexural strengths in environment A would be caused by the high RH available in this condition, in combination with an optimum temperature, which allowed an adequate progress of pozzolanic and hydration reactions (Wang et al., 2004; Papadakis, 1999; cakır and Aköz, 2008; Khankhaje et al., 2023; Umar Khan et al., 2021), as has been previously explained, producing a progressive formation of solids, which would improve the performance of the mortars. These higher strengths noted for environment A would agree with the results registered with porosimetry test, especially with pore size distributions, because a more refined microstructure would entail better mechanical properties, as has been observed.

With respect to conditions B and C, the lower environmental relative humidity would slow down the progress of pozzolanic and hydration reactions (Ortega et al., 2015, 2017), so their influence in the development of mechanical properties was reduced compared to an optimum condition (Ramezanianpour and Malhotra, 1995; Barnett et al., 2006). Additionally, the carbonation produced in those environments, previously explained, may also affect the mechanical performance, resulting in a worsening of mechanical strengths (Atiş, 2003; Khan and Lynsdale, 2002). Moreover, the abovementioned possible development of drying shrinkage, together with the consequent formation of microcracks, would lead to get worse the mechanical properties (Ramezanianpour and Malhotra, 1995; Kanna et al., 1998; Ortega et al., 2018). Therefore, the results of strengths for real conditions B and C would be compatible with the harmful processes produced in those environments, as well as with the lower pore refinement observed under these conditions, already discussed.

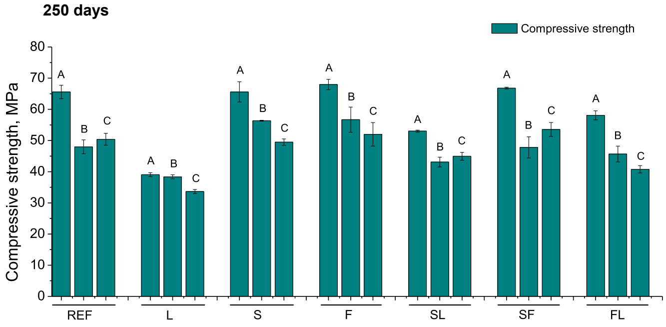

Fig. 7. Compressive strengths obtained for the studied mortars.

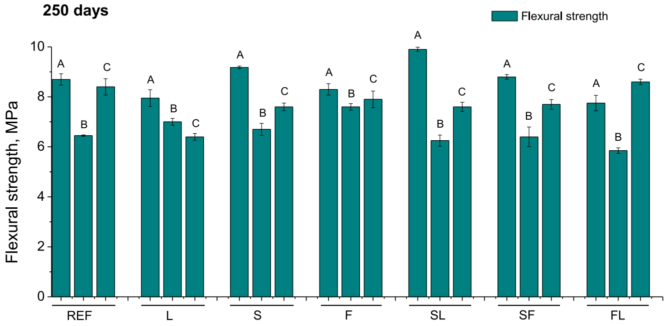

Fig. 8. Flexural strength results at 250 days for the different binders and environmental conditions studied.

If the results of compressive strength for both real environments B and C are compared, the differences between them were not high, although this parameter was overall lower in environment C for most of the tested series (L, S, F and FL). This result would suggest that in general the compressive strength would be slightly more affected by a real environment with predominance of carbonation, which may be relevant regarding the application of these results. In the case of REF, SL and SF series, the differences regarding compressive strength between both real environments were very low, even though this parameter was slightly higher for condition C than B. This would show that an environment with the predominance of deleterious processes related to drying would affect the compressive strength of REF, SL and SF mortars more than the other tested series, in comparison with another environment where the carbonation is the main process, which is interesting to highlight. In addition, this would be compatible with the lower total porosity noted for REF, SL and SF series matured in environment C compared to B, a with the result that the three lowest carbonation depths observed in both real environments corresponded to these REF, SL and SF mortars. Finally, the flexural strength was overall lower for environment B, so it seemed that an environment with higher drying shrinkage would affect more the flexural strength of the studied series.

Regarding future lines of research in order to continue the work, whose results have been described and discussed here, it is noteworthy to highlight the study of the evolution of the microstructure and properties of the mortars tested in this research at higher exposure ages (i.e. several years), the study of other binary and ternary binders exposed to the same environments analyzed in this work, and testing the behavior of the mortars studied exposed to other real environments compatible with other exposure classes defined in Eurocode 2. On the other hand, the study of the performance of cement-based materials which incorporate new additions not yet standardized exposed to real exposure environments could be also a suitable future topic of investigation in the line of the work presented here.

4. Conclusions

The main conclusions of this work can be summarized as follows.

- All the studied binders showed a more refined microstructure for condition A, with a higher percentage of pores of the size intervals <10 nm and 10–100 nm. This may be explained in relation to the high environmental relative humidity, in combination with an optimum temperature of this condition, which would allow an adequate progress of slag and clinker hydration, and pozzolanic reactions of fly ash. These reactions would form additional solid phases which reduce the pore sizes. This also led to a better mechanical performance of the binders, in comparison with real environments, as revealed the higher compressive and flexural strengths overall noted for optimum condition A.
- The lower relative humidity present in real in-situ exposure conditions B and C would make difficult the progress of hydration and pozzolanic reactions, also entailing a progressive drying shrinkage of the specimens, as suggest the mercury intrusion porosimetry results. In addition, the carbonation development was noted for all binders in

both real environments B and C. The effects of this harmful processes overall gave as a result a lower pore refinement (higher percentages of pores with diameters >100 nm) and worst mechanical properties of the mortars, with lower compressive and flexural strengths in comparison with optimum environment A.

- The development of drying shrinkage seemed to be the predominant deleterious process in real environment B, while the carbonation was the main process for condition C, according to the higher carbonation front depths observed for condition C compared to B.
- The microstructure of reference mortars (REF series), ternary binder with both fly ash and slag (SF series) and binary binder with fly ash (F series) was more negatively affected by environment C, as would indicate their lower proportion of finer pores (diameters <100 nm) for this condition. The environment B produced a higher harmful influence in the pore structure of ternary and binary binders with limestone (SL, FL and L series) and binary binder with slag (S series), shown by the smaller percentages of pores with sizes lower than 100 nm in comparison with environment C.
- Mortars which incorporated at least one active addition in the binders (fly ash and/or slag) generally presented similar or higher microstructure refinement, with higher percentages of finer pores, compared to reference mortars. This has been observed for all the environments studied. Therefore, they would be the most suitable mortars for being used as cement-based coatings of buildings, at least in the conditions studied in this work, with additional benefit of contributing to sustainability.
- The differences regarding the compressive strength between the real environments studied were not high, although this parameter was overall slightly lower in environment C for most of the studied binders, suggesting that the compressive strength was probably more affected by a real environment with predominance of carbonation. On the contrary, lower flexural strengths were noted for environment B, which would indicate that an exposure condition with higher drying shrinkage would affect the flexural strength to a greater extent.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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