INFLUENCE OF EARLY SULFATE EXPOSURE IN THE PORE NETWORK DEVELOPMENT OF MORTARS

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ABSTRACT

The objective of this paper is to evaluate the influence of sulfate exposure on the pore network development of several Portland cement matrices. MIP, XRD and SEM analysis were performed at different ages in samples exposed to sulfates after 2 days of casting. Results suggest that patterns of precipitation of the expansive products are linked to the degree of refinement of the pore network. During early stages of exposure, large pores concentrate a higher proportion of the expansive product formed. At later stages, precipitation evolves towards finer pore sizes.

Keywords: Concrete; Durability; External sulfate attack; Pore structure; Ettringite; Precipitation pattern; Curing

1. INTRODUCTION

External sulfate attack (ESA) has been recognized as a complex degradation phenomenon that may cause severe damage in cement based materials [1,2]. The stresses generated by precipitation of expansive phases (ettringite and gypsum) in the pore network are reflected on the macro-scale in the form of expansions and cracking. After decades of extensive research, important aspects such as the precipitation pattern of expansive products are not fully understood. Because of that, codes have adopted simplified approaches to mitigate ESA in real structures. Moreover, numerical models to predict the damage include simplifications regarding the precipitation of expansive products, requiring several fitting parameters to correctly reproduce the effects of ESA [3,4].

The uncertainties in fundamental issues might be explained by the fact that most of the research conducted in this field is focused on the dimensional variation and cracking, which are the macro-scale response of the precipitation of expansive phases in the pore network. However, according to recent publications [5-7], to correctly assess the potential damage is key to understand the relationship between ettringite formation and pore network. When it comes to evaluate the damage generated, K. Tosun et al. [5] suggested that the location and morphology of the ettringite precipitation may be more relevant than the total quantity of ettringite formed. In fact, the crystallization pressure theory [6,7] states that only expansive products precipitated in small pores are likely to cause damage. Unfortunately, few experimental studies focusing on

these aspects are found in the literature due to limitations in the techniques available to characterize the precipitation in the pore structure of the cement-based materials. Another important issue hardly ever evaluated is the early sulfate exposure. In reality, the source of external sulfate ions is usually found in sulfate-rich soils and underground waters in contact with concrete. Therefore, ESA is especially significant in underground structures like foundations, tunnels or waste containers. Due to their massive size, these structures are usually built *in situ*, hence being exposed to sulfates since casting. However, most studies about the ESA in laboratory rely on testing of specimens cured several days in lime water prior immersion in the aggressive solution with sulfates.

To illustrate this, Table 1 summarizes some of the recent studies on the ESA performed in laboratory, including data on the mineral admixtures used and the age at which the specimens were exposed to the sulfate solution. Even though it only represents a small part of studies published, the table indicates that in most of them specimens are cured at least 28 days before sulfate exposure. If mineral admixtures are used, this non-aggressive curing may be extended to 90 days. This contrasts with the reality found in most structures, which are subjected to sulfates shortly after casting.

Table 1. Age of sulfate exposure in a selection of recent publications

Authors	Year	Additions				Age of exposure [days]
		FA ^a	SF ^b	LF ^c	S ^d	
M.T. Bassuoni, M.L. Nehdi [8]	2009	x	x	x	x	56
T. Schmidt et al.[9]	2009			x		28
B. Lothenbach et al. [10]	2010					28
T. Aye, C.T. Oguchi [11]	2011	x	x			28
El-Hachem [12]	2012					3 and 28
W. Kunther et al. [13]	2012	x	x	x	x	28
J. Gao et al. [14]	2013	x			x	60
W. Müllauer [15]	2013					28
Zhang et al. [16]	2013					28
I. Sirisawat et al. [17]	2014	x		x		28
J. Stroh et al. [18]	2015	x			x	28
Yu et al. [19]	2015				x	90

a: Fly ash, b: Silica fume, c: Limestone filler and d: Slag

Despite the influence of pore characteristics on the precipitation of expansive phases and the importance of early sulfate exposure, there is little or no research focused on the combination of these aspects. The objective of this study is to assess the pore network development and estimate qualitatively the pore ranges at which the alterations might occur in specimens subjected to early sulfate exposure. Since these aspects are expected to vary depending on the initial pore size distribution of the material, five mortars with different pore systems were evaluated: one without any mineral admixture (reference), three with mineral admixtures (fly ash, silica fume or limestone filler) and one with air-entrainer. In addition to that, the influence of two different sulfate concentrations representative of field and laboratory conditions were evaluated.

The evolution of the pore structure was assessed by mercury intrusion porosimetry (MIP). Although this technique may be affected by several experimental factors [20,21], it is one of the

few that may provide an overview on the pore distribution. Moreover, a qualitative comparison should provide valuable information regarding the influence of early sulfate exposure and highlight possible differences on the precipitation patterns depending on the characteristics of the material. X-ray diffraction (XRD) combined with Rietveld analysis was performed to evaluate the presence of expansive phases at the end of the curing period. Scanning electron microscopy (SEM) was also performed to assess the influence of the external sulfate concentration and the degree of refinement of the matrix on the morphology and crystallinity of the ettringite formed.

The results obtained shed light on important issues related with the ESA. It provides a different view on the evolution of the attack, suggesting possible explanations for the alteration patterns observed in the porous network over time. The conclusions derived from this study may help to further understand the phenomenon behind the ESA, being useful for future development of prediction models and guidelines.

2. EXPERIMENTAL

2.1. MATERIALS AND MIXTURE CHARACTERISTICS

Table 2 shows the properties of the Portland cement and mineral admixtures used in this work. Chemical composition of Portland cement (CEM I 52.5 R) was determined by X-ray fluorescence (XRF) and phase compositions were calculated using Bogue equations. Due to the presence of ferromagnetic particles, elemental compositions of the fly ash and silica fume were determined by ICP-MS. The fly ash used is equivalent to ASTM C618 class F. A low-calcium fly ash was chosen for its little or no self-cementing properties and to avoid a supplementary addition of the crystalline phases that may be present in high-calcium fly ashes, such as C_3A or C_4A_3S . Siliceous sand with maximum particle size of 2 mm was chosen for all binders. Particle size distribution of the cement and mineral admixtures estimated by laser diffraction are presented in Figure 1.

Fig. 1. Particle size distribution.

Table 2. Properties of cement and mineral admixtures.

	PC ^a	LF ^b		FA ^c	SF ^d
<i>Chemical comp. [%]</i>			<i>Elemental comp. [%]</i>		
SiO ₂	19.5	1.99	Si	23.56	46.26
Al ₂ O ₃	5.9	1.05	Al	8.74	0.35
Fe ₂ O ₃	1.7	0.46	Fe	6.92	1.26
CaO	63.1	54.16	Ca	3.70	0.32
MgO	2.1	0.63	Mg	0.50	0.07
SO ₃	3.5	-	S	0.20	-
K ₂ O	0.78	0.10	K	0.55	0.21
Na ₂ O	0.35	0.02	Na	-	0.61
Cl ⁻	0.02	-	P	0.11	-
MnO	-	0.01	Mn	0.01	0.04
TiO ₂	-	0.05	Ti	0.28	-
Ignition loss	2.96	42.39		1.68	3.35
<i>Physical prop.</i>					
Spec. surf. area (BET) [m ² /g]	1.10	3.74		1.56	19.84
<i>Phase comp. [%]</i>					
C ₃ S	65.4				
C ₂ S	10.6				
C ₃ A	12.3				
C ₄ AF	5.6				

a: Portland cement, b: Limestone filler, c: Fly ash and d: Silica fume

Table 3 shows the composition of the 5 matrices included in the study, which intend to simulate the typical composition of the mortar that surrounds the coarse aggregate in a conventional concrete applied in foundations. In certain applications, mineral admixtures are used to replace a fraction of the cement, which reduces the C₃A content of the binder and its expansive potential. However, in this work, the additional volume from the mineral admixtures was fully compensated by a reduction in the content of sand. This way, the content of cement remained the same for all mixtures, ensuring a constant amount of C₃A per unit of volume and similar potential expansion. All compositions had a water/cement ration (w/c) of 0.45.

The mixing procedure defined in UNE-EN 196-1:2005 was adopted, assuming small modifications to cover the specificities of the admixtures added and the cylindrical molds used. In the case of compositions with mineral admixtures, the latter was first thoroughly mixed with cement prior to adding water. GLENIUM ACE 456 superplasticizer was added to all compositions mixed with the deionized water in contents to assure flow extents of 20 cm ± 0.5 cm. In the case of composition PC_A, air-entrainer admixture MasterAir 100 was added at the end of the mixing procedure and mixed at high speed for 60 s.

Table 3. Mortar composition.

	PC	PC_FA	PC_LF	PC_SF	PC_A
Cement [kg/m ³]	580	580	580	580	580
Sand [kg/m ³]	1330	1235	1210	1245	1325
Water [l/m ³]	261	261	261	261	261
Fly ash [% ^a]	-	30	-	-	-
Limestone filler [% ^a]	-	-	20	-	-
Silica fume [% ^a]	-	-	-	10	-
Air-entrainer [% ^a]	-	-	-	-	0.3
Superplasticizer [% ^a]	0.25	0.55	0.55	1	0.25

a: Percentage by cement weight

2.2. EXPERIMENTAL PROCEDURE

2.2.1. SPECIMEN PREPARATION

Mortars were cast into Ø2x16 cm² cylindrical molds. The specimen size was chosen according to the results of the size effect study by R. El Hachem et al. [22], who determined that 2x2x16 cm³ prisms reached a good balance between test duration and representativeness. In the present study, cylindrical specimens were used to avoid the typical corner spalling experienced in rectangular prisms during the ESA. The specimens were cast individually to avoid presence of cut sand on the surface.

Figure 2a depicts a schematic representation of the molds used, which had a longitudinal opening to ease the demolding process. Prior to casting, this opening was sealed with a high strength duct tape. As shown in Figure 2b, the mortar was poured gradually in three steps. After each step, the material was manually compacted. Specimens were demolded 24 hours after casting and water sealed with epoxy resin at both ends to ensure radial penetration of the sulfate ions at the lateral surface (Figure 2c).

Fig. 2. Schematic representation of (a) cylindrical molds and (b) casting process, (c) specimen with epoxy coating and (d) specimen layout.

2.2.2. EXPOSURE CONDITIONS

Once sealed, specimens were cured in water at 25 °C ± 1 °C for one day. Then, 2 days after mixing, they were placed vertically inside plastic containers and submerged in a sulfate rich

water solution, as shown in Figure 2d. Sulfate concentrations of 3 and 30 g of $\text{Na}_2\text{SO}_4/\text{l}$ were used to reproduce field and accelerated laboratory testing conditions (referred to as C3 and C30, respectively). The solution was renewed weekly during the first month and every other week until the end of the test. The volumetric ratio of sulfate solution to mortar was 12. This should be representative of field conditions where the material is exposed to continual supply of sulfate ions.

Water pumps were used at low speed to ensure a continuous flow from the bottom to the top of the container. The containers were filled up to the top and covered to reduce contact with the air, thus limiting CO_2 dissolution and further carbonation. Duration of exposure for all mortars with mineral (PC_FA, PC_LF and PC_SF) and an air-entrainer (PC_A) admixtures was set to 90 days. In mortars without admixtures (PC) the period evaluated was shortened to 28 days. Test duration was set to cover typical curing periods before sulfate exposure reported in the literature (see Table 1). Reference samples of each composition were also exposed to non-aggressive curing with water without sulfates for comparative purposes.

2.2.3. MICROSTRUCTURAL ANALYSIS METHODS

The pore characteristics of the mortars were examined by mercury intrusion porosimetry (MIP) with a Micrometrics AutoPore IV 9500 (contact angle 140° and Hg surface tension 485 dynes/cm) at 48 h, 7, 28 and 90 days. Following the recommendations by [23,24], samples for MIP measurements were core drilled from original specimens (Figure 3a) using a column drill equipped with a diamond drill bit cooled with water, as this extraction method exhibited less sample-to-sample variation. Due to the symmetric radial sulfate exposure conditions, each sample was divided in two and analyzed separately (Figure 3b). Freeze-drying was applied to the samples to ensure full desaturation prior to mercury intrusion.

Quantitative results obtained by MIP may be prone to variations. Some studies found a shift towards finer pore sizes in intrusion curves by one or two orders of magnitude [20, 21]. Therefore, the pore sizes obtained do not necessarily correspond to the real pore sizes of the material. Nevertheless, a qualitative comparison should provide valuable information regarding the influence of early sulfate exposure and highlight possible differences on the precipitation patterns depending on the characteristics of the pore structure of the material.

Fig. 3 (a) Core drilled sample and samples tested in (b) MIP, (c) XRD and (d) SEM.

Phase composition at the end of the curing period was investigated by X-ray diffraction (XRD). Samples for this test were obtained as mentioned previously and depicted in Fig. 3. Additionally, in order to analyze separately the external (in contact with the sulfate solution) and internal fractions of the samples, they were divided in half with a low speed diamond saw cooled with water (Figure 3c).

Samples for XRD were freeze-dried, grinded and mixed with 10 wt.% Al_2O_3 as an internal standard. The powder samples were sandwiched between polyester films of 3.6 μm and tested with a PANalytical X'Pert PRO MPD Θ/Θ diffractometer of 240 mm of radius in a configuration of convergent beam with a focalizing mirror and transmission geometry. $\text{CuK}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) and PIXcel detector with active length of 3.347° were used. Work power was set to 45 kV – 40 mA. $2\Theta/\Theta$ scans from 4 to $88^\circ 2\Theta$ with a step size of $0.026^\circ 2\Theta$ and a measuring time of 200 seconds per step were performed.

Rietveld analysis was performed with the XRD results for the quantitative study of the crystalline phases at the end of the curing period. All structures used in the refinement are listed in Table 4. The global variables refined were the background polynomial with 4 coefficients and the zero shift. For all phases detected, individual scale factors and lattice parameters were refined. A pseudo-Voigt function was chosen to model the peak shape. The phase profile width (w) was refined for all phases with wt.>2 %. For the main phases (wt.>10 %), the profile parameters U , V and the peak shape were also refined. Preferred orientation corrections were applied when necessary for alite (-1 0 1), gypsum (0 2 0) and quartz (1 0 1) as long as the phase content was above 2 %. Phase compositions in the whole sample was calculated by a weighted average taking into account the thickness of the surface and inner sample.

Table 4. Structures used for Rietveld refinement.

Phase	Chemical composition	ICSD Code	Reference
Alite	Ca_3SiO_5	94742	[25]
Belite_o	Ca_2SiO_4	81097	[26]
Portlandite	$\text{Ca}(\text{OH})_2$	15471	[27]
Calcite	CaCO_3	79673	[28]
Ettringite	$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}26\text{H}_2\text{O}$	155395	[29]
Gypsum	$\text{CaSO}_42\text{H}_2\text{O}$	15982	[30]
Ferrite	$\text{Ca}_2\text{AlFeO}_5$	9197	[31]
Quartz	SiO_2	200721	[32]
Monocarboaluminate	$3\text{CaOAl}_2\text{O}_3\text{CaCO}_311\text{H}_2\text{O}$	59327	[33]
Mullite	$\text{Al}_{4,74}\text{Si}_{1,25}\text{O}_{9,63}$	66448	[34]
Corundum	Al_2O_3	73725	[35]

Additional samples were extracted and examined by scanning electron microscopy using secondary and backscattered electrons as well as EDS X-ray analysis. The analysis was performed in a JEOL JSM 7100F microscope at the voltage of 20 kV. Sections were cut perpendicular to the exposed surfaces, freeze-dried, impregnated with epoxy resin, polished and coated with carbon (Figure 3d).

3. RESULTS AND DISCUSSION

3.1. PORE STRUCTURE DEVELOPMENT IN NON-AGGRESSIVE WATER

The pore structure development of the different mixtures in non-aggressive curing conditions (without sulfates) is initially assessed to distinguish the effects caused by the sulfate presence from the microstructure transformations due to normal cement hydration.

Figure 4 depicts the evolution of the cumulative intrusion curves in non-aggressive conditions for all dosages at 48 h, 7 days, 28 days and 90 days. Results at 48 hours for the air entrained mortar are not available due to problems during sample extraction. All dosages show a refinement of the pore structure due to the hydration process along the evaluated period. The mortars with mineral admixtures (PC_LF, PC_FA and PC_SF) show higher refinements due to the replacement of a fraction of sand by finer particles. Amongst these compositions, PC_FA and PC_SF show the finest pore size distributions due to the additional refinement induced by the pozzolanic activity of the mineral admixtures used [36]. On the other hand, the addition of an air-entrainer produces a coarser pore structure due to the intrusion of air voids ranging from 0.1 μm to 2 μm . The total mercury intruded in PC_A is considerably higher than in any other composition studied. At 90 days, PC_SF offers the highest refinement of the pore structure, followed by PC_FA, PC_LF and PC_A. These results are in agreement with the particle size distribution of the additions presented in Figure 1.

Fig. 4. Cumulative intrusion curves of PC, PC_SF, PC_LF, PC_FA and PC_A at (a) 48h, (b) 7days, (c) 28 days and (d) 90 days.

Figure 5 shows the evolution of the critical pore diameter, which is a semi-quantitative parameter that can be related to the permeability of the specimens [37]. As expected from the cumulative intrusion curves, mortars with silica fume and fly ash present the smallest critical

diameters at the end of the curing period. For those compositions, the reduction is produced gradually during the 90 days of curing due to the pozzolanic reaction [36]. For mortars with limestone filler, no further refinement of the pore structure is observed after 28 days, displaying a critical diameter similar to that of the reference mortar (PC). Notice that Figure 5 does not include PC_A series. The use of an air-entrainer generates micro air bubbles that distort the definition of the critical diameter.

Fig. 5 Critical diameter evolution in lime water curing of PC, PC_SF, PC_LF and PC_FA.

3.2. PORE STRUCTURE DEVELOPMENT IN AGGRESSIVE CONDITIONS

3.2.1. MIP RESULTS

The evolution of the cumulative intrusion curves is evaluated separately for each of the five mortars studied. Results corresponding to the low aggressive solution representative of field conditions (C3) are available at the end of the curing period (28 days for PC and 90 days for the others). In order to ease the interpretation of the intrusion curves, the evolution of the critical diameter and the precipitation rates amongst 5 predefined pore ranges are evaluated.

Due to the known limitations associated to the MIP and the similar total mercury intruded by each sample, results are presented as percentage of the cumulative volume intruded, not in absolute values. Variations in the intrusion curves between non-aggressive and aggressive curing conditions are assumed to be mainly caused by the formation of expansive phases due to the presence of sulfate ions in the curing water. To simplify the analysis, possible alterations on other hydration processes due to the presence of sulfates are not taken into account, even though they might take place. The results from the MIP tests are compared to XRD analysis in section 3.2.2, which should confirm the presence of expansive phases.

Reference mortar (PC)

Figure 6 shows the evolution of the cumulative intrusion curves for high (C30) and low (C3) aggressive curing conditions in PC. At 7 days of exposition (Figure 6a), the intrusion profile for specimens under high aggressive curing has already shifted towards a more refined pore structure. At 28 days (Figure 6b), this trend is even more evident, thus indicating the possible precipitation of expansive phases. Conversely, low aggressive curing does not affect significantly the pore network during the period evaluated.

Fig. 6. Cumulative intrusion curves of PC at (a) 7 days and (b) 28 days.

In order to further analyze the MIP results, Figure 7a shows the evolution of the pore size distribution according to 5 predefined pore ranges (<10 nm, 10-50 nm, 50-100 nm, 100-500 nm and >500 nm) at different ages and curing conditions.

Figure 7a shows important modifications of the pore network at 7 days when C30 and non-aggressive curing are compared. A considerable reduction of the proportion of pores above 500 nm and 100-500 nm is observed. This is balanced by an increase of finer pores. At 28 days, the main difference on the pore size distribution between C30 and non-aggressive curing is found in the pore range 50-100 nm. An increase of the proportion of pores in this range indicates that the precipitation of expansive phases may be occurring preferentially in pores above 100 nm.

Notice that larger pore ranges are affected at the initial ages of exposure. However, alterations evolve towards finer pore sizes as the exposition time increases. On the other hand, as expected from the cumulative intrusion curves presented in Figure 6b, mortars under C3 curing condition show similar pore size distributions to those of specimens subjected to non-aggressive curing both at 7 and 28 days of exposition.

Figure 7b shows the evolution of the critical diameter. No change in the critical diameter occurs at 7 or 28 days for specimens subjected to the aggressive curing in comparison to those under non-aggressive curing. Such outcome may be explained by the fact that modification in the pore network occurs in pores larger than the critical diameter presented in Figure 5 (around 50 nm).

Fig. 7. Evolution of (a) pore size distribution and (b) critical diameter of PC.

Mortar with limestone filler (PC_LF)

Figure 8 presents the cumulative intrusion curves of PC_LF mortars at 7, 28 and 90 days of exposition to different curing conditions. At 7 days, no significant difference is observed between high (C30) and non-aggressive curing. However, from 28 days on, specimens submerged in the C30 solution displayed a more refined pore structure, which may indicate a precipitation of expansive phases such as ettringite or gypsum. At 90 days, specimens in the low sulfate concentration (C3) also showed a finer pore network compared to specimens under non-aggressive curing. This result suggests that the influence of an early sulfate exposure is not only significant in accelerated tests with high sulfate concentrations but also in concentrations representative of field conditions since alterations in the pore network are also observed.

Fig. 8. Cumulative intrusion curves of PC_LF at (a) 7 days, (b) 28 days and (c) 90 days.

Figure 9a shows the evolution by pore range. At 28 days, results indicate a higher precipitation rate of expansive phases in pore sizes between 100-500 nm. Due to this precipitation, the proportion of pores between 50-100 nm increases. At 90 days, this trend is maintained, also leading to an increase in the proportion of pores between 10-50 nm. The results suggest that the evolution of pore refinement over time affects the additional deposition of expansive products, reaching smaller pore sizes. Like in the case of the reference PC mortar, a bigger refinement is achieved in samples exposed to C30 in comparison with those exposed to C3. Despite that, the critical diameter is not affected by the different curing conditions evaluated at 28 days and 90 days (see Figure 9b).

Fig. 9. Evolution of (a) pore size distribution and (b) critical diameter of PC_LF.

Mortar with fly ash (PC_FA)

Figure 10 depicts the cumulative intrusion curves of PC_FA mortars at 7, 28 and 90 days for the different curing conditions considered. Results at 7 days already show a slight refinement of the pore structure for the samples submerged in the high aggressive solution (PC_FA_C30). From 28 days on, this trend is confirmed and the shift towards a more refined pore structure becomes clearer. In the case of the specimens under low aggressive curing conditions (PC_FA_C3), at 90 days the cumulative intrusion curve also deviates towards a thinner pore network.

Figure 11a shows that specimens with fly ash submerged in high aggressive conditions present alterations in the pore network in low pore ranges as early as at 7 days of exposition. In fact, a significant increase in the relative volume of pores between 10-50 nm is observed. This trend is maintained for samples at 28 days and 90 days.

Interestingly, specimens submerged in low aggressive conditions reach similar pore size distribution to the ones under high aggressive conditions. This behavior of the PC_FA in the precipitation patterns is also reflected on the evolution of the critical diameter. Figure 11b illustrates how sulfate exposure decreases the critical diameter for all ages tested here. Results suggest that the finer pore system observed in samples with fly ash force the deposition of expansive phases in smaller pores in comparison with equivalent composition without mineral admixtures and with limestone filler.

Fig. 10. Cumulative intrusion curves of PC_FA at (a) 7 days, (b) 28 days and (c) 90 days.

Fig. 11. Evolution of (a) pore size distribution and (b) critical diameter of PC_FA.

Mortar with silica fume (PC_SF)

According to the results presented in the section 3.1, silica fume addition leads to the most refined pore network during the period evaluated among the compositions studied. Figure 12 presents the evolution of cumulative intrusion curves for this series. As can be seen, differences observed between aggressive and non-aggressive curing are minor at all curing ages for both high and low aggressive conditions. This behavior seems to indicate that the amount of expansive phases precipitated during the first 90 days of curing in aggressive environments is

less significant when the pore structure of the matrix is highly refined. The differences on the cumulative intrusion curve between 70-300 nm for PC_SF_30 at 28 days cannot be explained by normal hydration or deposition of expansive products, being probably a consequence of inaccuracies related to sample extraction or testing.

Fig. 12. Cumulative intrusion curves of PC_SF at (a) 7 days, (b) 28 days and (c) 90 days.

Figure 13a shows the evolution of the pore size distribution according to 5 predefined pore ranges. No evident deposition pattern is observed. Despite that, significant variations are identified in the critical diameter shown in Figure 13b. This figure highlights a reduction in the critical diameter in aggressive curing conditions. This indicates that, despite the absence of clear alterations due to early sulfate exposure in MIP curves, precipitation could occur in pores smaller than 40 nm.

Fig. 13. Evolution of (a) pore size distribution and (b) critical diameter of PC_SF.

Mortar with air-entrainer (PC_A)

According to the analysis of the pore structure conducted in section 3.1, specimens with air-entrainer should have the most favorable conditions for ettringite and gypsum formation, as the high permeability might promote the penetration of sulfates. Figure 14 represents the evolution of cumulative intrusion curves for PC_A mortars. At 7 days, a slight refinement of the pore structure is already observed in samples exposed to C30 in comparison to equivalent ones exposed to non-aggressive environment. Differences between both curing conditions become more significant over time. At 28 days, the intrusion curve of the specimens in the high sulfate environment (C30) shows a shift towards thinner pores. At 90 days, the higher refinement of the pore structure is accentuated. Specimens submerged in low sulfate concentration solution (C3) also show a thinner pore network if compared with the one from samples under non-aggressive curing conditions, although differences are not as pronounced as in comparison with samples exposed to C30 solution.

Fig. 14. Cumulative intrusion curves of PC_A at (a) 7 days, (b) 28 days and (c) 90 days.

The evolution of the pore size distribution depicted in Figure 15 suggest that these differences may be attributed to a significant reduction of the proportion of pores above 500 nm, increasing the ratio of pores between 50-100 nm and 100-500 nm. Even though compositions with air-entrainer might seem prone to penetration of sulfates and precipitation of expansive phases, results indicate that this precipitation occurs mainly in large pores, while smaller pore ranges remain unaltered.

Fig. 15. Evolution of the pore size distribution of PC_A.

Discussion of MIP results

The results show significant differences between the cumulative intrusion curves of mortars cured in aggressive and non-aggressive conditions. The dosage that presents the greatest influence is the PC_A series. For this mortar, the presence of entrained air voids connected to the pore network may enhance the ingress of sulfate ions towards the inner layers of the material and promote ettringite and gypsum formation. On the other hand, the dosage that presents the lowest influence by early aggressive curing is the PC_SF series. In this case it seems that the high pore refinement leads to a matrix with lower permeability, which was barely penetrated by sulfates. Notice that the alterations in the pore network are observed not only in specimens submerged in the high aggressive solution (C30), but also in the solution representative of field conditions (C3) for PC_LF, PC_FA and PC_A.

In compositions PC, PC_FA and PC_A the alterations in the pore network due to early sulfate exposure are observed as early as at 7 days. Consequently, typical curing periods of 28 to 90 days (see Table 1) prior to sulfate exposure adopted in accelerated laboratory testing might not reproduce the behavior of the structures cast *in situ*, which will be affected by sulfate since casting. According to R. El Hachem et al. [12], the expansive product formed during early curing is less likely to cause damage due to the coarser pore network in which it is formed. Therefore, if the age of sulfate exposure in laboratory testing is not consistent with the field conditions, the damage predicted might not be realistic. A more realistic approach in accelerated tests would be to expose sample to sulfate at earlier ages.

Another relevant outcome derived from the analysis of the MIP results is related to how the pore size distribution of the matrix influences the precipitation pattern. Some models from the literature used to evaluate the ESA assume that the precipitation occurs evenly in the pore network. If this assumption was true, the proportion of pores in samples exposed to aggressive and non-aggressive curing conditions should be similar. Conversely, results indicate that different pore ranges have different precipitation rates. In fact, the precipitation pattern depends strongly on the original pore size distribution of the material. As a general trend, it seems that initially larger pore sizes are more affected by early sulfate exposure. At later ages, finer sizes are affected by the alterations.

Results also indicate that the pore size distribution of the material defines which is the lowest pore range affected. In more refined matrices, the precipitation of expansive phases reached the pore range of 50-100 nm (PC_FA). On the other hand, in coarser pore network of the mortar with air-entrainer (PC_A), the precipitation was mainly found in pores bigger than 500 nm. The exact reasons for this differential alteration depending on the refinement of the pore system are not completely clear. However, it may be explained by the higher rate of penetration of the sulfates through paths that include coarser pore sizes, which exert smaller restriction to the diffusion and would also accommodate a bigger total sulfate content inside. This higher availability of sulfates would favor the formation of ettringite in the larger pores [38]. At the same time, the precipitation in coarser pores could act as a buffer that hinder the increase of concentration in smaller pores connected to them. Therefore, the concentration in smaller pores would not built up to allow ettringite precipitation. As time passes and the refinement of the system increases, the same phenomenon would extend to smaller pores.

The results also seem to indicate that mortars with air entrained bubbles (PC_A) and with silica fume (PC_SF) might be less affected by early aggressive curing conditions. Notice that each of these two mortars would reach this performance by two different reasons. In the case of PC_SF, the reduced permeability of the matrix would limit the sulfate ingress and, consequently, the extent of the ESA. In the case of PC_A, the large amount of big pores would act as a buffer that hinders the increase of the crystallization pressure in the system. The small levels of pressure generated in smaller pores would be unlikely to generate damage since the majority of the precipitation takes place in larger pores.

3.2.2. XRD RESULTS

This section presents the results from XRD tests in order to verify the presence of expansive phases (ettringite and gypsum) that could explain the alterations of the pore network observed in aggressive curing conditions. Figures 16a and 16b depict ettringite, gypsum and portlandite contents in the whole sample (average of external and internal) for high (C30) and low (C3) aggressive curing conditions, respectively. The XRD confirms a significant presence of expansive product that may explain the alterations presented in section 3.2.1.

Results obtained for high aggressive condition are also consistent with the cumulative intrusion curves since mortars with silica fume shows the lowest amount of expansive products whereas specimens with air entrained have the highest content of ettringite and gypsum. In C30 curing condition, the formation of expansive phases increases with the porosity of the material.

Figure 16b shows the results obtained for low aggressive curing conditions. As expected, ettringite and gypsum contents are lower than in the high aggressive solution due to a more limited amount of sulfates that penetrate the sample. Except for the composition with air-entrainer (PC_A_C3), the content of expansive product formed is also directly related to the porosity of the material, although this relation is less evident than in samples subjected to C30 given the smaller sulfate content available in the solution.

In Figures 16a and 16b, portlandite contents in PC_SF and PC_FA are considerably lower than in PC_LF and PC_A. These results can be explained by the pozzolanic activity of the silica

fume and fly ash, which consumes reactive silica of the pozzolan and calcium hydroxide, producing calcium silicate hydrate [36].

Fig. 16. XRD results of PC_SF, PC_LF, PC_FA and PC_A at 90 days for (a) C30 and (b) C3.

Figure 17 shows separately the ettringite, gypsum and portlandite contents obtained in the external (close to the surface) and the internal (close to the core) fractions of the sample, for high and low aggressive curing conditions. As expected, ettringite contents are higher in the external fraction of the samples for both aggressive curing conditions due to a higher sulfate concentration (Figures 17a and 17c). However, gypsum and portlandite contents exhibit an opposite trend, being higher in the internal fractions.

These results might be partially explained by a calcium leaching phenomenon from the soluble phases towards the aggressive solution. The solubility of $[Ca^{2+}]$ of the phases of interest are listed in Table 5, along with their ion activity and solubility products. This table shows that the solubility of portlandite and gypsum is considerably bigger than the solubility of ettringite, which is thermodynamically more stable. In this context, the calcium leached may be provided by portlandite and, in a lesser extent, gypsum dissolution from the surface of the sample.

Another possible reason is that ettringite formation promoted by the high sulfate concentration in the external layer also consumes calcium ions from the pore solution. The combination of calcium leaching towards the external solution with high ettringite formation rates causes a reduction of calcium ions close to the external surface. To reach equilibrium, the dissolution of more soluble phases (portlandite and gypsum) might increase, thus explaining the differences in content between the surface and the inside of the sample.

Fig. 17. XRD results of PC_SF, PC_LF, PC_FA and PC_A at 90 days for (a) the external and (b) internal fraction for C30, and (c) external and (d) internal for C3.

Table 5. $[Ca^{2+}]$ solubility of portlandite, gypsum and ettringite.

Phase	Ion activity product	$\log(k_{sp})$ 25°C	Solubility $[Ca^{2+}]$ [mmol/l]
Portlandite	$[Ca^{2+}][OH^-]^2$	-5.18 [39]	11.82
Gypsum	$[Ca^{2+}][SO_4^{2-}][H_2O]^2$	-4.58 [39]	5.13
Ettringite	$[Ca^{2+}]^6[Al(OH)_4^-]^2[SO_4^{2-}]^3[OH^-]^4[H_2O]^{26}$	-45 [40]	1.50

3.2.3. SEM RESULTS

The study of the microstructure and morphology was performed in samples that presented dissimilar trends in terms of initial pore system and alteration patterns after sulfate exposure in order to explain and justify previous results. For that reason, samples from mortars with air-entrainer (PC_A) and fly ash (PC_FA) after 90 days of exposition were selected.

Figure 18 shows SEM images of air voids and pores as well as the magnification of the hydrated products found in high (C30) and low (C3) aggressive curing conditions. Regions analyzed by EDS are indicated by a red circle. The Ca, S and Al ratios calculated from the counting are indicated in the upper right corner of each image. According to the EDS spectra, the needle-like hydrated product found in all cases should correspond to ettringite. However, evident

differences are identified regarding the morphology and degree of crystallinity of the ettringite formed between the two mortars and between both aggressive solutions.

In the case of PC_A_C30 (Figure 18a), the air void is partially filled with clusters with less than 10 μm of diameter formed by ball-shaped ettringite crystals with lengths that go from 1 μm to 5 μm . On the other hand, the ettringite formed in PC_FA_C30 (Figure 18c) is more uniformly spread within the surface of the pore, with most crystals length over 15 μm . In the case of PC_A_C3 (Figure 18b), ettringite is observed in the form of well-defined crystals that grow perpendicular to the surface of the pore, indicating a slower formation. Notice that the length of the crystals reach 20 μm . The same is also depicted in PC_FA_C3 (Figure 18d), where ettringite formed presents high crystallinity, with defined and separated crystals.

These results indicate that the degree of crystallinity of the ettringite formed increases with the refinement of the pore system and decreases with the aggressiveness of the media. Therefore, poorly crystallized ettringite is associated with formation under high supersaturation of the pore solution. The differences observed in the length of the crystals between the high and low aggressive curing conditions can be explained by the fact that the nucleus formation takes place far more rapidly than crystal growth, leading to the formation of a large number of small crystals in high supersaturated environments [41]. Moreover, small crystals formed in low aggressive curing conditions may dissolve because they are not stable with respect to larger crystals in equilibrium with lower concentrations [15].

Figure 18. SEM images of air voids and its magnification for (a) PC_A_C30, (b) PC_A_C3, (c) PC_FA_C30 and (d) PC_FA_C3.

4. CONCLUSIONS

The following conclusions may be derived from this study.

- Results from cumulative intrusion curves indicate significant differences on the pore network between mortars cured in aggressive and non-aggressive conditions. The alterations are observed in both high and low aggressive solutions for most compositions. XRD tests indicate that these alterations may be attributed to the precipitation of ettringite and gypsum.
- The modifications in the pore network are observed as early as at 7 days after early exposition to sulfates. Therefore, typical curing periods of 28 days or 90 days commonly adopted in accelerated laboratory tests prior to sulfate exposure might lead to imprecise damage estimations for structures cast *in situ*. In these cases, a more realistic approach would be to expose samples to sulfate at earlier ages.
- MIP results indicate that the expansive products do not precipitate equally in all pores, as assumed in some models regarding the ESA. Initially, larger pores concentrates a higher proportion of the expansive product. As pore refinement increases with time, the precipitation evolves towards finer pore sizes.
- Results also suggest that the degree of refinement of the pore network defines which is the lowest pore range affected by precipitation. In refined pore structures precipitation reaches smaller pore ranges than in coarser networks, where the precipitation is mainly produced in large pores.
- SEM images of ettringite formed in air voids indicate that the morphology and degree of crystallinity varies depending on the availability of connected air voids and the external sulfate concentration. Crystallinity of ettringite increases with the degree of refinement of the pore system and decreases with the aggressiveness of the media.

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