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Effects of healing start time and duration on conventional and high-performance concretes incorporating SAP, crystalline admixture, and sepiolite: A comparative study

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ABSTRACT

This research investigates the self-healing capability of conventional and high-performance concrete containing either a superabsorbent polymer (SAP), a crystalline admixture (CA), or water-encapsulated in sepiolite by quantifying the recovery of water tightness through the water permeability test and chloride permeability via cracks and matrix penetration on healed specimens. Specimens were pre-cracked to a crack width range of 50–450 μm at 28 days. Specimens were healed under water in four time combinations: healing starting at the concrete age of 28 days or 56 days and a healing duration of 28 or 56 days. Additionally, a healing condition of presaturation during 1 day of water immersion and storage in a humidity chamber for 27 days was studied. The results show that delayed healing reduced the self-healing efficiency, and extending the duration to 56 days enhanced healing, especially for narrow cracks (≈100 μm), and reduced chloride permeability. Specimens with SAP showed superior early-stage healing, but low delayed healing. Sepiolite enhanced healing for delayed cracks with variable effectiveness. CA improved healing for both early and delayed healing, exhibiting low chloride penetration in healed specimens.

1. Introduction

Reinforced concrete is a key material in the construction of modern structures. It is a composite material that combines steel reinforcement and a concrete matrix. Due to the low tensile strength of concrete, it is a material that frequently works with small cracks in service conditions. Some cracks can reduce concrete's durability by allowing deteriorating substances to penetrate inside the element [1]. The crack widths that are allowed depend on the environmental conditions of the structure. Structural codes like Model code 2010, Eurocode 2, 1992, or BS 8110–1,1997 [2,3], usually limit the recommended maximum crack width to 300 μm, but this value varies depending on the environment.

Autogenous healing in cracked concrete is its natural capacity to recover partially or completely initial properties [1]. The process of autogenous (or natural) healing is mainly produced by carbonation and further hydration and needs the direct presence of water to

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promote the reactions. In the literature, cracks with width below 50 μm are considered to display a rapid and complete autogenous healing [4]. The term autonomous healing in concrete refers to the healing produced by engineered materials introduced into concrete with this purpose, such as some chemical additions like crystalline admixtures [5–8], encapsulated polymers [9–12], and biological additions [13–15]. Another strategy to promote self-healing reactions focuses on improving the autogenous healing of concrete, such as with the use of Superabsorbent polymers (SAPs) as water reservoirs [16–19].

Visual crack closure is the most direct method to evaluate self-healing; however, it does not always indicate improved durability-related properties [20]. Water absorption [21], water permeability [22–27], and air permeability [28] tests conducted under cracked conditions are commonly used to measure the effectiveness of healing. Different properties have been reported to have different critical crack widths [29]. It has been observed that water permeability increases rapidly as crack widths increase from 50 to 200 μm, but the increase becomes steady for cracks larger than 200 μm [30]. Chloride penetration also increases with the size of cracks. Usually, it is considered that the threshold crack width for chloride penetration is 10 μm, and smaller cracks are generally not susceptible to chloride penetration [31]. One study [17] reported that cracks of 60 μm showed complete healing in terms of chloride diffusion. Another study [29] identified 13 μm as the critical crack width to prevent additional chloride penetration in the short term. In comparison, 40 μm was reported as the critical crack opening in the long term. These values depend highly on the test setup and parameters chosen, as indicated in [29].

The exposure conditions during the healing process significantly impact the healing process. This has been emphasized in various publications, where cracked samples stored in air or humidity chamber conditions showed similar levels of performance before and after the healing stage [23,32–34].

The time when concrete elements start the healing process and the time that they are allowed to heal is also critical to ensure a high healing performance. On the one hand, higher concrete maturity has been reported [35] to have a diminished capacity for self-healing (cracks formed at 218 versus 28 days), but moderate self-healing was still observed. Instead, another study [36] has reported that concrete samples that were allowed to heal for 100 days exhibited nearly the same permeability as samples without cracks. The differences in healing performance depending on the start healing time or healing duration have also been reported in concrete incorporating SAPs, where concrete with SAPs [20,37], and cracks induced after 7 days of aging were more capable of self-healing than those induced after 28 days of aging. This difference was considered to be produced by the low degree of hydration in the young cracks [37].

Crystalline admixture (CA) is a specific type of permeability-reducing admixture (PRAs) [38] that can promote self-healing of cracks below 0.3 mm [39]. Several studies indicate that incorporating CA into cementitious materials results in more consistent healing properties with reduced variability [23,39,40]. It has been reported that cracks smaller than 0.4 mm in concrete without crystalline admixtures showed similar healing potential after 3 and 6 months compared to those with crystalline admixtures after 1 and 3 months of healing [41]. Crystalline admixtures are considered to significantly enhance self-sealing in cracks up to 0.15 mm wide that are continuously submerged in water, and their effect can persist for up to a year through multiple cycles of cracking and healing [42]. Several experiments found that CA did not enhance crack self-healing at 95 $\pm$ 5% relative humidity [23]. However, some studies have suggested that CA could accelerate self-healing in an air exposure [39]. The effect of CA has been reported to be even better for high-performance fiber-reinforced concrete, showing better mechanical performance of the healed material than the uncracked pristine material [43]. The concentration of chloride decreases gradually with the distance from the exposure surface; however, in mixes with CA, the chloride profile reaches a stable value at a depth much closer to the exposure surface than those without CA [41]. The ability of crystalline admixtures to prevent chloride entry is less evident when healing in a condition with wet/dry cycles [41].

Superabsorbent polymers (SAPs) can enhance the self-healing ability of concrete due to their ability to absorb water and promote autogenous healing by further hydration and precipitation of the calcium carbonate [16,20,44,45]. The introduction of SAP can result in a reduction in compressive strength due to the formation of pores [21,46] and due to an early release of water [44,47,48], with higher reduction when the dosage of SAP increases [16,21,49]. It has been reported that the strength reduction can be mitigated by adding the right amount of water [50]. Studies show that using SAP in high-performance concrete samples can improve healing capacity in the samples stored under water and specimens stored in the air [51,52]. Water is required for enhanced autogenous healing as storage within the SAPs [16,53]. SAP is added to the concrete mix and swells slightly because of the mix water's high pH and ionic concentration upon contact with the cement [54]. After forming the matrix, the water is released for additional hydration and to maintain the relative humidity within the matrix. The SAPs can then absorb water again when in contact with fluids [54,55], which promotes autogenous healing by narrowing the crack pathway and reducing flow [54]. When the cement hydrates, the pores left behind by the formerly saturated SAP particles reduce the tensile strength due to the matrix's reduced active cross-section [16]. The amount of absorbed fluid by the SAP depends on the nature of the SAP and the cementitious composition. According to previous research, the ideal dosage SAP to achieve optimal sealing and healing capabilities is approximately 1% of the binder weight, as suggested by various studies [21,29,30,32]. Greater levels of healing have been observed in samples containing SAP that were healed in relative humidity levels above 90% compared to those healed in relative humidity of 60% [20].

Sepiolite is a microcrystalline-hydrated magnesium silicate with the formula of $Mg_4Si_6O_{15}(OH)_2 \cdot 6\ H_2O$, known for its low specific gravity and high porosity in various forms including fibrous, fine-particulate, and solid. It has been used in cementitious composites to encapsulate chemical agents, such as bacteria, showing higher self-healing effectiveness compared to simply adding minerals [56–59]. In addition, replacing cement with 2% and 10% sepiolite as natural clay has been shown to increase the mechanical strength of mortars by filling cavities and improving compressive and bending strengths [60,61]. In this work, sepiolite has been used as an agent to store water in order to verify its influence in promoting autogenous healing reactions.

1.1. Research significance

The delay in initiating the healing process extends concrete exposure to corrosive agents, potentially compromising its long-term durability. The diverse healing agents can contribute to varied healing capacities in concrete, depending on whether the healing process starts immediately or is delayed. This study analyses the efficiency of superabsorbent polymers, crystalline admixtures, and sepiolite in enhancing the self-healing properties of conventional and high-performance concrete. The evaluation parameters are water permeability tests to assess tightness recovery and chloride penetration resistance after healing. The research compares two healing durations and two initiation timings and considers the impact of presaturation and humidity chamber storage. This work aims to contribute to a deeper understanding of effective healing techniques by incorporating the study of self-healing agents within the same experimental program.

2. Materials and methodology

2.1. Mix designs and materials

This paper investigates two different types of concrete: conventional concrete (C30/37), denoted as OC, and High-Performance Concrete (C70/80), denoted as HPC. Additionally, enhanced versions of conventional concrete incorporating superabsorbent polymer (SAP), sepiolite, crystalline admixture (CA), and high-performance concrete containing CA were investigated.

The mix designs for OC and HPC are presented in Table 1, which includes Lafarge's CEM I 42.5 R-SR5 cement and Elkem's undensified micro-silica fume as the binder components. To achieve the targeted workability, the mixes included the Superplasticizer ViscoCrete 5970 from Sika. Additionally, each mix contained 40 kg/m^3 of steel fiber Dramix 65/35 3D from Bekaert (L=35 mm, $\Phi =$ 0.55 mm) to regulate and maintain crack opening during the pre-cracking and healing phases.

The superabsorbent polymer (SAP) employed in this study has a particle size of approximately 100 μm. It is estimated to absorb demineralized water between 200 to 500 times its own mass in water and between 10 and 30 times in the presence of salts. In this study, OC0.3 and OC0.6 denote conventional concrete mixes with 0.3% and 0.6% SAP by weight of cement, respectively. Due to SAP's water absorption, concrete mixes frequently contain additional water [28,62]. For the calculation of the additional water added to the OC mix, an absorption rate of 20 times the mass of the SAP was assumed. Therefore, in the conventional concrete, 16.8 l/m^3 of water was added in the OC0.3 mix and 33.6 l/m^3 in the OC0.6 mix to compensate for the SAP's water absorption. Regarding the mixing procedure, dry SAP and cement were introduced to the concrete mix before adding water.

In this study, sepiolite porous sand with particles ranging between 0.25 to 1.18 mm in size and a density of 0.64 gr/ml was included in the concrete mix at a 5% dosage by the weight of the cement, in replacement of the same amount of 0/4 fine aggregate. Two sepiolite conditions were investigated: dry sepiolite (OCDS) and pre-saturated sepiolite (OCSS) in which the sepiolite was saturated with an 80% water-to-dry-sepiolite-mass ratio. The pre-saturated mix was used to analyze the effect of encapsulated water as an additional water source to facilitate the internal self-healing of the concrete.

Penetron ADMIX, a crystalline admixture composed of Portland cement and active chemical formulations, was used in this study. The admixture induces a catalytic reaction in the presence of moisture and by-products of cement hydration, forming a non-soluble crystalline structure that seals microcracks against liquid penetration. In this research, the crystalline admixture was added at a dosage of 1% by weight of the binder, labeled as OC1CA and HPC1CA.

SAP and sepiolite were only studied in OC mixes since they reduce the strength of the concrete mix, and therefore, they would have only limited applications in HPC mixes.

Table 1
Mix designs of Conventional and High Performance concrete.

Material (kg / m^3)	OC	OCDS	OCSS	OC0.3	OC0.6	OC1CA	HPC	HPC1CA
Cement I 42.5 R-SR	280	280	280	280	280	280	400	400
Silica Fume							40	40
Water$_{Effective}$	185	185	185	185	185	185	170	170
Water $_{additional}$		11.2	11.2	16.8	33.6	0		0
Sand 0/2	449	449	449	449	449	449	310	310
Sand 0/4	535	495	495	535	535	495	549	549
Gravel 8/16	852	852	852	852	852	852	875	875
Dramix 65/35	40	40	40	40	40	40	40	40
Superplasticizer	2.3	3.5	3.5	3	3	2.3	3.8	4
Superabsorbent polymer				0.84	1.68			
Crystalline admixture						2.8		4.4
Sepiolite		14	14					
(w/c) $_{Effective}$	0.66	0.66	0.66	0.66	0.66	0.66	0.43	0.43
(w/c) $_{Total}$	0.66	0.70	0.70	0.72	0.78	0.66	0.43	0.43

2.2. Self-healing methodology

2.2.1. Concrete mix characterization

Each concrete mix was characterized by the slump test following EN 12350–2, fresh air content evaluation following EN 12350–7 and compressive strength at 28 days, determined by testing three 150 mm cubes following EN 12390–3.

2.2.2. Evaluation of the self-healing properties

To analyze the self-healing capabilities, procedures were based on those proposed by the COST SARCOS Interlaboratory test groups, some of which have already been published [63–65]. From each concrete mix, 8 cylindrical specimens with dimensions of ϕ100× 200 mm were prepared for each mix. After casting, the specimens were stored in a humidity chamber at 20ºC and 95% relative humidity for 28 days. The cylindrical specimens were then cut into three ϕ100× 50 mm disks using a concrete circular saw, and the two ends were discarded to ensure the uniformity and consistency of the samples (Fig. 1).

Some of these disks were pre-cracked and used to assess self-healing properties through water permeability measurements. Permeability tests were performed 28 days after curing, before the healing period, to obtain the initial reference permeability. The same test was performed in the same specimens after each healing period. Furthermore, chloride penetration experiments were carried out on completely healed specimens to assess the level of protection provided by the healed crack against chloride penetration.

2.2.3. Pre-cracking process and crack analysis

The disk specimens were pre-cracked at the age of 28 days using a splitting test to obtain a residual crack width ranging from 150 to 450 μm and were then subjected to healing under different conditions. Disks are loaded until cracks near 500 μm are formed during loading (before unloading). After unloading, the crack obtained is smaller and within the desired range. A manually-controlled hydraulic press is used to produce the cracks. During the test, once a crack is formed, the loading process is paused (the load is maintained), and the maximum crack opening is measured using a crack meter. If the crack width is lower than the target, the load is increased slowly until it reaches the target crack width. The amount of steel fibers used in the mixes allowed good control of the crack formation throughout the pre-cracking process, with a single crack formed in the center of the disks. The crack width was measured immediately after pre-cracking. Disks with crack openings exceeding this range were excluded from this investigation.

A YINAMA wireless optical microscope with 50–1000X magnification and a 2-megapixel camera was used to capture images of the cracks before healing. The crack width was measured at three points spaced 2.5 cm apart along the crack on each surface to obtain an average crack width for each disk. In a few cases where multiple cracks exist at a point, the total crack size was considered, and if the point had a surface pore, the crack size was measured at the nearest point, bypassing the pore.

At least 6 specimens for each mix and healing condition have been tested using the water permeability and chloride penetration analyses. Further details of the tests are included in the next subsections.

Additionally, several reference disks were analyzed. On the one hand, four uncracked reference disks (labeled R) were tested in each mix in order to add more insights to the results of the chloride penetration test. These disks were stored in a humidity chamber for 84 days, and their chloride penetration was assessed at the same moment when the chloride penetration test was done in the main series of pre-cracked and healed disks. On the other hand, in the series without healing agents and the mixes containing CA, four pre-cracked reference disks (labeled PR) were also studied at the same age as the main series of pre-cracked and healed disks. The objective is to analyze different trends in the penetration produced in different areas due to healing or maturing; therefore, only the mixes with clear results were selected. In total, at least 26 disks have been tested per mix (more than 200 disks in total).

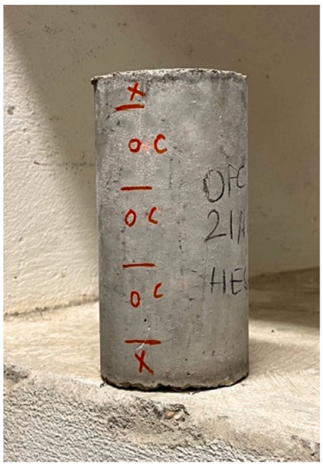

Fig. 1. Cylinder marks before cutting the disks.

2.2.4. Low-pressure water permeability test

The water permeability test setup is depicted in Fig. 2. The test procedures were based on previous studies and Sarcos COST Action Interlaboratory studies [64,66,67]. The lateral surfaces of pre-cracked disks were sealed with resin (Sikaflex 11 FC) to avoid the leakage of water. PVC tubes of 100 mm of internal diameter and with a height of 250 mm were glued on the disks using the same resin. The bottom crack of the disks was sealed with PVC tape to prevent water leakage before the test. The tubes were then filled with a 200 mm water column, and the initial water level was recorded before removing the bottom tape to initiate the test (time 0). The reduction in water head was measured after 30 min to determine the water flow in 30 min (ml/30 min). Permeability tests were performed before and after each healing period. Normalized initial water flow was calculated to compare its relation with the initial crack width using Eq. 1. The effect of healing on permeability was assessed by calculating a Healing Ratio using Eq. 2:

$$Normalized \quad water \quad flow = \frac{Flow \quad in 30\,\mathrm{min} before \quad healing}{Initial \quad water \quad volume} \times 100 \tag{1}$$

$$Healing \quad Ratio = 1 - \frac{Flow \quad in 30\,\mathrm{min} after \quad healing}{Flow \quad in 30\,\mathrm{min} before \quad healing} \tag{2}$$

2.2.5. Modified chloride penetration test

The present study employed a modified water penetration test as suggested in previous research [67,68] to evaluate the extent of chloride penetration through concrete surfaces and crack pathways. The penetration was quantified by measuring the extent of silver nitrate pigmentation.

The penetration of chlorides through water across fully or partially healed cracks was evaluated using the same disks and tubes utilized for the low-pressure water permeability test. After the final water permeability test, the bottom crack of the pre-cracked disks was sealed with Sikaflex 11 FC to prevent water leakage. Subsequently, the samples were placed in the test setup with tubes filled with water with a 33 g NaCl/liter solution (height of 250 mm), and the solution was kept in the tubes for three days. After removing the tubes and resin, the samples were cut perpendicular to the crack direction the following day (Fig. 3). The cutting procedure used dry cutting to prevent contamination [69]. The cut samples were pigmented using a 0.1 mol/liter $AgNO_3$ solution, and digital photographs of the penetration patterns were taken. The penetration pattern was quantified based on two parameters (Fig. 3): the penetration through the crack (W) and the penetration depth through the matrix in contact with the chloride solution (P_0). Four locations were measured to quantify P_0, at 2 cm intervals, beginning 1 cm from the surface. Three locations were measured to quantify W, keeping a 2 cm distance from the surface to avoid matrix and crack penetration overlaps. The representative value of each disk was determined using a total of 8 P_0 values and 6 W values.

2.3. Healing conditions

2.3.1. Effect of concrete age at healing start time and healing duration

Previous research has shown that storage in high humidity chamber conditions do not activate the healing reaction [40]. In this study, a humidity chamber was used as a storage that does not promote healing reactions and water immersion was used as the evaluated healing condition.

To investigate the impact of different starting times of the self-healing process, a set of disks initiated the self-healing process under water immersion immediately after pre-cracking when concrete age was 28 days, while another set was placed under water immersion after being stored for 28 additional days in a humidity chamber. In both cases, to examine the effects of self-healing duration on water permeability, the pre-cracked disks were tested after 28 and 56 days of water immersion. The chloride penetration test was performed only after healing for 56 days in water immersion since it is a destructive test. The labels used for these four series are 28WI, 56WI,

Fig. 2. Water permeability test setup.

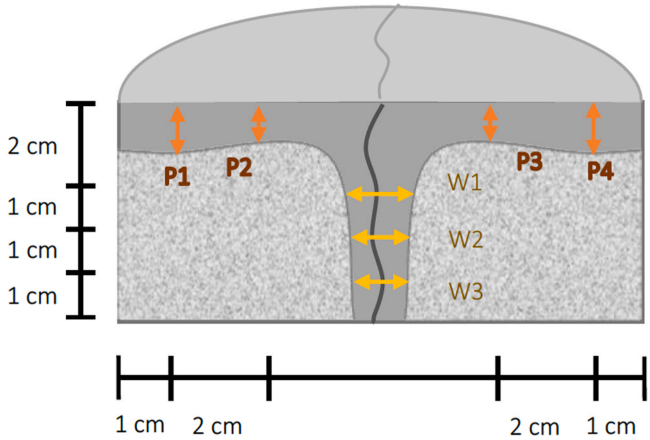

Fig. 3. Diagram of a sawed disk and measurement points for the penetration of chlorides through the matrix (P1, P2, P3, and P4) and through the crack (W1, W2, and W3).

28HC28WI, and 28HC56WI and refer to the exposition and time that experienced the disks, where WI means Water Immersion and HC Humidity Chamber. The process and series labels are included in Fig. 4.

The tubes attached to the disks for the water permeability test were left intact during the healing process until the chloride penetration tests were conducted. To avoid cross-contamination between the different series of samples, each set of disks containing a particular type of agent was placed in separate tanks for healing under immersion conditions.

2.3.2. Effect of presaturation

This study also investigated the effectiveness of a short presaturation period (1 day) under water immersion, followed by 27 days of storage in a controlled high-humidity environment (RH=95%, 20 °C), as a means of promoting healing by maintaining the saturation level of the matrix. This analysis focused specifically on the OC series with SAP and sepiolite (and the reference mix). Due to the low performance observed, the evaluation was limited to assessing water permeability.

3. Experimental results and discussion

3.1. Characterization tests

Table 2 summarizes the results of the slump test and entrapped air content for all series tested. The lower workability of OC mixes with 0.3 and 0.6 SAP was compensated using slightly higher superplasticizer content, resulting in a similar slump value as the OC mix, around 21–23 cm. However, the OC mix's workability was decreased to 6, 18, and 13 cm in the mixes that contained dry sepiolite (OCDS), saturated sepiolite (OCSS), and crystalline admixture, respectively. HPC-based mix is a dryer mix (with a slump test value of 8 cm); therefore, higher content of superplasticizer was used if compared with OC mixes. The HPC1CA mix had only slightly higher

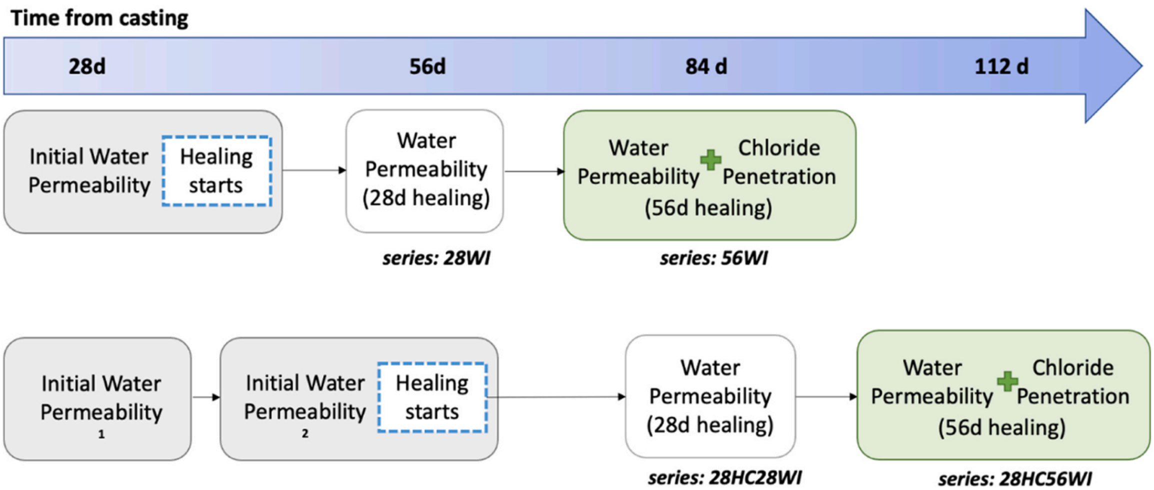

Fig. 4. Diagram showing the healing steps and conditions.

Table 2
Slump value and the percentage of entrapped air in the series tested.

Test \ Mix		OC	OCDS	OCSS	OC0.3	OC0.6	OC1CA	HPC	HPC1CA
Slump value (cm)		21	6	18	23	21	13	8	14
Entrapped air (%)		1.1	1.3	0.4	1.4	1.3	1.8	0.8	1.3
$f_{cm,28d}$ (MPa)	**avg.**	40.8	38.8	37.5	38.3	30.9	39.3	84.0	74.8
	std. dev	*0.78*	*0.50*	*0.80*	*0.49*	*0.07*	*1.40*	*3.92*	*1.88*

superplasticizer content but was more workable than its reference mix, reaching a 14 cm slump.

Table 2 presents the compressive strength values at 28 days for each mix tested. The reference OC mix had an average compressive strength of 40.84 MPa. The addition of CA, sepiolite, and 0.3 SAP resulted in a decrease in compressive strength of less than 9%. The OC0.6 mix exhibited the lowest strength, with 30.08 MPa. On the other hand, the HPC reference mix had an average compressive strength of 84.03 MPa. The compressive strength of the HPC1CA mix was 11% lower than the reference mix.

3.2. *Self-healing by means of water permeability*

3.2.1. *Initial water permeability vs. initial crack width*

The average crack widths obtained for each OC and HPC series are presented in Table 3. The average crack width for OC specimens ranges from 190 to 280 μm, while for HPC specimens, it ranges from 150 to 210 μm. The dispersion of crack widths can be observed in both the graphs depicting normalized initial water flow versus initial crack width (Fig. 5), and the healing graphs since the properties analyzed in this study are plotted against the crack width of the specimen in the horizontal axis, highlighting the variation across the different series.

The normalized initial crack width values were compared with the initial normalized water flow percentage in 30 min. This value represents the total volume of water that has passed through the unhealed crack in 30 min, based on the initial volume of water. A concentrated distribution of data points across all the tested series can be seen in Fig. 5. In the HPC series, narrower initial crack widths correspond to higher values of initial water flow when compared to the OC series. This observation can be attributed to the lower tortuosity of the crack in HPC mixes, resulting from the higher strength of the matrix [67,70,71].

3.2.2. *Effects of age of concrete at healing start time and healing duration*

Fig. 6 and Fig. 7 present the results of the water permeability test using the Healing ratio (Eq. 2) separated into rows according to the duration of the water immersion period. The effectiveness of the healing agent can be visually assessed for each healing condition.

Each column of Fig. 6 and Fig. 7, shows the results of the same disks at different stages of healing. Subsequently, the water permeability test results for specimens subjected to 28WI and 56WI and the chloride penetration results for specimens subjected to 56WI are obtained from the same disks. Additionally, the water permeability test results for specimens subjected to 28HC+ 28WI and 28WI+ 56WI and the chloride penetration results for specimens subjected to 28HC+ 56WI also show the results of the same disks healed during different durations.

As expected, all the series tested show decreasing trends of healing ratio as the initial crack width increases.

In the case of OC specimens (without healing admixtures) that started healing at the age of 28 days and healed for 28 days, healing ratios ranged from 60–80% for cracks below 250 μm. However, the healing ratio dropped to 0–30% for cracks around 400 μm. OC specimens that had delayed the start of healing with a duration of 28 days experienced an increase in healing efficiency, with healing ratios ranging from 40 to 85% for cracks up to 400 μm.

Compared to the reference series (OC), specimens with SAPs (OC0.3 and OC0.6) had significantly improved healing when the healing started at 28 days and lasted for 28 days. In that case, the OC0.3 series achieved healing ratios of over 60%, and the OC0.6 series achieved healing ratios of over 90% for cracks below 350 μm. Extending the healing duration to 56 days further increased the healing ratios, with values consistently above 80% for the OC0.3 series and nearly complete healing (over 95%) for the OC0.6 series for cracks below 350 μm. However, when the healing start was delayed, the results were inferior to those of the reference mix, with healing ratios ranging from 40–80% for 28 days and only 10–50% for 56 days of healing in cracks close to 350 μm.

Specimens incorporating crystalline admixtures (OC1CA) exhibited similar results to SAP mixes when the healing began at 28 days, albeit with slightly lower improvements. Crystalline admixture specimens also show enhancement of healing when the healing start was delayed, in contrast to the SAP mixes.

Table 3
Average crack width of the mixes allocated to their healing conditions.

Condition	Crack width (μm)	OC mixes						HPC mixes	
		OC	OC0.3	OC0.6	OCDS	OCSS	OC1CA	HPC	HPC1CA
28WI	**avg.**	279.4	220.8	223.4	215.4	223.8	191.8	208.0	171.4
	std. dev	*95.8*	*52.7*	*29.6*	*61.6*	*81.8*	*46.7*	*72.0*	*59.1*
28HC28WI	**avg.**	254.2	262.5	252.8	244.6	235.3	189.3	153.0	180.4
	std. dev	*51.3*	*83.4*	*51.9*	*75.2*	*84.9*	*37.5*	*42.0*	*56.0*

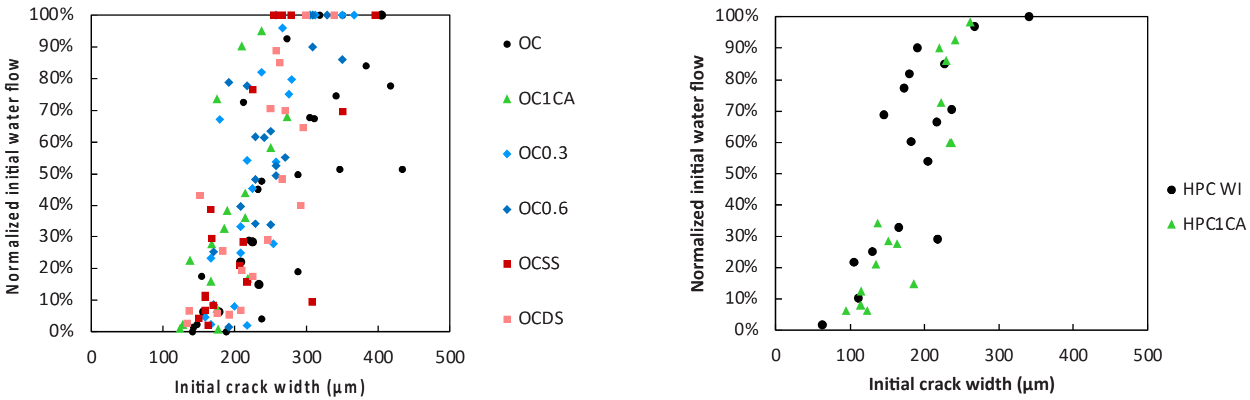

Fig. 5. Initial normalized water flow vs. initial crack width for all the mixes tested.

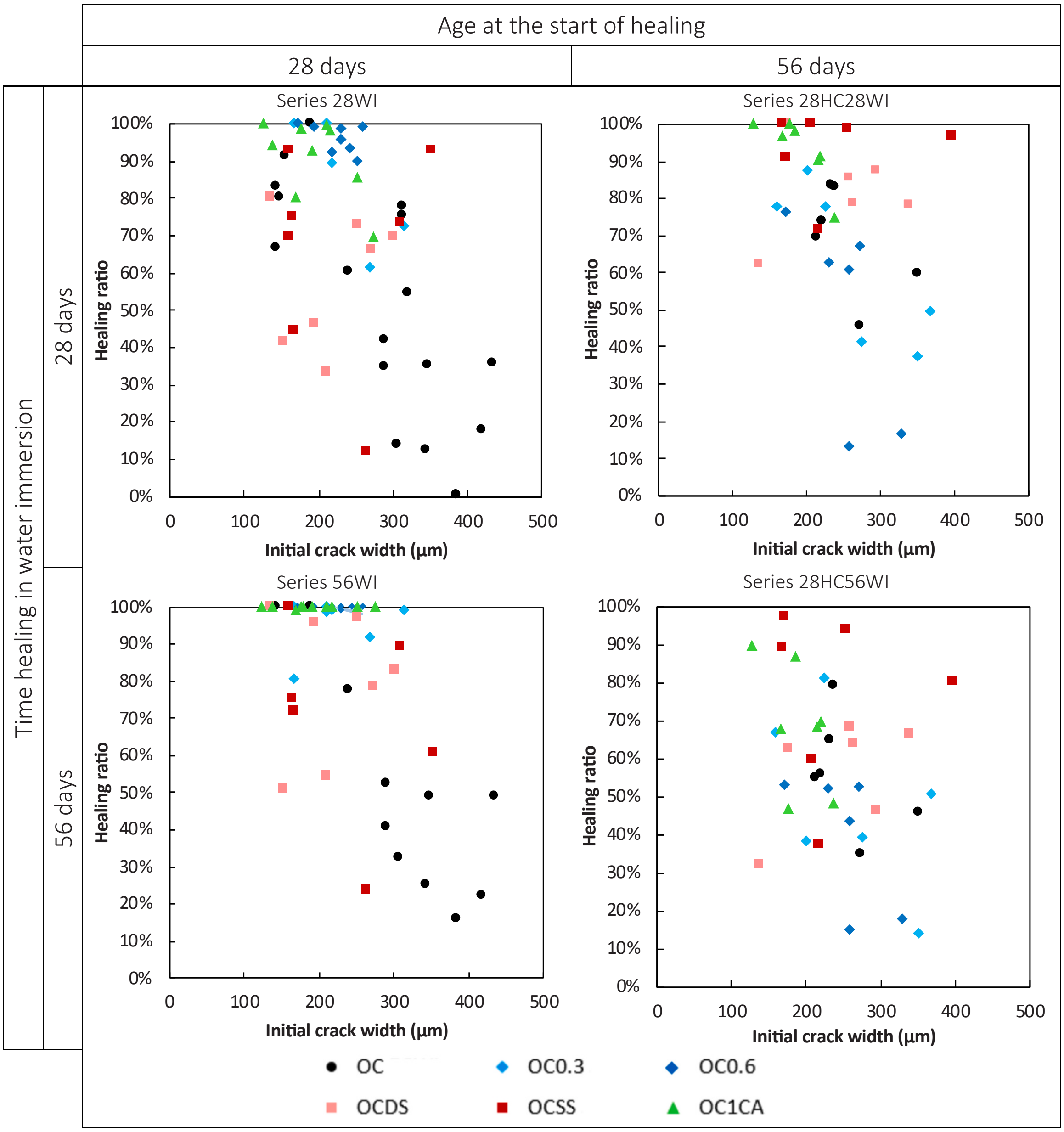

Fig. 6. Healing ratio of OC mixes depending on initial crack width.

Regarding the use of sepiolite in dry conditions (OCDS) or saturated conditions (OCSS), these series exhibited a response similar to the reference mix (OC) when the healing started at 28 days, with high dispersion. However, a benefit was observed when the healing start time was delayed, particularly in OCSS specimens, which displayed the highest healing ratios. Specifically, in the series 28HC56WI conditions, OCSS specimens achieved healing ratios of 80–100% for cracks around 350 μm, with a decreasing but dispersed trend for larger cracks.

Fig. 7 shows the healing ratios obtained for the HPC mixes. The healing ratio values for the reference HPC mix (without healing admixtures) were similar to the OC mix. However, a significant decrease in the healing ratio was observed when healing was delayed, with values between 0% and 45% for cracks below 200 μm after 28 days of healing. Extending the healing duration to 56 days improved these values, but only high healing ratios (over 70%) were achieved for very narrow cracks (around 100 μm), while wider cracks exhibited low healing ratios.

Adding crystalline admixture to the HPC mix (series HPC1CA) improved healing ratios, especially for delayed healing. The healing ratio of the HPC1CA samples with delayed healing exhibited values exceeding 60% and 80% for cracks of less than 300 μm, following a healing period of 28 days and 56 days, respectively. In contrast, reference samples' healing ratios were less than 40% for the same crack width. However, HPC series with healing starting at the age of 28 days did not show a clear enhancement from adding the CA

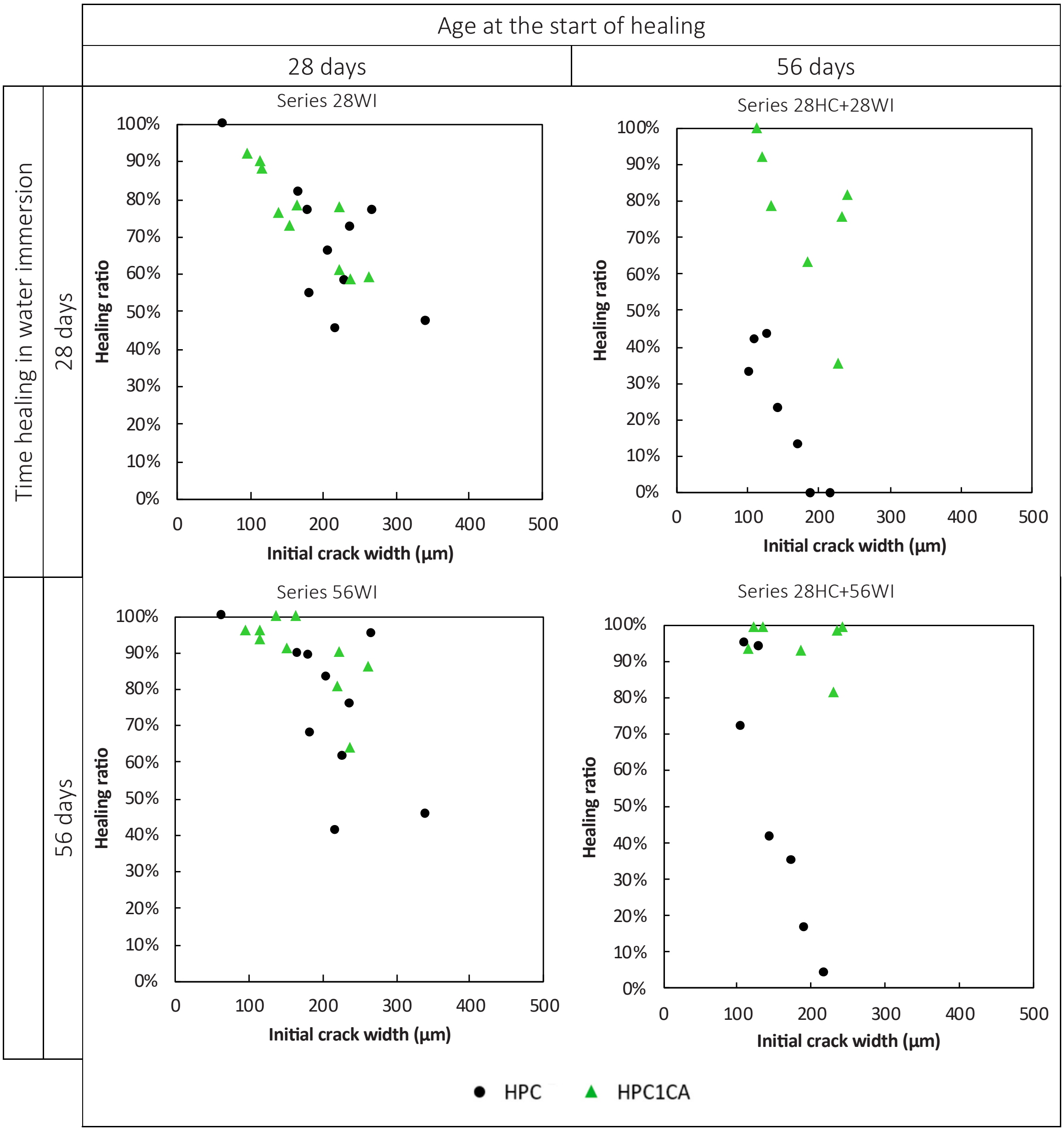

Fig. 7. Healing ratio of HPC mixes depending on initial crack width.

agent.

3.2.3. Effects of presaturation in SAP and sepiolite specimens

OC specimens that were saturated during water immersion for one day and subsequently healed in a humidity chamber showed a healing ratio of zero even when incorporating SAP or sepiolite, as displayed in Fig. 8. This result clearly indicates the insufficiency of high humidity conditions to initiate healing processes, even when incorporating these admixtures.

3.3. Self-healing through chloride penetration

3.3.1. Chloride penetration through the crack and the matrix

Results of the crack width and penetration through the crack (W) in all studied groups are shown in Table 4. Fig. 9 and Fig. 10 show chloride penetration through crack walls (W) and the matrix (P_0) depending on the mix and healing conditions. Each graph represents the average results of W along the width and P_0 along the height of the graph, mirroring their visual positions on the actual pigmented disk after the chloride penetration test.

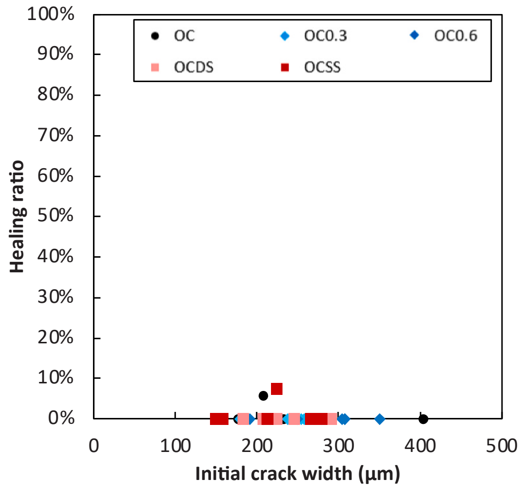

Fig. 8. Healing ratio of OC mixes after presaturation.

Table 4
Values of penetration through the crack (W) in all the groups studied.

		OC	OC0.3	OC0.6	OCDS	OCSS	OC1CA	HPC	HPC1CA
WI	Avg. Crack width (µm)	279	221	223	215	224	192	208	171
	std. dev	*95.8*	*52.8*	*29.6*	*61.7*	*81.8*	*46.7*	*72.0*	*59.1*
	W (mm)	10.0	2.5	2.7	8.8	17.5	2.9	9.5	1.5
	std. dev	*7.3*	*6.1*	*4.5*	*6.4*	*3.2*	*4.0*	*5.2*	*2.3*
HC+WI	Avg. Crack width (µm)	254	262	253	245	235	189	153	180
	std. dev	51.3	83.5	52.0	75.2	84.9	37.6	42.0	56.0
	W (mm)	13.6	17.6	18.8	11.9	10.5	8.0	3.0	2.5
	std. dev	*1.4*	*4.7*	*4.3*	*5.4*	*6.4*	*7.7*	*2.1*	*3.9*

The results from the reference mixes, OC and HPC, indicate that OC specimens have greater chloride penetration (W and P_0) than HPC specimens after healing, which aligns with the expected performance due to the better quality of the HPC matrix. Due to the almost complete healing of pre-cracked OC and HPC samples under all healing conditions, their matrix penetration was lower than 3 mm. However, those containing CA showed a higher ability to reduce chloride penetration.

Regarding OC mixes (Fig. 9), the 56WI series, in which healing starts at the age of 28 days and lasts for 56 days in water immersion, show that the mixes containing SAP and CA (OC0.3, OC0.6, and OC1CA) exhibit reduced penetration of chloride (W and P_0) than the reference mix. The values for these parameters are consistently below 3 mm on average for the two parameters. Conversely, the mix incorporating saturated sepiolite (OCSS) shows increased chloride penetration compared to the reference OC mix, while the mix with dry sepiolite (OCDS) has results similar to the reference OC, lower than 10 mm in the W parameter. In the case of delayed healing (series 28HC56WI), all series experienced increased penetration, and the benefit from using SAP disappeared. In this case, the mixture with crystalline admixture (OC1CA) demonstrates the lowest W and P_0 penetration, with values below 10 and 1 mm, respectively. Specimens containing sepiolite may also reduce chloride penetration slightly under delayed healing.

Chloride permeability after healing has reduced in the same cases in which self-healing improved. This suggests that the self-healing reaction produces these improvements. Specifically, OC specimens with SAP when the healing started at 28 days and lasted for 28 and 56 days (28WI and 56WI) exhibit > 80% healing for disks with initial cracks up to 300 µm. In that case, the chloride penetration after healing was less than 5 mm.

Regarding HPC mixes (Fig. 10), the 56WI series, in which healing starts at the age of 28 days and lasts for 56 days in water immersion, show that the mixes containing CA (HPC1CA) exhibit reduced penetration of chloride (W and P_0) compared to the reference HPC mix. These parameters have constant values of 0.5 mm for P0, and 1.5 mm for W in HPC1CA. In the case of delayed healing in HPC mixes, the two series show comparable results, with P_0 lower than 1 mm and W values in all cases below 3 mm.

3.3.2. Reference samples for chloride penetration

The chloride penetration of two types of reference disks were evaluated, one type were uncracked disks (R) and the second were cracked disks (PR). The average values of chloride penetration through the matrix (P_0) were obtained from R and PR samples of each group. Additionally, the penetration through the crack (W) was obtained in PR samples of each group.

The results of P_0 for all the series are shown in Table 5. In uncracked specimens, the OCSS mix had the highest penetration through the matrix in uncracked specimens with an average of 8.72 mm, followed by OC0.3, OCDS, OC0.6, OC1CA, and OC with 6 ± 1 mm. Due to the dense matrix of HPC, in the mixes of this group less than 2 mm of average matrix penetration was obtained in all uncracked

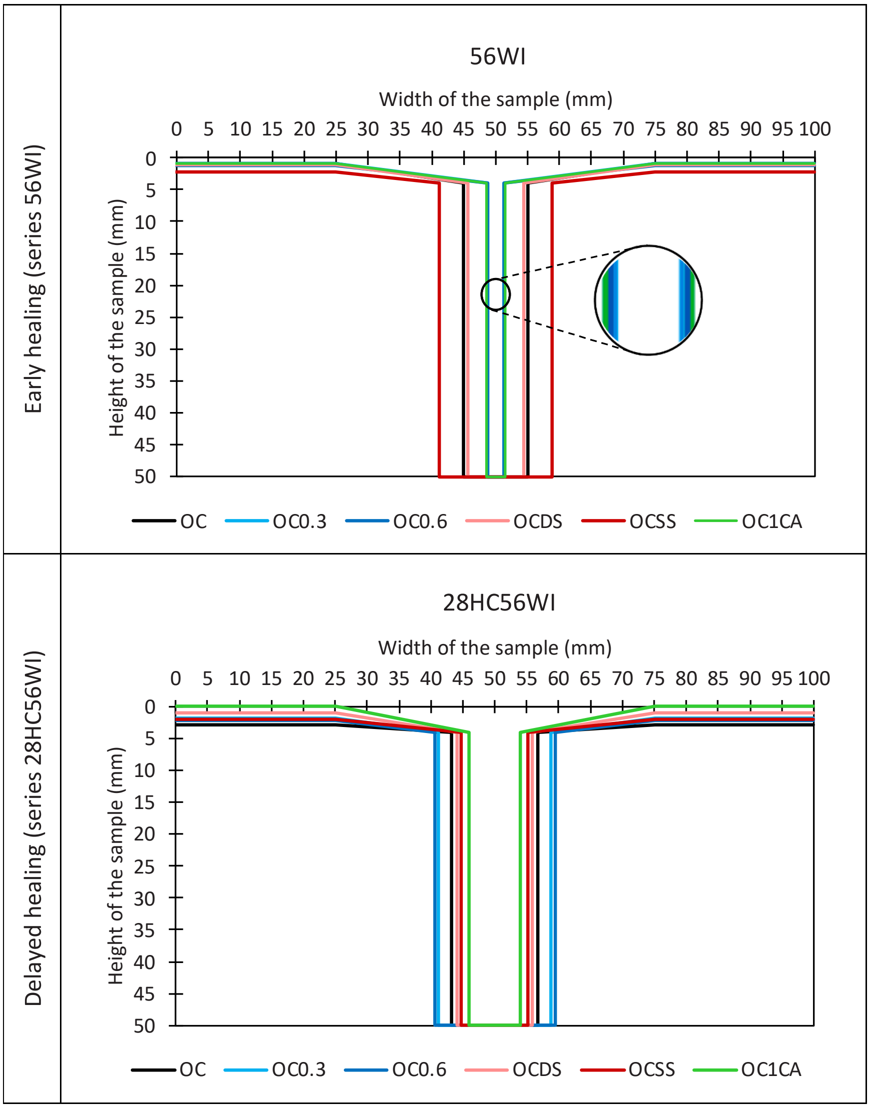

Fig. 9. Chloride penetration profile of OC mixes along the crack (W) and P_0 along depth after healing, depending on their healing condition.

specimens. Comparing the obtained findings of PR and R samples, penetration through the matrix P_0 in Table 5, it can be concluded that the values are similar for both series.

The chloride penetration through the crack (W) obtained in the PR samples (Table 6) is consistent across all groups, with values of 15 ± 1 mm in OC and 4 ± 1 mm in HPC, despite variations in the crack width range. This finding suggests that the penetration depth in the unhealed crack is not influenced by the crack width. It should be highlighted that the ratio of W/P_0 for PR samples is close to 2 ± 1. This indicates that the measurement of W in the PR samples can be regarded as a representation of the combined penetration depth (P_0) on both sides of the crack, which is consistent with previous studies [67].

Due to the destructive aspect of the chloride penetration test, getting a representative reference sample is challenging. In prior research [68,72], the chloride penetration of healed samples was compared by utilizing uncracked samples stored in the same humidity chamber as the healed samples of the same age. Since these samples were not cracked, the acquired results would provide information only about the matrix penetration. Introducing PR samples as cracked reference samples of the same age as the healed samples will provide information on matrix penetration and penetration through cracks.

Excluding OCSS samples, most OC mixes with a healing agent had negligible matrix penetration (P_0) after healing, indicating the influence of the healing agents in the matrix's densification and potentially the surface's healing processes, as shown in previous research [67]. The effect of the healing agents in the matrix's densification adds further complexity in evaluating their self-healing performance enhancement.

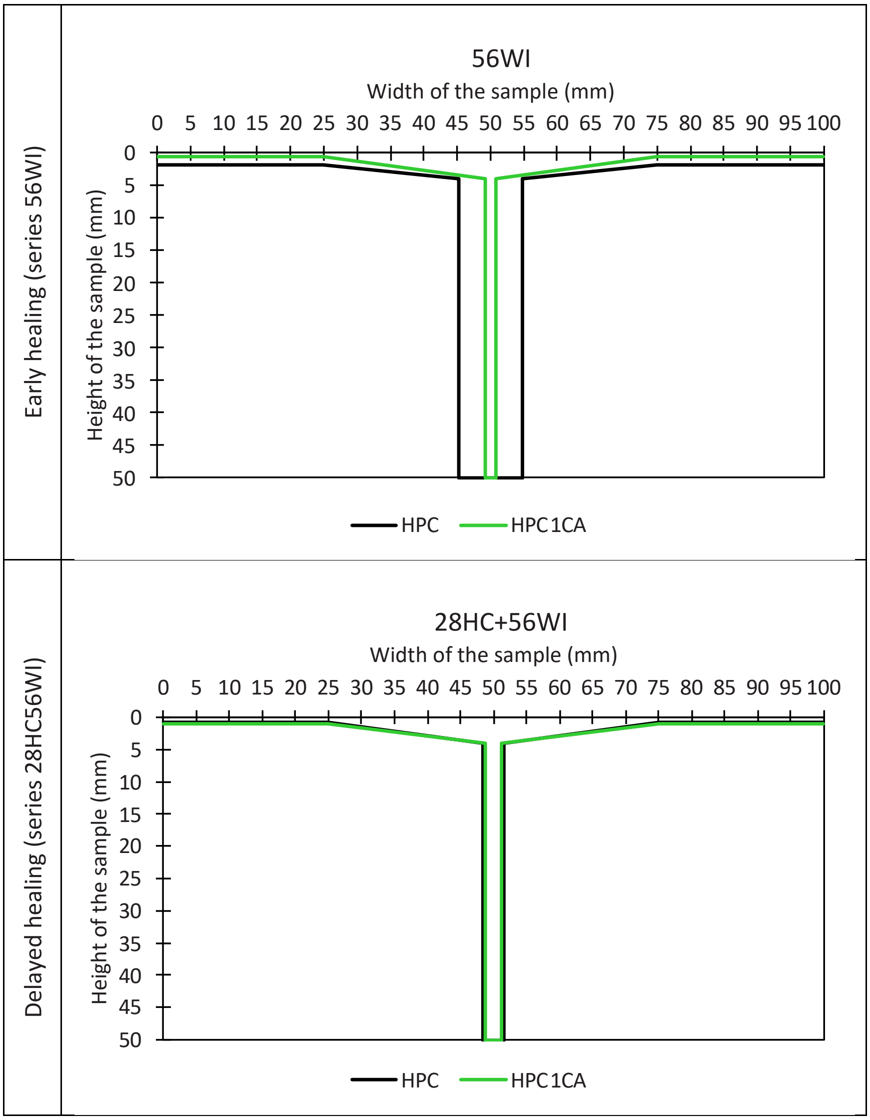

Fig. 10. Chloride penetration profile of HPC mixes along the crack (W) and P_0 along depth after healing, depending on their healing condition.

Table 5
Values of penetration through the matrix (P_0) in all the groups studied.

	P_0 (mm)	OC	OC0.3	OC0.6	OCDS	OCSS	OC1CA	HPC	HPC1CA
WI	avg.	0.88	0.94	1.19	1.09	2.22	0.82	1.76	0.52
	std. dev	*1.23*	*0.65*	*0.69*	*0.98*	*1.61*	*0.98*	*1.60*	*0.87*
HC+WI	avg.	2.81	1.75	2.22	0.99	1.97	0.00	0.91	1.06
	std. dev	*1.86*	*0.56*	*0.82*	*1.16*	*1.51*	*0.00*	*0.55*	*0.70*
R	avg.	4.73	6.82	5.76	6.09	8.72	5.29	1.87	1.11
	std. dev	*1.64*	*1.47*	*1.64*	*0.95*	*1.21*	*1.05*	*0.54*	*0.21*
PR	avg.	5,78					6.07	1.81	1.73
	std. dev	*2.97*					*0.63*	*0.84*	*0.55*

3.4. Discussion on the effectiveness of the healing process in the studied mixes

This study analyzed the self-healing effectiveness provided by the studied healing agents under different healing conditions and in two concrete qualities, a conventional (OC) and a high-performance concrete (HPC), measured by means of water permeability and through the evaluation of the protection to chloride penetration in the healed or partially healed elements.

Table 6
Values of the penetration through crack W of cracked reference samples (PR) with their crack width.

		OC	OC1CA	HPC	HPC1CA
Crack width (μm)	**avg.**	283.33	124.63	121.11	49.375
	std. dev	*100.51*	*69.93*	*27.75*	*15.09*
W (mm)	**avg.**	15.59	15.73	3.84	3.86
	std. dev	*1.13*	*3.08*	*2.37*	*1.07*

Permeability in uncracked concrete measures the capability of water to penetrate inside the concrete matrix [73]. In cracked specimens, the fluid flow passing through the sample at a determined pressure can be measured using test methods similar to those for porous materials, such as soil mechanics. Water permeability results in cracked specimens being conditioned by the crack rather than the properties of the matrix. In the case of chloride penetration measured with the test used in this study, chlorides can penetrate inside concrete through capillary sorption, permeability, and diffusion. To gain a deeper understanding of the process, two parameters were studied, namely P_0, which measured the penetration through the matrix, and W, which measured the penetration through the crack area. Although both parameters convey similar information regarding enhancements in chloride penetration protection, further studies are recommended to clarify their specific influences. The results also indicate that if self-healing improves when measured by water permeability tests, it also shows an improvement in the protection against chloride penetration.

The values of the average crack width and healing ratios (measured by water permeability) for each healing interval of each mix are presented in Table 7, where an improvement of more than 10% compared to the reference mix has been indicated with an upwards arrow, worsening larger than 10% with a downward arrow, and similar results with an almost equal symbol.

Observing the OC reference samples, regardless of the healing initiation time and duration, the healing ratios are between 50–60%. However, HPC samples with healing initiation at 28 days obtained higher healing than those with delayed healing. The main cause producing autogenous healing in HPC, which has a low water-to-cement ratio, is considered to be the hydration of the unhydrated cement grains on cracked surfaces [74]. The new crystals' stiffness has been reported to be comparable to the original calcium silicate-hydrates [32,75], and therefore, it could be an efficient healing mechanism. Autogenous healing by further hydration will happen more readily in younger materials because they have a higher content of unhydrated particles, which is consistent with the results obtained in this study.

OC specimens with SAP when healing started at 28 days and lasted for 28 and 56 days (28WI and 56WI) exhibit > 80% healing for disks with initial cracks up to 300 μm. In that case, the chloride penetration after healing was less than 5 mm. The enhancement detected for early healing is compatible with the findings reported in references [54,55], where it was observed that the initial absorption of SAP particles leads to the release of water, facilitating additional hydration and ensuring the maintenance of relative humidity during the hardening process. Nevertheless, when there is a delay in the healing process (specifically, in 28HC+28WI and 28HC+56WI series), the effectiveness of healing is observed to be lower than in the reference mixture. In accordance with the results mentioned in [76], sealing the inner crack area through physical blocking by swollen SAP may hinder further healing during subsequent healing periods. Additionally, the presence of pores generated by the SAP particles will increase the concrete's permeability [76], which could affect the higher penetration to chlorides measured under the late healing conditions. However, this point would need verification from further studies. Additionally, SAPs in the OC mixture studied did not promote healing reactions in high humidity conditions, even when a presaturation period is implemented. This finding aligns with the conclusions presented in another study [76], which indicate that the self-healing capacity of SAP was diminished when there is inadequate exposure to external water following the hardening process.

The series containing sepiolite had similar or higher healing effectiveness with delayed healing (28HC+28WI and 28HC+56WI), especially those with saturated sepiolite, which had nearly complete healing. This could be produced by sepiolite's high surface area and microporosity, which can potentially encapsulate water that would be slowly released, as mentioned in several studies [13,21,77].

Crystalline admixtures in OC and HPC mixes exhibited enhanced healing when the healing began at 28 days, and when the healing start was delayed. In the case of chloride penetration, regardless of the initiation time of healing, OC and HPC samples with CA had the lowest chloride penetration. This could probably be due to the rapid formation of water-insoluble, pore/crack-blocking deposits and integration into the matrix by CA following contact with water, which contributes to the increased density of Calcium Silicate Hydrate (CSH) and its resistance to water penetration [23,38]. The incorporation of CA in HPC had considerable effects on the HPC mix, consistent with the conclusion of the study [1], which indicated that CA performance is significantly impacted by mix design.

4. Conclusions

The effect of healing start time and duration on the self-healing capability of over 200 specimens of OC and HPC incorporating SAP, CA, and sepiolite was determined by measuring water permeability and chloride permeability. The following conclusions can be drawn:

1. In general, delayed healing reduced the healing capability compared to healing starting at 28 days, especially for the HPC mixes. Extending the healing duration from 28 to 56 days improved healing in all the cases, including in delayed healing groups, especially for narrow cracks (around 100 μm). Chloride permeability after healing improved in the same cases in which self-healing improved as measured by the water permeability test.

Table 7
Values of the average crack width and healing ratio ↑ indicate > 10% benefit, ↓ a worsening > 10%, and ≈ indicate similar results compared to the average healing ratio in the reference mix.

			OC		OC0.3		OC0.6		OCDS		OCSS		OC1CA	
Start healing at (days)	**healing time (days)**	**Code**	**Crack width (μm)**	**Avg. healing**	**Crack width (μm)**	**Avg. healing**	**Crack width (μm)**	**Avg. healing**	**Crack width (μm)**	**Avg. healing**	**Crack width (μm)**	**Avg. healing**	**Crack width (μm)**	**Avg. healing**
28	**28**	**28WI**	279	52.0%	221	89.1% ↑	223	96.1% ↑	215	58.7% ≈	224	65.8% ↑	192	91.0% ↑
		Std. dev	*95.8*	*30.5%*	*52.8*	*15.8%*	*29.6*	*3.8%*	*61.7*	*18.0%*	*81.8*	*28.7%*	*46.7*	*10.5%*
56		**28HC28WI**	254	55.9%	263	48.2% ≈	253	38.8% ↓	245	56.4% ≈	235	76.2% ↑	189	68.1% ↑
		Std. dev	*51.3*	*15.20%*	*83.5*	*23.57%*	*52.0*	*17.90%*	*75.2*	*14.40%*	*84.9*	*23.35%*	*37.6*	*16.67%*
28	**56**	**56WI**	279	51.3%	221	95.5% ↑	223	99.9% ↑	215	80.0% ↑	224	74.4% ↑	192	99.9% ↑
		Std. dev	*95.8*	*29.48%*	*52.8*	*3.01%*	*29.6*	*0.26%*	*61.7*	*20.16%*	*81.8*	*26.72%*	*46.7*	*0.28%*
56		**28HC56WI**	254	69.4%	263	62.0% ≈	253	49.5% ↑	245	81.9% ↑	235	93.1% ↑	189	93.2% ↑
		Std. dev	*51.3*	*14.70%*	*83.5*	*21.70%*	*52.0*	*27.35%*	*75.2*	*12.60%*	*84.9*	*11.03%*	*37.6*	*8.86%*

			HPC		HPC1CA	
Start healing at (days)	**healing time (days)**	**Code**	**Crack width (μm)**	**Avg. healing**	**Crack width (μm)**	**Avg. healing**
28	**28**	**28WI**	208	68.1%	171	75.7% ↑
		Std. dev	*72.0*	*16.98%*	*59.1*	*12.63%*
56		**28HC28WI**	153	22.1%	180	75.3% ↑
		Std. dev	*42.0*	*18.40%*	*56.0*	*21.15%*
28	**56**	**56WI**	208	74.9%	171	89.7% ↑
		Std. dev	*72.0*	*20.40%*	*59.1*	*10.92%*
56		**28HC56WI**	153	51.5%	180	95.4% ↑
		Std. dev	*42.0*	*36.33%*	*59.1*	*6.68%*

2. OC specimens containing SAP yielded the highest healing ratios at early healing with 28- and 56-day durations. If healing is delayed, the healing ratios of OC specimens with SAP were lower than in the reference mix.
3. OC specimens with dry and saturated sepiolite showed enhancement of healing for delayed cracks (healing starts 28 days after cracking), but no enhancements were detected if healing started immediately after cracking. In delayed healing, sepiolite specimens with 200 μm cracks had 90-100% healing ratios when incorporated in saturated conditions (OCSS). On the other hand, OCSS specimens experienced greater chloride penetration after early healing than the reference OC mix, while OCDS has W values like the reference OC mix. Therefore, sepiolite may minimize chloride penetration, but only in some conditions with delayed healing.
4. CA significantly improved healing in OC and HPC specimens in early and delayed healing conditions. In addition, OC1CA and HPC1CA had the lowest chloride penetration (W and P_0), both below 3 mm, regardless of healing initiation time.
5. The healing condition of one day of presaturation in water immersion and 27 days of storage in a high humidity condition could not promote healing reactions even when SAP or sepiolite agents were included.

CRediT authorship contribution statement

Formagini Sidiclei: Conceptualization, Methodology, Validation. **Doostkami Hesam:** Conceptualization, Data curation, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Roig-Flores Marta:** Methodology, Supervision, Validation, Writing – review & editing. **Serna Pedro:** Methodology, Resources, Supervision, Validation, Writing – review & editing.

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.

Data availability

Data will be made available on request.

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