



Crystalline Admixture as Healing Promoter in Concrete Exposed to Chloride-Rich Environments: Experimental Study

Estefanía Cuenca¹; Stefano Rigamonti²; Enricomaria Gastaldo Brac³; and Liberato Ferrara⁴

Abstract: The requirements on service life of reinforced concrete structures, as prescribed by design codes, may be difficult to be fulfilled in highly aggressive environments such as marine ones, in which premature degradation is most likely to occur. In the aforementioned situations, to avoid expensive repair activities, different protective systems, including, among the others, self-healing concrete, could be adopted. Researchers have found *self-healing* as a way to face degradation problems in chloride-rich environments. If a significant degree of crack sealing can be achieved, the physical properties of a cracked element can trend back to those of an identical uncracked element, which may also result in a slower penetration rate of aggressive substances. The main problem in exploiting this methodology is related to its reliability. In this context, an experimental program aimed at investigating the effectiveness of crystalline admixtures as healing stimulating agent in chloride-rich environments was carried out. The influence of the exposure conditions on the compressive strength development and on its recovery in predamaged specimens was first analyzed. Afterwards, crack sealing and chloride permeability of sealed cracks were evaluated for specimens continuously immersed or subjected to wet/dry cycles in a 16.5% NaCl aqueous solution. Both an enhanced recovery of compressive strength and an improved crack sealing ability were observed for samples containing the healing agent. A microstructure study of the healing products was conducted by means of scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis as well. DOI: 10.1061/(ASCE)MT.1943-5533.0003604. This work is made available under the terms of the Creative Commons Attribution 4.0 International license, <https://creativecommons.org/licenses/by/4.0/>.

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Introduction

During the last years, the civil and building engineering community has been paying increasing attention to the concept of sustainability, specifically to the repair and conservation of reinforced concrete structures (Dossche et al. 2016) to guarantee their strength and durability. Cracks, which naturally form in reinforced concrete structural elements, because of the inherently weak tensile strength of concrete, create an entry path for aggressive agents (e.g., chlorides) which could compromise the durability of the structure (Wu et al. 2015; Bonta et al. 2016). As a matter of fact, chlorides, entering the concrete matrix and penetrating up to the reinforcement level, can cause corrosion of the reinforcement together with degradation of concrete, primarily in the case of structures exposed to marine and chemical attack [exposure classes XS

and XA defined in EN 206-1 (CEN 2000), respectively]. Frequent repair actions may be hence needed to avoid time-dependent degradation related problems. It is well known that chloride-rich exposure conditions such as marine environments are one of the most aggressive (Li and Li 2011; Tsinker 1995) due to the composition of sea water consisting primarily of sulfates and chlorides (Maes and De Belie 2014).

Based on available studies, the yearly global cost of repairing the degradation due to corrosion is estimated to be USD 2.5 trillion, which is equivalent to 3.4% of the global gross domestic product (GDP) (Koch et al. 2016). These data indicate that the lack of corrosion management is very costly and that, by using proper corrosion control methods, significant savings on maintenance costs (about 15%–35%) could be obtained all along the service life of the reinforced concrete structure (Koch et al. 2016).

It is worth mentioning that improvements from a sustainability point of view must be assessed in an objective way, and a quantitative evaluation of the service life is also necessary. Currently, the life cycle assessment methodology (Guinee et al. 2011) is used together with *service life prediction models*, such as the model code for service life design (fib 2006) and Duracrete (Engelund 2000). As stated above, it is not possible to avoid crack formation in concrete and, it is also known that *permeability* of cracked concrete increases significantly with increasing crack width (Wang et al. 1997; Edvarsen 1999; Savija and Schlangen 2016; Ismail et al. 2008). In this context, self-healing, by controlling and repairing small initial cracks could be an interesting and viable solution for reducing the chloride penetration rate and therefore, extending the service life of reinforced concrete structures.

The interest on durability and self-healing technologies has been continuously increasing during the last years (Edvarsen 1999;

¹Assistant Professor, Dept. of Civil and Environmental Engineering, Politecnico di Milano, 20133 Milano MI, Italy (corresponding author). ORCID: <https://orcid.org/0000-0002-0810-9743>. Email: estefania.cuenca@polimi.it

²Civil Engineer, Dept. of Civil and Environmental Engineering, Politecnico di Milano, 20133 Milano MI, Italy. Email: stefano2.rigamonti@mail.polimi.it

³Chief Executive Officer and Architect, Penetron Italia, 10093 Collegno TO, Italy. Email: direzione.technica@penetron.it

⁴Associate Professor, Dept. of Civil and Environmental Engineering, Politecnico di Milano, 20133 Milano MI, Italy. Email: liberato.ferrara@polimi.it

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Cuenca and Ferrara 2017; Aldea et al. 2000; Darquennes et al. 2016; Cuenca et al. 2018; Ferrara et al. 2014, 2018; Snoeck and De Belie 2012), due to the likewise increasing awareness of scientists and society about deterioration of reinforced concrete structures and the costs of repair and maintenance of damaged structures. Self-healing technologies can provide a solution for an effective management of these problems. A few studies have addressed thoroughly all the aforementioned topics. Savija and Schlangen (2016) considered two types of concrete mixtures (Portland cement mix and blast furnace slag mix) under two different curing conditions (immersed in tap water and fog room), specimens were cracked by means of wedge splitting tests at different cracking ages (14 and 28 days). Specimens were cured after cracking for more than two months before chloride exposure, being tested at an age of three months (including the curing period). A methodology based on rapid chloride migration test was used after the healing period to evaluate the healing efficiency. They found that, without taking into consideration self-healing of cracks, an almost linear relation between crack width and maximum chloride penetration depth holds. Moreover, taking into consideration self-healing, they found that, for cracks narrower than $60\ \mu\text{m}$, the resistance against chloride ingress was fully recovered. De Nardi et al. (2017) studied the recovery of compressive strength on specimens healed after being pre-damaged at 14 and 84 days and at different levels of damage (70% of the compressive strength value in prepeak regime and 90% of the compressive strength value in postpeak regime). They found that the compressive strength in healed specimens increased compared with the one determined at precracking age, from 25% to 40% depending on the precracking age, being higher for specimens pre-damaged at a young age. Sahmaran et al. (2007) investigated the chloride diffusivity of mortars with different crack widths and found that for crack widths larger than $135\ \mu\text{m}$ the effective diffusion coefficient increases rapidly. Moreover, the formation of self-healing products diminished the rate of chloride penetration through the crack, reducing the effective diffusion coefficient of cracked mortar samples. Jacobsen et al. (1996) found that self-healing may be responsible for a reduction of chloride migration rate between 28% and 35% on specimens precracked by means of freeze/thaw tests and healed by immersing them in lime saturated water at 20°C for 3 months. Penetration time was also significantly increased compared with migration in newly cracked specimens. The rate of chloride migration and penetration time were calculated by linear regression of the steady-state flow rate. Ismail et al. (2008) analyzed the chloride penetration in mortar specimens cracked with a mechanical expansive core and observed that, for crack widths lower than $30\ \mu\text{m}$ no chloride diffusion occurs along the crack path, regardless the age at which the crack was induced. Maes et al. (2014) studied specimens containing glass capsules filled with polyurethane as a healing agent. This polyurethane healing agent consisted of two components: one was a prepolymer of polyurethane and the other was a mixture of 10% accelerator and distilled water. Specimens were precracked by means of splitting tests and also by means of thin steel plates introduced into the concrete in the fresh state. The specimens were cured into a solution of water and NaCl for 7 weeks. The results showed that for crack widths of 100 and $300\ \mu\text{m}$ almost no chloride penetration was measured around the healed crack in 83% and 67% of the cases, respectively. They also observed that some of the specimens did not benefit at all by the presence of healing agent because of improper or nil release of the polyurethane (PU) into the crack. Li and Li (2011) tested high performance fiber reinforced concrete specimens preloaded in tension up to 0.5%, 1.0%, and 1.5% tensile strain level and immersed in a 3% chloride solution for 30, 60, and 90 days. When they reloaded the specimens after curing, they found that, due to self-healing,

reloaded specimens still featured multiple microcracking behavior and tensile strain capacity greater than 2.5%. Moreover, the results showed that under chloride exposure, the specimens remained durable in terms of tensile strain capacity and recovery of the initial material stiffness. Ling and Chunxiang (2017) studied the effects of self-healing cracks in bacterial concrete on the penetration of chlorides. They considered ordinary Portland cement mortar specimens (control) and one mortar containing a microbial self-healing agent consisting of bacteria powder (*Paenibacillus mucilaginosus*) and substrate. It was observed that self-healing led to a reduction of chloride content for both mixes, but the chloride content in the specimens having the self-healing agent was lower. Borg et al. (2018) studied the crack sealing capacity of mortars containing supplementary cementitious materials (fuel ash and silica fume) or crystalline admixture (same as used in this research) in chloride-rich environments. They observed that sea water may lead to an enhancement of the self-healing capacity of mortars with respect to distilled water, especially for higher chloride contents (16.5% NaCl aqueous solution). It may be due to a sort of chloride binding capacity and that the compounds deriving from the precipitate healing product in the cracks contribute to closing them. Moreover, they noticed that both the addition of fuel ash (with a replacement ratio lower than 20%) and silica fume (with a content of 15% by mass of cement) have a beneficial effect on the sealing capacity of cracks up to intermediate widths (0.15–0.3 mm). The mix containing the crystalline admixture, thanks to its hydrophilic behavior, guaranteed the highest crack sealing capacity in almost all the investigated conditions, especially for cracks up to 0.3 mm. Van Belleghem et al. (2017) used a concrete mixture containing fly ash and a PU-based healing agent encapsulated into glass capsules. Two different PU healing agents were used. The first healing agent was a noncommercial PU that essentially consisted of a polyether polyol and methylene diphenyl diisocyanate (MDI). The second healing agent was also an MDI and polyether polyol based prepolymer with an inert hydrophobic to control the viscosity and rheological behavior. Some of the specimens were precracked up to a crack width of $300\ \mu\text{m}$. The results showed that chloride ingress depends on the crack opening and decreases almost exponentially along the depth of the crack. After the curing time, it was observed that the self-healing agent led to a reduction of the chloride ingress rate up to 75%. Maes and De Belie (2016) also studied the improvement due to self-healing in service life of concrete specimens suffering chloride attack, introducing into their life prediction model also a variable depending onto the crack width.

In this paper, an experimental campaign is proposed to evaluate the effects of crack healing on the mechanical and durability properties of concrete exposed to chloride-rich environments, with reference to both autogenous self-healing and stimulated through the addition of crystalline waterproofing admixtures. In fact, the main objective of this research is to analyze the effectiveness of the crystalline admixtures as healing promoters in concrete exposed to chloride-rich environments. The effects of the self-healing of cracks on the recovery of compressive strength and improvement on chloride penetration resistance have been evaluated. In particular, the chloride content (% mass) has been quantified at different distances from the exposure surface on specimens healed for 1, 3, and 6 months. Moreover, the microstructure of healing products was analyzed to explain the improvements obtained from a mechanical and durability point of view.

Research Significance

Durability requirements prescribed by current design codes could be difficult to accomplish in concrete structures exposed to highly

aggressive environments, in which premature degradation takes place. Self-healing may be a protective system of concrete structures against chloride-rich environments, such as marine environments, in which repairing small crack widths is able to extend the service life of the concrete structure. Research have been carried out thoroughly on the aforementioned topics but, to the knowledge of the authors, the literature on self-healing of concrete exposed to chloride-rich environments (sodium chloride solution at a concentration up to 165 g/L) is still scarce, being the most studied concentration values of sodium chloride solutions up to 33 g/L. Moreover, most of the research on self-healing of concrete structures exposed to chloride environments is focused on self-sealing of cracks (crack repairing of the concrete surface against environmental actions). In this paper, not only self-sealing of cracks has been studied but also self-healing of cracks (recovery against mechanical actions). To this purpose, self-sealing has been evaluated by means of permeability tests and self-healing by means of the recovery of compressive strength in healed specimens.

Mixture Proportions and Exposure Conditions

Two concrete mixes were analyzed: a reference mix and a mix adding to the reference one a crystalline admixture (0.8% by cement weight) to study its effectiveness as a healing agent. Crystalline admixtures were directly added during the mix. Table 1 contains the proportions of both mixtures. The employed crystalline admixture consists of a mix of cement, sand, and patented active chemicals, characterized by particles of irregular shape ranging from 1 to 20 μm with the presence of calcium, oxygen, silicon, magnesium, aluminum, and potassium. More details can be found in (Ferrara et al. 2014). Crystalline admixtures are *permeability-reducing admixtures* as described by the American Concrete Institute (ACI) Committee 212 (ACI 2016). To analyze the effectiveness of this crystalline admixture as a healing agent on chloride-rich environments, specimens were subjected to the following three exposure conditions:

1. Climate room at a temperature of 20°C and a relative humidity of 95%;
2. Continuous immersion in a 16.5% NaCl aqueous solution; and
3. Wet/dry cycles in a 16.5% NaCl aqueous solution. For these cycles, a 2-2-3 day scheme was adopted, meaning that the specimens were immersed for two days, stayed out of the aqueous solution for the subsequent two days (and kept inside the laboratory), and then was immersed again for three days, and so on.

Continuous immersion and wet/dry cycles were chosen to simulate the chloride-rich environments in which reinforced concrete elements can be found (for example, areas subjected to splashes of water containing deicing salts). Therefore, a high salt content (16.5% NaCl aqueous solution) was used herein. The specimens

Table 1. Concrete mix proportions (kg/m³)

Constituent (kg/m ³)	Mix without crystalline admixture	Mix with crystalline admixture
Portland cement CEM II 42.5 R	360	360
Water	180	180
Fine aggregate (sand 0–4 mm)	814	811
Coarse aggregate (gravel 4–16 mm)	1,077	1,077
Acrylic superplasticizer ^a	3.5	3.5
Crystalline admixture (CA)	0	2.9

^aDensity = 1.050 ± 0.02 kg/dm³ at 20°C.

cured in the climate room act as control samples cured under ideal conditions, thus providing a reference for comparison.

Objectives and Test Methodology

The recovery of both mechanical and durability properties on concrete specimens has been analyzed as follows:

1. Mechanical recovery was analyzed on undamaged and damaged concrete cylinders (Ø100 × 200 mm). Samples were predamaged (microcracked) by loading them up to 90% of the compressive strength. Subsequently, they were exposed to chloride-rich environment (section “Compressive Strength Tests”);
2. The recovery of durability properties was carried out on concrete cylinders Ø100 × 100 mm precracked by the Brazilian splitting test. Crack sealing and recovery of chloride penetration resistance was assessed (section “Chloride Penetration Tests and Microscopic Analysis to Quantify Crack Sealing”);
3. Finally, the mechanical and durability behavior has been linked to the analysis of the microstructure of the healing products by means of SEM and EDS analysis. With SEM analysis, the morphology of the healing products was observed and, with EDS analysis their composition was determined (identifying the elements present in the healing products).

Compressive Strength Tests

Analysis of Compressive Strength Development

To analyze the influence of crystalline admixtures on compressive strength development in specimens subjected to chloride-rich environments, the average compressive strength of concrete cured for 7, 14, 28, 56, and 84 days in the above-listed environmental conditions (section “Mixture Proportions and Exposure Conditions”) was measured. For each curing age and type of concrete, three concrete cylinders (Ø100 × 200 mm) were tested. These samples are hereafter called undamaged samples.

Analysis of Compressive Strength Recovery

Cylinder specimens were predamaged by loading them up to 90% of their average compressive strength after being cured for 7 or 28 days; the compressive strength values were obtained from compressive tests mentioned above in the “Analysis of Compressive Strength Development” section. Predamaged specimens were then further cured for 1, 3, or 6 additional months, and compression strength tests were performed again after the curing period (damaged and healed samples). For each curing age and type of concrete, three concrete cylinders (Ø100 × 200 mm) were predamaged. Comparison with the previously determined strength development curve for sound (undamaged) specimens with the same curing conditions allowed us to clearly quantify the effects of healing on the recovery of the strength, if any. It is important to highlight that for long healing periods (6 months) the analogous experimental compressive strength value of a sound cylinder was not available because, as underlined in the “Analysis of Compressive Strength Development Analysis of Compressive Strength Development” section, compressive strength values on undamaged samples were available up to 84 days. Therefore, when the corresponding experimental value was not available for an undamaged cylinder specimen, the compressive strength value was predicted by using the Eurocode 2 -EC2- (CEN 2004). The Eurocode 2 -EC2- (CEN 2004), in 3.1.2(6), states that for a mean temperature of 20°C and curing in accordance with EN 12390-3 (CEN 2019), the compressive strength of concrete at various ages $f_{cm}(t)$ may be estimated from Eqs. (1) and (2):

$$f_{cm}(t) = \beta_{cc}(t) \cdot f_{cm} \quad (1)$$

$$\beta_{cc}(t) = \exp \left[s \cdot \left[1 - \left(\frac{28 \text{ days}}{t} \right)^{\frac{1}{2}} \right] \right] \quad (2)$$

where $f_{cm}(t)$ = mean concrete compressive strength at an age of t days; f_{cm} = mean compressive strength at 28 days; $\beta_{cc}(t)$ = coefficient which depends on the age of the concrete t ; t = age of the concrete in days; and s = coefficient which depends on the type of cement (it is equal to 0.20 for cement of strength class CEM 42.5 R).

Chloride Penetration Tests and Microscopic Analysis to Quantify Crack Sealing

Chloride ion penetration in both uncracked and cracked-healed specimens was measured. To this purpose, cylinder specimens ($\varnothing 100 \times 200$ mm) were casted, to be further cut into two 100 mm high halves. The specimens were cured in a climate room at 20°C and a relative humidity of 95% up to the precracking age (7 or 28 days), when the thus obtained cylinder specimens ($\varnothing 100 \times 100$ mm) were precracked by means of a splitting tensile test. The two halves were then reunited and kept in place by means of a waterproofing tape around the entire outer surface of the cylinder. Subsequently specimens were immersed in 16.5% NaCl aqueous solution or subjected to wet/dry cycles (following the procedure explained in the ‘‘Objectives and Test Methodology’’ section) for 1, 3, or 6 additional months.

The ingress of chlorides into the samples was planned to take place only from the upper face of each sample because all the other surfaces had been waterproofed to water, and, hence, the chloride penetration profiles were determined perpendicular to the crack path after the splitting tests. As a consequence, a decrease in the chloride content was expected for increasing depth, where depth is the distance from the exposure surface. For that reason, to obtain the samples for titration tests, cylinders were cut into 3–4 mm thick slices perpendicular to the longitudinal axis of the cylinder.

Moreover, before and after curing the specimens, a visual inspection to assess the degree of crack sealing was carried out, followed by a more accurate analysis of the healed surface of the precracked specimens by means of a digital microscope and an image-editing software, aimed at quantifying the extent of crack closure. The detailed procedure has been intensively explained in Cuenca et al. (2018) and will be briefly summarized hereafter. Fourteen pictures of each sample were taken both immediately after

precracking the samples and at the end of the scheduled curing time. These pictures were then processed by means of the image-editing software, thus allowing the identification of the crack surface width before and after the curing period and so the determination of the percentage of crack closure that had occurred. For each case (uncracked, or precracked at 7 or 28 days), the type of concrete (with and without crystalline admixtures), exposure condition (immersion or wet/dry cycles), and healing period (1, 3, and 6 months), three concrete cylinders ($\varnothing 100 \times 100$ mm) were tested.

On the other hand, the chloride penetration depth was determined for both uncracked and precracked specimens indicated above. To do that, specimens were split into two halves (for precracked specimens in the direction orthogonal to the initial crack) to perform color boundary tests. In this method [thoroughly explained in Ferrara et al. (2018)], an aqueous silver nitrate (AgNO_3) solution with a concentration equal to 0.1 mol/L was sprayed on the freshly split crack surfaces. When this solution contacts with concrete, it forms a boundary with brown and white zones. The color of the area contaminated by chlorides changed to white or light grey, and the free-chloride zone changed to light brown. As an example, Fig. 1(a) shows one cracked specimen, of the present experimental campaign, subjected to a color change boundary test. Pictures were taken and analyzed by means of an image-editing software. This allowed the determination of the area penetrated by chloride ions.

Finally, other specimens (different from those used for color boundary tests) were subjected to a potentiometric titration [Fig. 1(b)] according to the Standard EN 14629 (CEN 2007) and RILEM TC 178-TMC (Vennesland et al. 2013). Because the parameter of interest was chloride ion penetration, only immersed specimens and samples undergoing wet/dry cycles were considered in this stage.

For each case (uncracked or healed for 1, 3, or 6 months, the type of concrete (with or without crystalline admixtures) and exposure condition (immersion or wet/dry cycles) one sample from the concrete cylinder ($\varnothing 100 \times 100$ mm) was used to perform the chemical titration test.

Methods for Characterization of Healing Products

The microstructural changes on the concretes due to the action of the crystalline admixtures and the effect of the 16.5% NaCl aqueous solution were analyzed by using a scanning electron microscopy (SEM, ZeissEvo 50P equipped with Oxford Inca Energy 200EDS having an ultra-thin window detector from 133 eV, ZEISS, Oberkochen, Germany). SEM analyses were carried out on tested specimens (with and without crystalline admixtures) after being

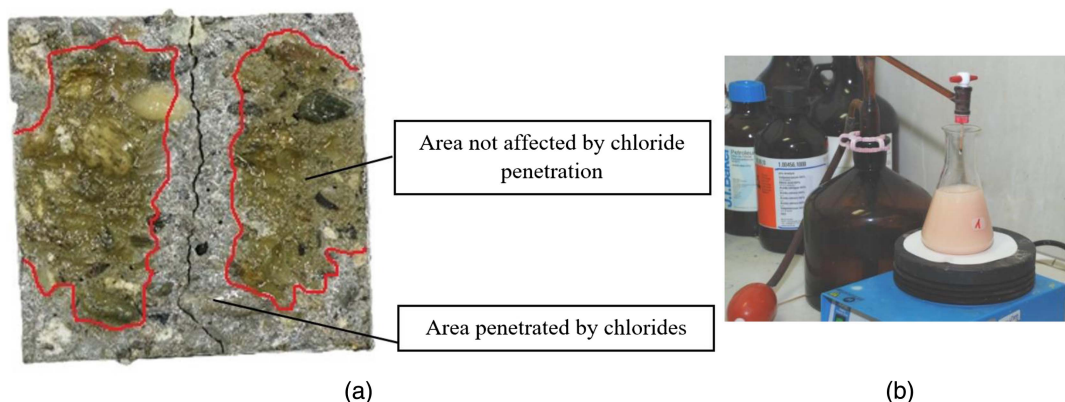


Fig. 1. Chloride penetration tests: (a) cracked specimen after being subjected to color change boundary test; and (b) chemical titration test.

immersed in 16.5% NaCl aqueous solution for 6 months. To carry out SEM observations, small samples of $1 \times 1 \times 1$ cm were removed from the precracked plane and on freshly fractured surfaces just after the splitting test, then the small samples were dried at 60°C for 24 h. Finally, they were metallized with gold (Au) to improve the image quality of observations at SEM. The SEM images were obtained in high vacuum mode, 20 kV of accelerating voltage and variable working distance. Energy dispersive X-ray spectroscopy (EDS) analyses were also carried out to identify the main elements present in the healing products. This chemical microanalysis technique was carried out in combination with the SEM.

Results and Discussion

Characterization of Self-Healing Based on Mechanical Properties: Compressive Strength

The compressive strength of specimens made with both mixes and cured in different environmental conditions (climate room, immersed in 16.5% NaCl aqueous solution and subjected to wet/dry cycles in the same solution) was investigated first. The development of average compressive strength values over time for all the analyzed exposure environments is shown in Fig. 2. A limited influence of the curing conditions on the development of strength can be observed. Moreover, a slight decrease in compression strength was associated with the use of the crystalline admixture, coherently with what is known in the literature (Ferrara et al. 2014). Table 2 also shows the coefficient of variation, CoV (%), of the average values plotted in Fig. 2. The CoV (%) values are satisfactory because they are small (lower than 13%).

To assess the self-healing related recovery of strength by means of compressive strength tests on predamaged specimens cured under different environmental conditions, the following *Strength recovery index* was calculated according to the Eq. (3):

$$\text{Strength recovery index}[\%] = \frac{f_{cm,damaged\&healed}}{f_{cm,undamaged}} \cdot 100 \quad (3)$$

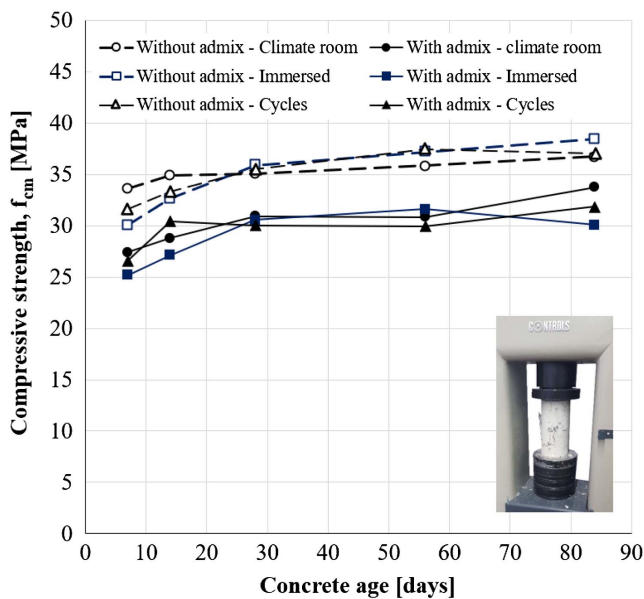


Fig. 2. Influence of curing conditions and type of concrete on the development of compressive strength.

where $f_{cm,damaged\&healed}$ is the average compressive strength obtained from testing the predamaged specimens after 1, 3, or 6 months exposed to different healing conditions (section “Analysis of Compressive Strength Recovery”) and $f_{cm,undamaged}$ is the average compressive strength of the undamaged samples tested at the same age (section “Analysis of Compressive Strength Development Analysis of Compressive Strength Development”).

As explained in the “Analysis of Compressive Strength Recovery” section, it is pointed out that, despite not having an exact coincidence among the age of specimens predamaged after 7 days and cured for both 1 and 3 months and undamaged ones (after 28 and 84 days), the latter were used as reference values for $f_{cm,undamaged}$. This was done because it is shown that by interpolating the results described in the “Analysis of Compressive Strength Development Analysis of Compressive Strength Development” (Table 2), and calculating the actual values of strength by means of the prediction formula of Eurocode 2 (CEN 2004), the differences between the considered results and the computed ones were negligible.

The obtained results are summarized in Table 3. To analyze the possible mechanical recovery after healing due to the presence of crystalline admixtures, a new parameter called $\Delta_{recovery}$ was calculated as the difference between the strength recovery index for the mix with crystalline admixtures and the strength recovery index for

Table 2. Influence of curing conditions and type of concrete on the development of compressive strength

Type of concrete	Curing environment	Concrete age (days)	$f_{cm,undamaged}$ average (MPa)	Coefficient of variation, CoV (%)
Without crystalline admixtures	Climate room ^a	7	33.6	8.4
		14	34.9	3.2
		28	35.1	13.0
		56	35.8	4.1
		84	36.7	9.2
		84	37.0	3.7
	Immersed ^b	7	30.1	13.1
		14	32.6	7.4
		28	35.9	5.5
		56	37.1	4.7
		84	38.5	11.7
		84	37.0	3.7
With crystalline admixtures	Climate room ^a	7	27.4	6.3
		14	28.8	2.4
		28	30.9	7.3
		56	30.8	2.4
		84	33.7	4.0
		84	31.9	5.1
	Immersed ^b	7	25.2	11.2
		14	27.1	8.2
		28	30.6	8.4
		56	31.6	4.6
		84	28.3	9.3
		84	31.9	5.1
Cycles ^c	7	31.6	6.2	
	14	33.4	2.9	
	28	35.5	10.6	
	56	37.5	1.2	
	84	37.0	3.7	
	84	37.0	3.7	

^aClimate room: temperature = 20°C and relative humidity = 95%.

^bImmersion in 16.5% NaCl aqueous solution.

^cWet/dry cycles (3 days immersed in 16.5% NaCl aqueous solution and 3 days not immersed) during 1, 3, and 6 months.

Table 3. Compressive strength recovery for predamaged specimens with and without crystalline admixture (results are average of three nominally identical specimens)

Specimen age at damage (days)	Exposure condition	Age of reloading (months)	Without crystalline admixtures				With crystalline admixtures				$\Delta_{\text{recovery}} (\%) \text{SRI2-SRI1}$
			$f_{cm_{\text{damaged and healed}}} \text{ (MPa)}$	Coefficient of variation, CoV (%)	$f_{cm_{\text{undamaged}}} \text{ (MPa)}$	Strength recovery index, SRI1 (%)	$f_{cm_{\text{damaged and healed}}} \text{ (MPa)}$	Coefficient of variation, CoV (%)	$f_{cm_{\text{undamaged}}} \text{ (MPa)}$	Strength recovery index, SRI2 (%)	
7	Climate room ^a	1	38.1	6.0	35.1	108.8	33.8	4.1	30.9	109.2	+0.4
		3	38.7	6.3	36.7	105.5	32.7	5.3	33.7	97.0	-8.5
		6	42.9	4.3	39.5 ^b	108.6	39.8	3.7	34.8 ^b	114.4	+5.8
28		1	36.0	12.3	35.8	100.4	27.0	7.9	30.8	87.7	-12.7
		3	43.1	9.7	38.8 ^b	111.1	36.8	3.3	34.2 ^b	107.6	-3.5
		6	41.7	3.7	39.7 ^b	105.1	36.9	9.3	35.0 ^b	105.4	+0.3
7	Immersed ^c	1	30.5	0.3	35.9	80.1	29.8	8.9	30.6	97.4	+12.3
		3	39.2	5.9	38.5	101.9	33.3	7.4	30.1	110.8	+8.8
		6	39.0	3.4	40.4 ^b	103.0	35.4	4.2	34.5 ^b	102.8	+6.2
28		1	34.0	10.9	37.1	91.7	32.0	2.1	31.6	101.2	+9.5
		3	39.7	3.6	39.6 ^b	100.1	34.3	6.8	33.8 ^b	101.5	+1.4
		6	40.2	9.4	40.6 ^b	105.9	35.9	2.8	34.7 ^b	103.7	+4.7
7	Cycles ^d	1	39.1	4.9	35.5	110.2	34.3	12.0	30.0	114.3	+4.1
		3	38.7	10.1	37.0	104.5	34.6	9.0	31.9	108.7	+4.2
		6	38.1	11.1	39.9 ^b	95.5	35.4	4.4	33.8 ^b	104.7	+9.2
28		1	30.9	1.7	37.5	82.4	26.1	10.2	29.9	87.2	+4.8
		3	36.0	4.1	39.2 ^b	91.8	32.0	7.0	33.2 ^b	96.5	+4.7
		6	37.0	8.8	40.2 ^b	92.1	34.1	10.5	34.0 ^b	100.2	+8.1

^aClimate room: temperature = 20°C and relative humidity = 95%.^bValue predicted by EC2 formulation.^cImmersion in 16.5% NaCl aqueous solution.^dWet/dry cycles (3 days immersed in 16.5% NaCl aqueous solution and 3 days not immersed) during 1, 3, and 6 months.

the reference mix (without crystalline admixtures) as indicated by Eq. (4):

$$\Delta_{\text{recovery}}(\%) = \text{Strength recovery index}(\%)_{\text{WITH crystalline admix}} - \text{Strength recovery index}(\%)_{\text{WITHOUT crystalline admix}} \quad (4)$$

In most of the cases, the obtained recovery of strength (strength recovery index, in %) was slightly higher than 100%, meaning that the compression strength of the predamaged samples turned out to be slightly higher than that of companion undamaged ones. This phenomenon can be justified by the possibility for cement particles inside the specimen to undergo further hydration reaction thanks to the formation of microcracks during the predamage. The particles would otherwise remain unhydrated in undamaged concrete samples where the hydration of the skin would prevent further water to reach the inner parts of the specimen.

The influence of crystalline admixture on the recovery of strength could be evaluated by comparing the results obtained for the two types of concrete. The highest benefits from the use of the healing agent were observed for specimens continuously immersed in the chloride solution (16.5% NaCl aqueous solution), especially in the first months of curing (1 and 3 months) for the specimens predamaged at 7 days. For these samples, an improvement up to 12% was observed (Table 3). Anyway, a strength enhancement was also observed for samples subjected to wet/dry cycles, even though a longer curing time (6 months) appeared to be necessary in this case for both predamaging ages, 7 and 28 days. No clear trend could be identified for the specimens cured in the climate room. This is also consistent with the results obtained in previous studies (Ferrara et al. 2014). This confirms the importance of water availability to exploit at its best the healing stimulating effects of the employed crystalline admixture.

Moreover, the influence of the age of the predamage was also investigated. The results showed that specimens predamaged 7 days after casting featured a slightly higher recovery of strength (up to 10% of improvement) than samples predamaged at 28 days especially for specimens immersed in chloride solution (Table 3). This is probably due to the higher expectable and available amount of unhydrated particles, with respect to specimens damaged at later ages, whose delayed hydration is responsible for the self-healing.

Characterization of Self-Healing Based on Durability Properties

Crack Sealing Quantification Using Microscopic Techniques

Crack monitoring and chloride penetration were assessed as shortly addressed in the “Chloride Penetration Tests and Microscopic Analysis to Quantify Crack Sealing” section and hereafter explained in detail. To this purpose, after precracking and at the end of the healing period, microscopic analysis was carried out on the precracked specimens to determine the crack closure (%). Fig. 3 shows the graphical evolution of a crack explaining the different crack closure levels observed throughout this research by means of microscopic techniques.

Using an image-editing software, the average crack width w_{average} and the crack closure (%) were determined according to Eqs. (5) and (6), respectively. This procedure is analogous to that used by Ferrara et al. (2016). In particular:

$$w_{\text{average}} = \frac{A_{\text{crack}}}{l_{\text{crack}}} \quad (5)$$

where

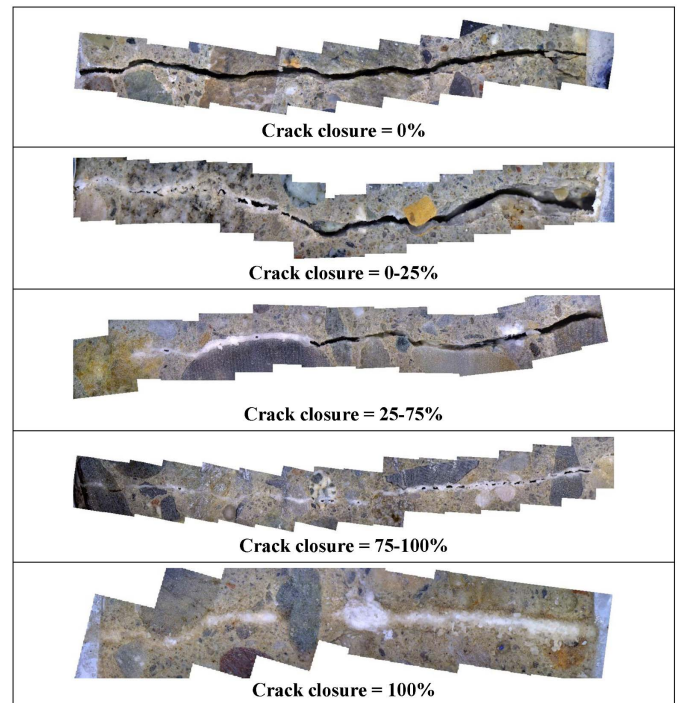


Fig. 3. Graphical evolution of a crack to show the different sealing degrees observed.

- A_{crack} is the area of the crack; and
- l_{crack} is the length of the crack obtained by approximating its middle line with a polygonal line

$$\text{Crack closure}[\%] = \frac{w_{\text{initial}} - w_{\text{post-sealing}}}{w_{\text{initial}}} \cdot 100 \quad (6)$$

where

- w_{initial} is the crack width just after the splitting test; and
- $w_{\text{post-sealing}}$ is the crack width of the same specimen after being exposed to the different exposure conditions (immersed in a 16.5% NaCl aqueous solution or wet/dry cycles).

A dependence of the crack closure with the crack width and the curing time was observed. As expected, the higher the crack width, the lower the percentage of crack closure. Moreover, for the same crack width value, the higher the curing time, the higher the percentage of crack closure.

Plotting the results obtained for immersed specimens [Fig. 4(a)] it is possible to identify at first glance the abovementioned existing relationship between initial crack width and percentage of closure. It is also possible to observe the beneficial effects of the crystalline admixture for wider cracks (0.5–1 mm). Moreover, focusing on smaller cracks (<0.4 mm), it is observed that the concrete samples with the healing agent have the potential to achieve a sealing capacity after 1 and 3 months of curing directly comparable with the one obtained after 3 and 6 months by the other mix, respectively. For larger cracks, longer healing times are needed, and the presence of the crystalline admixture always stimulates a higher crack closure. After 3 months healing, crack closures higher than 70% were only reached when the healing agent (crystalline admixtures) was present.

On the other hand, considering the samples subjected to wet/dry cycles [Fig. 4(b)] a generally lower healing capacity with respect to full immersed samples was observed. Indeed, when specimens were subjected to wet/dry cycles it was observed that crack widths

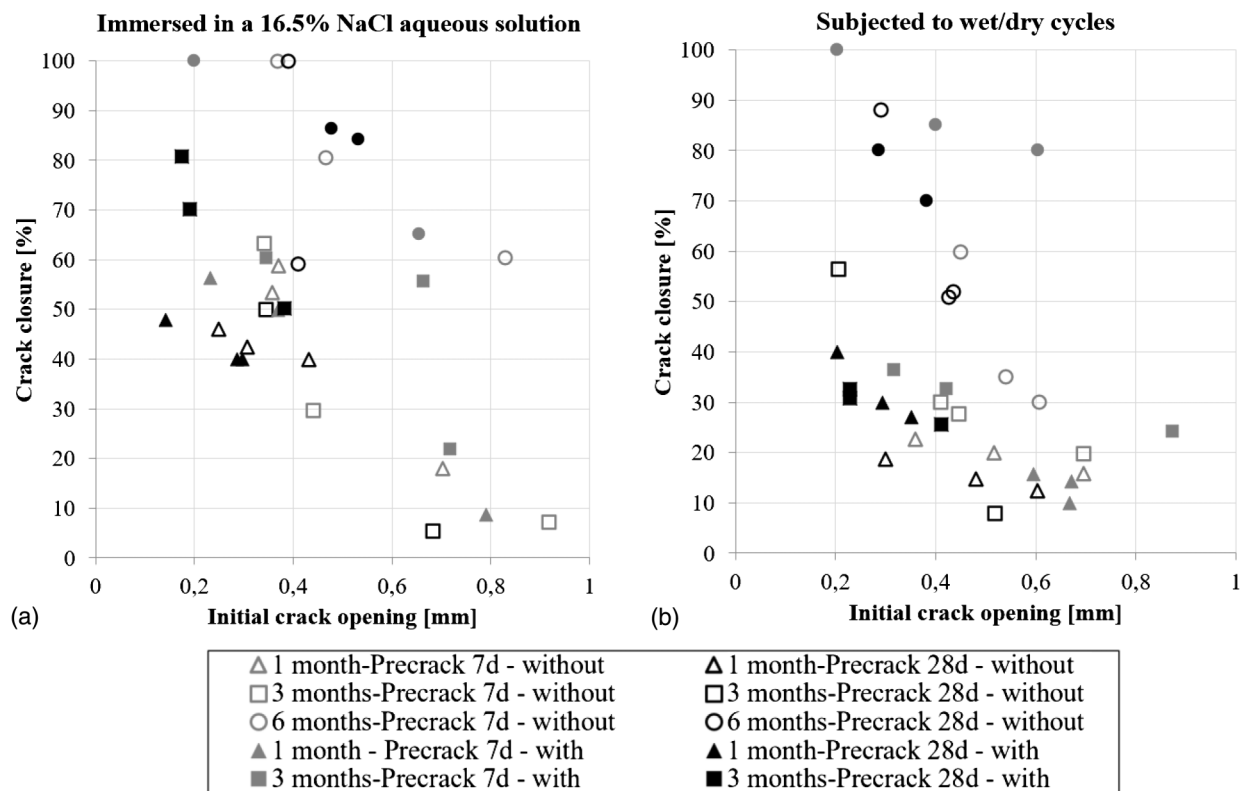


Fig. 4. Crack closure (%) versus initial crack opening (mm) for specimens with and without crystalline admixtures: (a) immersed in a 16.5% NaCl aqueous solution; and (b) subjected to wet/dry cycles with a 16.5% NaCl aqueous solution.

in the range 0.2–0.4 mm reached crack closure percentages around 30% (which is 25% lower than for permanently immersed specimens). Also, in the case of wet/dry cycles a relation between initial crack width and crack closure holds, and the use of crystalline admixture results in some benefits on the sealing capacity of cracks, even though its positive contribution seems not to be as relevant as for immersed specimens.

Focusing on the precracking age, it is noted that the cracks in specimens precracked after 7 days are generally wider than when precracking after 28 days; in fact, crack widths wider than 0.6 mm corresponded mostly to specimens precracked at 7 days. This outcome is probably because when precracking a younger concrete its tensile strength and fracture energy are not fully developed yet. This could make it more difficult to control the crack opening generated through a splitting test.

Chemical Titration Tests: Chloride Penetration Profiles

For both mixes, concrete cylinders were first precracked at 28 days and then, they were immersed in 16.5% NaCl aqueous solution or subjected to wet/dry cycles for 1, 3, and 6 months to be healed. For all these healed specimens, the chloride penetration profiles were determined and, as reference, also were determined for uncracked specimens immersed in 16.5% NaCl aqueous solution and subjected to wet/dry cycles for 1 month. Fig. 5 shows the experimental and fitted chloride profiles for the above-mentioned specimens. The theoretical fitting curves adjust very well to the experimental data. As a matter of fact, notably high coefficients of determination (R^2) were obtained as shown in Fig. 5.

When observing the evolution of the chloride profiles as a function of the healing time exposure (1, 3, and 6 months) it is evident that chlorides move inwards. As a matter of fact, the chloride content (% mass) increases gradually with the healing exposure time

for the same depth (distance from exposure surface) for both exposure conditions (immersion and cycles). For instance, for a specimen without crystalline admixtures immersed in 16.5% NaCl solution with a chloride content of 0.51%, 0.75%, and 0.85% were detected after 1, 3, and 6 months of exposure time, respectively.

According to previous studies (Guinee et al. 2011; Borg et al. 2018), it is well-known that the chloride ingress close to the exposed surface is usually not diffusion controlled, indeed is part of the convection zone. In fact, some researchers have detected an increased calcium leaching on the surface in contact with the exposure solution that results into a reduction of the chloride binding capacity (Álava et al. 2016; Elakneswaran et al. 2010). Because of this phenomenon, NT Build 443 (NT 1995) does not consider the first layer in the fitting process. For this reason, in this investigation the first layer (approximately 3 mm) in contact with the solution was discarded to avoid as much as possible the convection zone. Moreover, it is noticeable that the presence of crystalline admixtures is particularly positive from depths ranging from 4 to 30 mm for specimens immersed in the chloride solution for 3 and 6 months. As observed in a previous study of these authors (Cuenca et al. 2018), crystalline admixtures perform their best at longer exposure times. Anyway, when specimens are immersed for 1 month in the chloride solution the specimens with crystalline admixture is much closer to the reference uncracked specimen than the specimen healed without crystalline admixture. For the case of wet/dry cycles, the contribution of crystalline admixtures in terms of hindering the entrance of chlorides is not so evident.

The chloride content (% mass) decreases gradually with the distance from the exposure surface, but it has been detected that when crystalline admixtures are present into the mix, the chloride profile reaches a stable value in a lower depth (much closer to the exposure surface) compared with the mix without crystalline admixture.

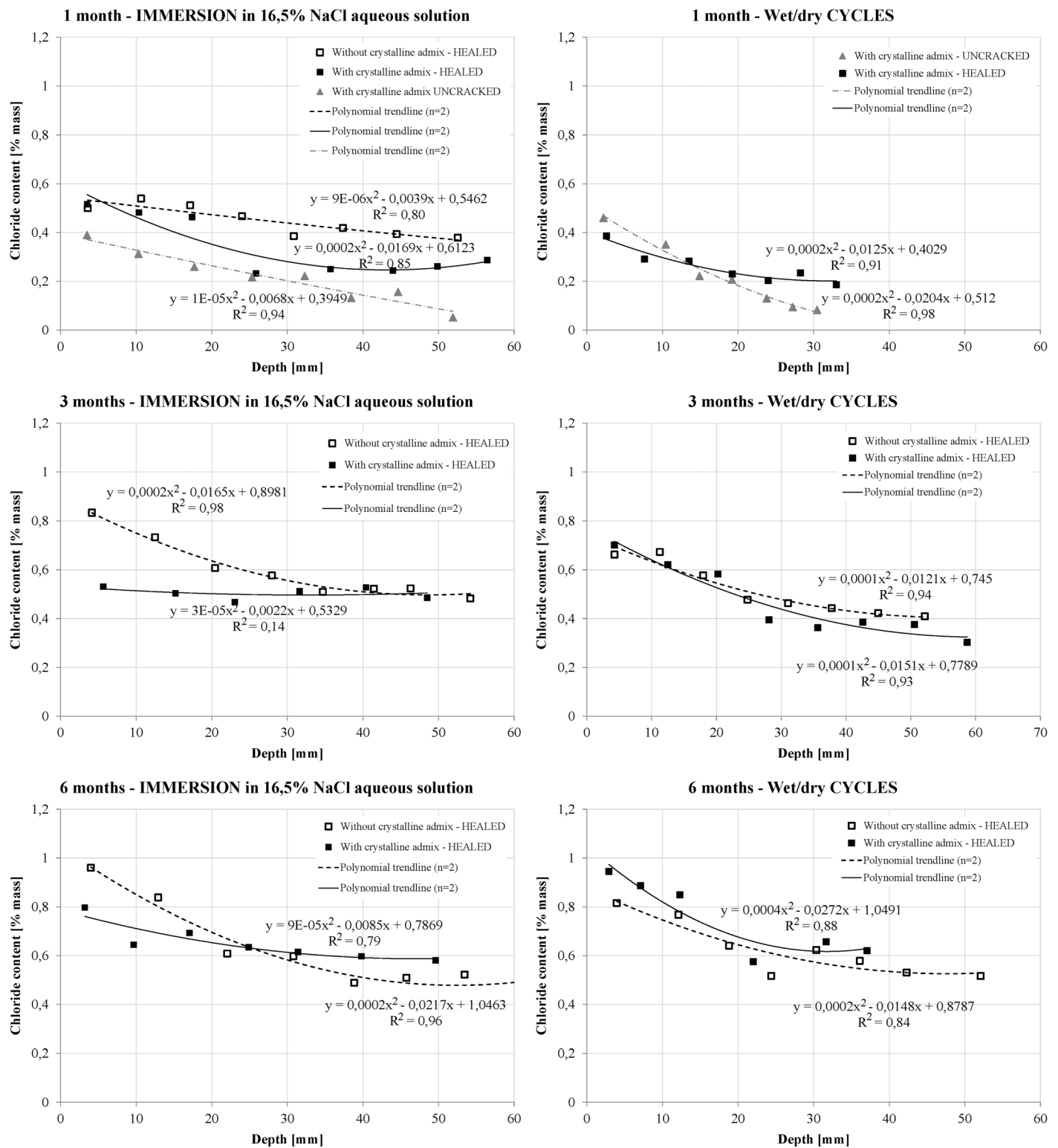


Fig. 5. Experimental and fitted chloride profiles for healed concrete after 1, 3, or 6 months immersed in 16.5% NaCl aqueous solution or subjected to wet/dry cycles, where depth is the distance from the exposure surface.

In other words, crystalline admixtures help to stabilize the chloride profile, limiting the depth with higher contents of chlorides to the region closer to the exposed surface.

Color Change Boundary Test

In cracked concrete, chlorides can directly diffuse inwards across cracks. Once reaction products of self-healing are formed in the

cracks, the chloride diffusion is hindered. As a matter of fact, after the healing period, and once the visual crack analysis was concluded, the specimens were broken in half, and the colorimetric test was performed [Fig. 1(a)]. Figs. 6 and 7 show the percentages of area penetrated by chlorides, crack closure (%), and initial crack width (mm) for the specimens precracked at 7 and 28 days and cured for 1, 3, or 6 months. Fig. 6 refers to specimens without

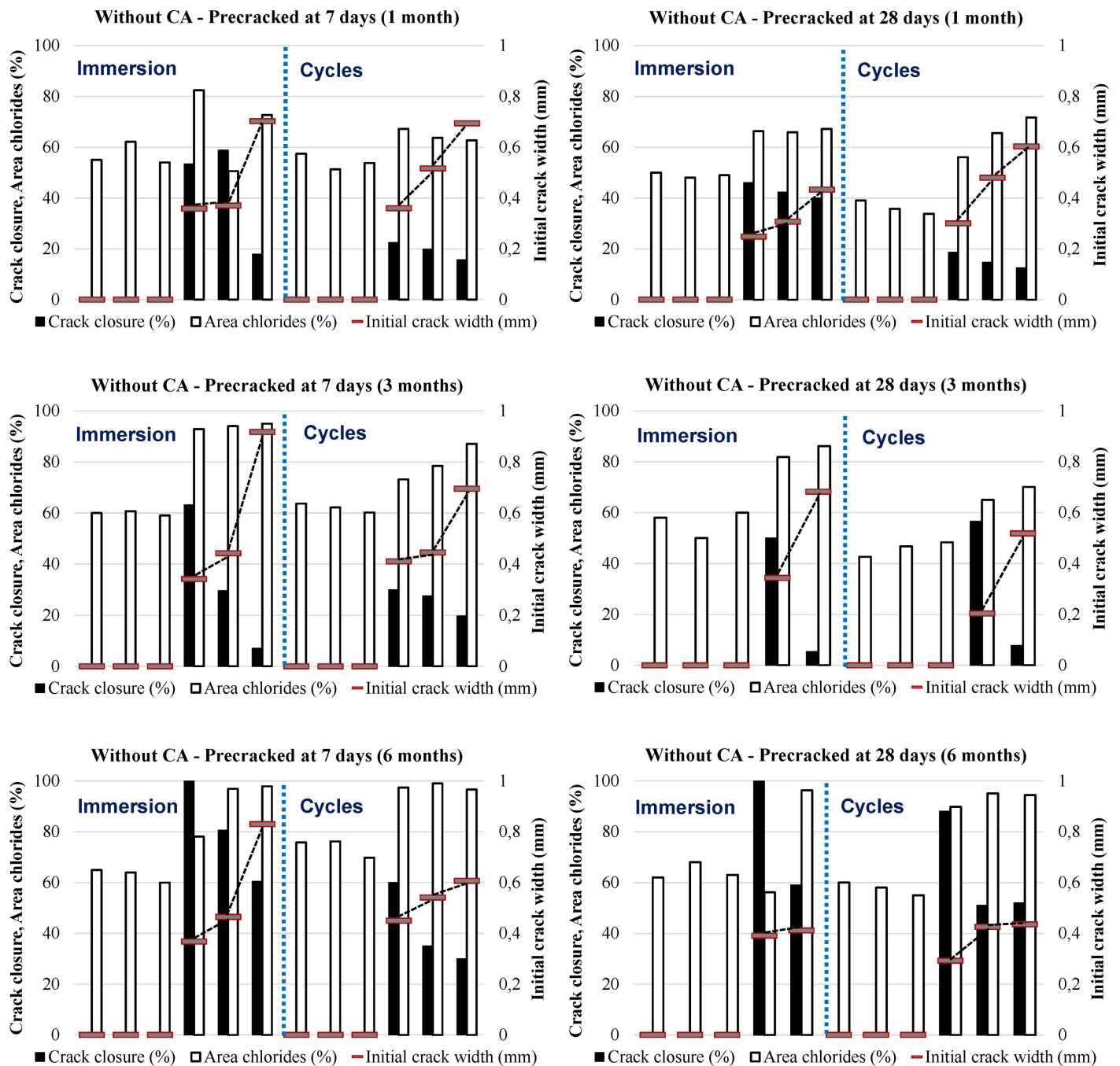


Fig. 6. Crack closure (%) and area of chlorides (%) versus initial crack opening for specimens without crystalline admixtures (CA) subjected to immersion and wet/dry cycles with a 16.5% NaCl aqueous solution.

crystalline admixtures, whereas Fig. 7 refers to those with crystalline admixtures. It is well-known that the crack closure (%) increases when the crack width decreases (Cuenca and Ferrara 2017; Ferrara et al. 2018) [see also Figs. 4(a and b)]. This is, when the crack opening is significant, the crack closure decreases, and the chloride penetrated area increases. For instance, for a specimen without crystalline admixtures precracked at 7 days and immersed for 3 months, a crack width of 0.342 mm reached a crack closure of 63.2% with an area penetrated by chlorides of 92.9%, whereas a crack width of 0.918 mm reached a crack closure of 7.1% with an area penetrated by chlorides of 95%.

The results (Figs. 6 and 7) show that the healing process was slower than the penetration of chlorides in the cement matrix,

because although high values of crack closure were obtained, the area penetrated by chlorides (Area chlorides, %) was also high. For example, for a specimen without crystalline admixtures precracked at 7 days and immersed for 6 months, a crack width of 0.368 mm reached a crack closure of 100% with an area penetrated by chlorides of 78.1%, whereas, a crack width of 0.465 mm reached a crack closure of 80.6% with an area penetrated by chlorides of 96.9%. Moreover, the area penetrated by chlorides (%) was greater in cracked specimens than for uncracked ones, as expected.

In the case of uncracked specimens, the chloride area slightly increased in the specimens without crystalline admixtures as the exposure time increased from 1 to 6 months (Fig. 6). To the contrary, this growth was slightly more reduced when the mixture

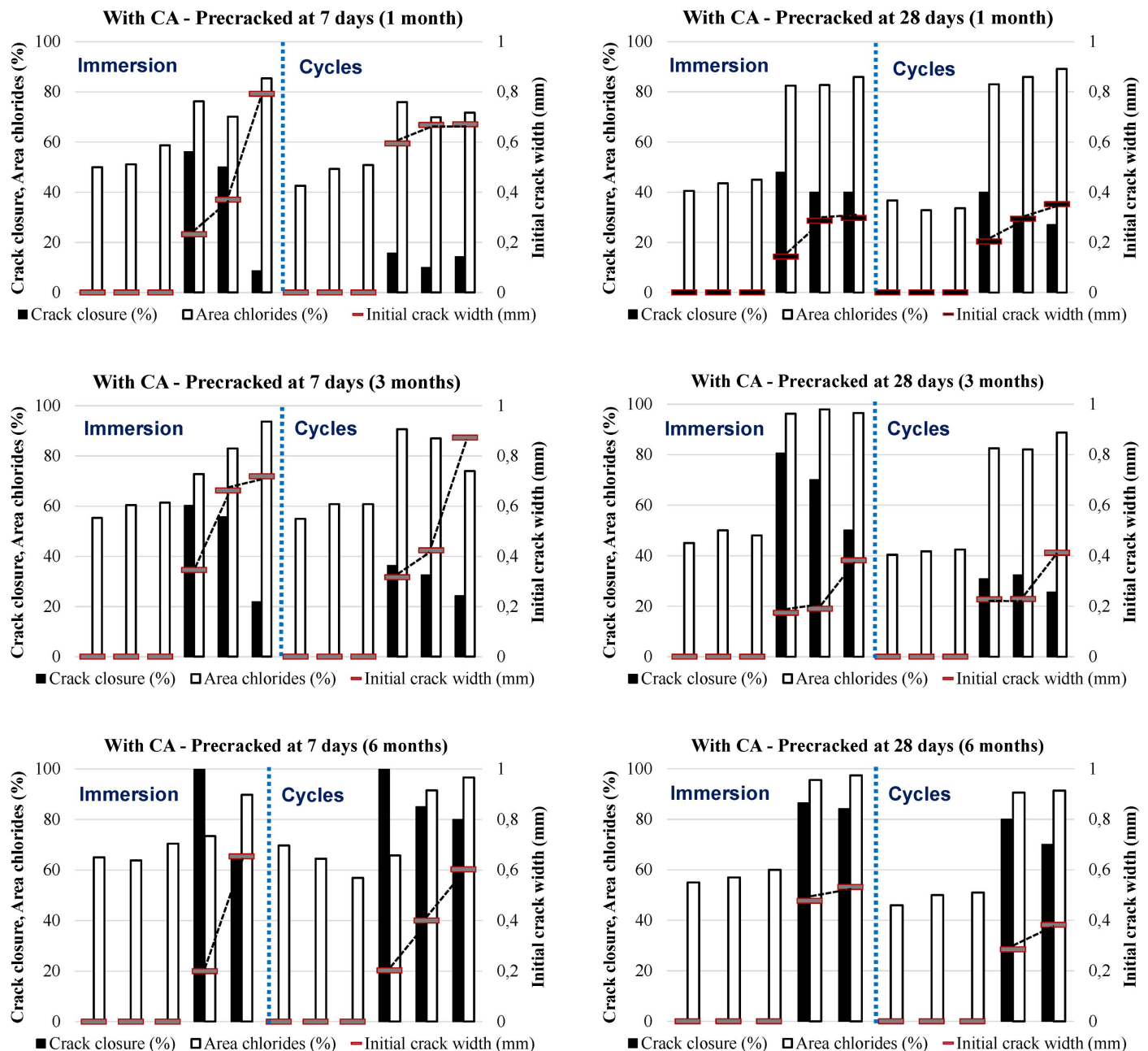


Fig. 7. Crack closure (%) and area of chlorides (%) versus initial crack opening for specimens with crystalline admixtures (CA) subjected to immersion and wet/dry cycles with a 16.5% NaCl aqueous solution.

contained crystalline admixtures (Fig. 7). Moreover, for a long-term period (6 months), the area affected by chlorides in uncracked specimens with crystalline admixtures (Fig. 7) was about 10% lower compared with their analogous specimens without crystalline admixtures (Fig. 6) for both exposures (full immersion and wet/dry cycles).

From Fig. 6 it is also observed that the crack closure in the matrix without crystalline admixtures precracked at 7 days is higher than that in the matrix without crystalline admixtures precracked at 28 days, no matter for a healing period of 1, 3, or 6 months. This result matches with the numerous results available in the literature (Ferrara et al. 2018) that show better healing ability for younger concretes than older concretes. Moreover, in Fig. 6, the *area chlorides* in the younger concretes, no matter cracked or not, are higher than those in the older ones. This result is understandable

considering that younger concretes have less dense microstructures. In Fig. 7, analogous results regarding the influence of the precracking age on self-healing can be observed.

SEM and EDS Analyses of Healing Products

The microstructure of the healing products due to the action of the crystalline admixtures was analyzed with SEM and EDS. To this purpose, two samples from two specimens healed for 6 months in 16.5% NaCl aqueous solution were analyzed: one from a specimen without crystalline admixtures and other from a specimen with crystalline admixtures. Figs. 8(a) and 9(a) show SEM images at the same magnification (500 \times) and EDS analyses for the specimen without [Fig. 8(b)] and with crystalline admixtures [Fig. 9(b)].

The main difference observed related to the presence of crystalline admixtures is the morphology of the healing product. In the

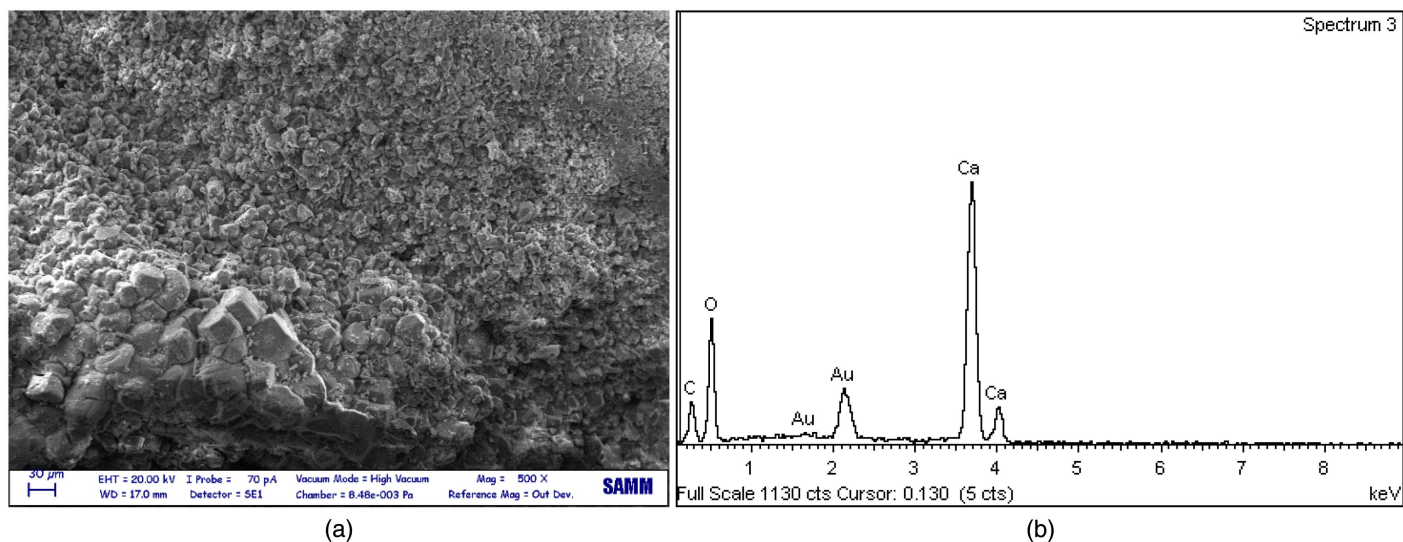


Fig. 8. (a) SEM image; and (b) EDS analysis of the healing product generated in a specimen without crystalline admixtures healed for 6 months in 16.5% NaCl aqueous solution.

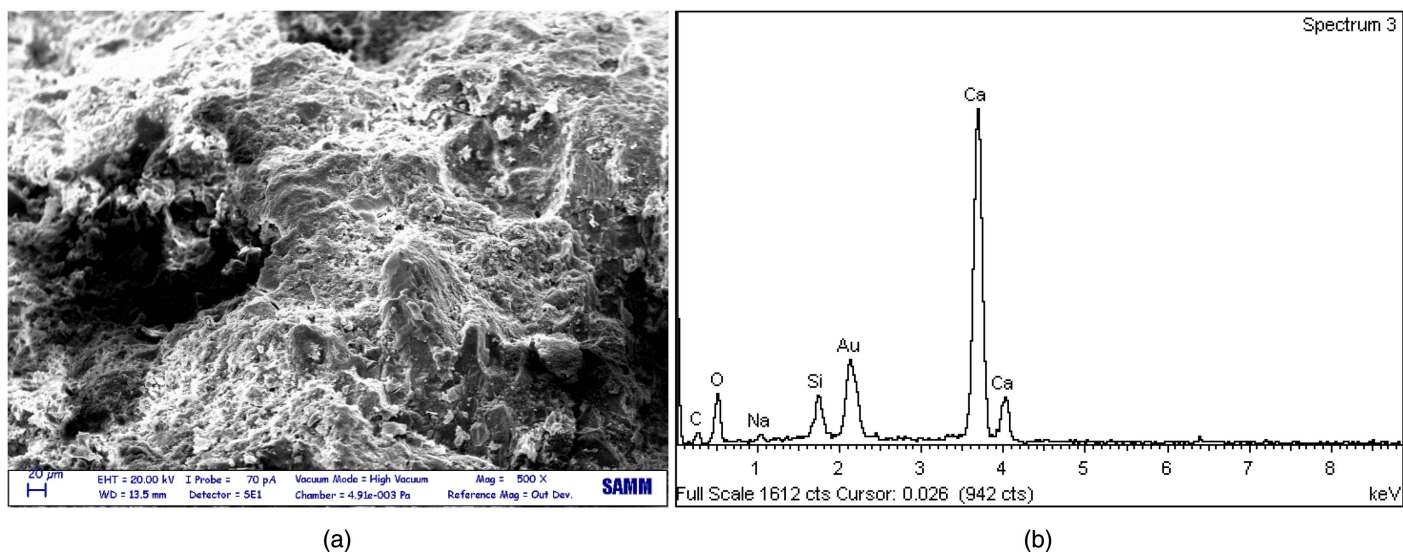


Fig. 9. (a) SEM image; and (b) EDS analysis of the healing product generated in a specimen with crystalline admixtures healed for 6 months in 16.5% NaCl aqueous solution.

case of the mix without crystalline admixtures, the healing product formed has a cubic shape, whereas when in the mix containing crystalline admixtures the healing product acquires a form of scab that, based on the SEM image, could be hypothesized as an amorphous structure. Consequently, the healing product generated in the presence of crystalline admixtures generate a continuous and dense scab very different from the discontinuous product formed by cubes observed when crystalline admixtures are not present. The presence of a continuous scab, which is also likely to be continuously generated thanks to the healing stimulating functionality of the admixture and guarantees also a rougher interface, is in agreement with the good performance observed in the chloride penetration profiles when crystalline admixtures were present (Fig. 5). EDS analysis of the healing products [Figs. 8(b) and 9(b)] shows primarily the typical elements of hydration products of cement (calcium, oxygen,

and silicon) being their chemical composition (precipitation of CaCO_3) very similar in both mixes. Moreover, from Fig. 9(b) it is observed a peak of silicon (Si) due to the presence of crystalline admixture that stimulates the production of new calcium silicate hydrates.

Conclusions

In this paper, the influence of crack healing on the recovery of mechanical properties (compressive strength) and on the reduction of chloride penetration was experimentally studied. Three different exposure conditions were investigated: water immersion in a 16.5% NaCl aqueous solution, wet/dry cycles with the same aqueous solution, and exposure to climate room (20°C and 95% RH). The influence of predamage, age of precracking, and curing periods were

also considered. Based on this experimental study, the following conclusions are drawn:

1. The samples cured in the 16.5% NaCl aqueous solution showed the highest benefits on the recovery of strength from the use of the healing agent (achieving an 5%–10% of strength improvement with respect to the reference mix without crystalline admixtures. The exposure to wet/dry cycles led to a slight enhancement of strength only when enough curing time was allowed.
2. Predamaging the samples with crystalline admixtures (by loading them up to 90% of their average compressive strength) appeared to not affect their mechanical behavior when cured in immersed condition because the recovery of compressive strength was, in most of the cases, slightly higher than 100%. This means that the strength of a healed specimen can be slightly higher than the strength of an undamaged companion analogously cured specimen at the same age. This could be explained by considering that the predamage allows some of the anhydrous particles inside the specimen to come into contact with water and further hydrate, thus contributing to its strength recovery.
3. Specimens predamaged at 7 days featured slightly higher recovery of strength rates and slightly higher crack closure percentages than those precracked at 28 days, especially for specimens immersed in chloride solution, reaching in both cases up to 10% of improvement for the specimens predamaged at 7 days compared with those predamaged at 28 days for the same healing period duration. This confirmed a better healing ability of younger concretes as compared with older ones. The area contaminated by chlorides in younger concretes, no matter cracked or not, was slightly higher (up to 10% of improvement) than those in the older ones as well.
4. For both types of concrete, with and without crystalline admixtures, it was observed that crack closure depends on crack width and curing time. The wider the crack, the lower the percentage of closure and, the longer the curing time, the higher the percentage of closure. However, a faster and more effective crack sealing was generally achieved by the samples containing the crystalline admixtures as healing stimulating agent. In fact, the sealing potential of small cracks (<0.4 mm) in concretes without crystalline admixtures after 3 and 6 months was comparable with the healing potential after 1 and 3 months, respectively, when crystalline admixtures were added in the mix. Moreover, after 3 months of healing, crack closures higher than 70% were only reached when crystalline admixtures were present.
5. According to the evolution of the chloride profiles, it has been observed that chloride content (% mass) increases gradually with the healing exposure time for the same distance from exposure surface. For instance, for a specimen without crystalline admixtures immersed in 16.5% NaCl solution a chloride content of 0.51%, 0.75%, and 0.85% were detected after 1, 3, and 6 months of exposure time, respectively. On the other hand, the chloride content (% mass) decreases gradually with the distance from exposure surface but, when crystalline admixtures are present in the mix, the chloride profile reached a stable value in a depth much closer to the exposure surface compared with the mix without crystalline admixtures.
6. A dependence between the area penetrated by chlorides ions and the crack width was generally observed. The higher the crack width, the lower the percentage of closure and the higher the area penetrated by chlorides. For instance, for a specimen without crystalline admixtures precracked at 7 days and immersed for 3 months, a crack width of 0.342 mm reached a crack closure of 63.2% with an area penetrated by chlorides of 92.9%, whereas, a crack width of 0.918 mm reached a crack closure of 7.1% with an area penetrated by chlorides of 95%.

7. SEM analysis showed different morphologies for healing products depending on the presence or not of crystalline admixtures. When crystalline admixtures are present, the healing product is a dense and rough scab very different from the discontinuous product formed by cubes when crystalline admixtures are not present. This result is in agreement with the good performance observed in the chloride penetration profiles for the mix with crystalline admixtures. EDS analysis of the healing products showed primarily the typical elements of hydration products of cement (calcium, oxygen, and silicon) being their chemical composition (precipitation of CaCO_3) very similar in both mixes. Moreover, when crystalline admixtures are present, silicon (Si) was detected in the sample that indicates that crystalline admixtures stimulate the production of new calcium silicate hydrates.

Data Availability Statement

All data, models, and code generated or used during the study appear in the published article.

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