An experimental methodology to assess the self-healing capacity of cementitious composites with “aero-crystallizing” additives

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ABSTRACT: The self healing capacity of cementitious composites employed for either new or reparing applications opens challenging perspectives for the use of a material intrinsically able to recover its pristine durability levels, thus guaranteeing a longer service life of the designed applications and a performance less sensitive to environmental induced degradation. One possibility of achieving the aforementioned self-healing capacity stands in the use of additives featuring a “delayed crystalline” activity, which, when in contact with water or atmosphere humidity, form chemical compounds which are able to reseal the cracks thus guaranteeing the partial recovery of the pristine mechanical performance. In order to quantify this self healing ability and its effects on the recovery of mechanical properties of the material, a methodology has been developed and will be presented in this paper. It consisted in pre-cracking up to different crack opening levels (a three point bending scheme with COD measurement was employed) prismatic beam specimens, made with both concrete added or not with the aforementioned additives. Specimens were then submitted to accelerated temperature and humidity cycles, representative of autumn climate conditions in northern Italy, for different exposure times. Finally, three point bending tests were performed on either uncracked or pre-cracked specimens and results, in terms of load-crack opening curves, were compared with those obtained from virgin specimens before any “conditioning”. This allowed crack “self-closure” to be evaluated and “self healing” indices to be defined and correlated, *e.g.*, to the load-recovery capacity.

1 INTRODUCTION

The self healing capacity of cement-based materials has been known for quite a long time, dating back to 1937, when Turner first recognized the occurrence of this phenomenon in several real cases, such as concrete water ducts and tanks, bridge piers and different kinds of prefabricated elements damaged by accidental impacts and vibrations.

Water, even in the form of environment moisture, is the foremost character of the play. The ability to self heal existing cracks is in fact primarily due to the hydration reactions of material constituents which are present on the cracked interfaces and ready to react with water penetrating into cracks. Due to these reactions, new hydrates and other minerals are formed, which are deposited along the surfaces of the crack, progressively reducing its width, and even until the continuity of the material can be fully recovered.

The mechanisms of self-healing of cracks was first explained by Lauer and Slate (1956), who demonstrated that the materials produced by the self-healing reactions consist of calcium hydroxide and calcium carbonate crystals. The latter are due to the reaction between calcium hydroxide, which is a product of cement hydration, and carbon dioxide present either in water or air. The consumption of calcium hydroxide on the crack surfaces generates its outward migration from inner concrete. At the same time, as long as the production of calcium carbonate continues, its crystals precipitate along the free surfaces of the crack.

Hearn and Moorley (1997) furthermore highlighted the importance of continuing hydration as a possible phenomenon to explain the self healing capacity of cementitious composites. In order continuing hydration to occur, not only water and anhydrous constituents are necessary but also free space for new hydration products is required. This, as explained by Neville (2002) is most likely to occur in early age concretes, where cracks are more tortuous, because of the lower strength and toughness of paste, and may expose to outdoor environment larger clusters of anhydrous cement particles. On the other hand, in old concretes, the material filling the cracks mainly consists of calcium carbonate, according to reaction mechanisms explained above.

Several variables, besides the presence of water and, in case, of carbon dioxide dissolved in it, may affect the phenomenon of self healing, such as:

- the mix constituents (Dhir et al., 1973, found that self healing is higher in mortars with a higher content of cement);
- the stress state along the cracks and the steadiness of the cracked state (Ngab et al., 1981);
- the temperature of the water (Reinhardt and Joos, 2003, found that a higher temperature of water acts in favor of self healing);
- or the alternation between water saturated conditions and exposure to air with different relative humidity.

If the mechanisms of self healing have been quite well understood and reaction products thoroughly characterized from a chemical point of view, the quantitative assessment of its effects on the engineering properties of concrete and cement based materials still needs and deserves a much deeper and more comprehensive dedicated investigation. Most of the surveyed studies (Hearn and Morley, 1997; Hearn, 1998; Edvardsen, 1999; Aldea et al., 2000) focused on the variation of water permeability and only very few among them (*e.g.* Dhir et al., 1973) the effects on strength recovery were analyzed.

The issue of self healing of cementitious composites has received new attention in these last years in the framework of two different cutting edge fields.

On one hand extensive research has been done and is currently on going with reference to the use in concrete of bacteria (de Boel, 2010), able to digest different substances and produce calcium carbonate which reseals the cracks.

The other main field of interest is represented by High Performance Fiber Reinforced Cementitious Composites (HPFRCCs), which are highly conducive to exhibit self healing capacity, as a concurrent outcome of the mix composition characterized by high dosages of cement and cement substitutes and low water/binder ratios and by the formation of stable multiple tiny cracks before the onset of unstable crack localization. As a matter of fact, because of the former, large amounts of anhydrous particles which feature either cementitious or pozzolanic activity can be exposed to atmosphere humidity and activate self-healing reactions upon cracking. Furthermore, because of the smaller width of each single crack, even complete resealing may be possible, which is also likely to result into a significant or even complete recovery of strength and strain capacity of the material, as a function of the exposure conditions and preexisting damage/cracking conditions (Yang et al., 2009). This opens, *e.g.*, interesting perspectives to the use of HPFRCCs in repairing old or damaged structures. First of all, the repairing materials is in fact intrinsically more durable, because of its high compactness and of the crack bridging effects exerted by fibers which help in controlling crack opening and hence prevents or reduces exposure to environment born aggressive agents. Furthermore, because of the self healing, the material is able to recovery its pristine level of durability and strength, with relevant outcomes, *e.g.*, on the whole life cycle of the structure.

Recently, so-called “aero-crystallizing” additives (ACI 2010) have also started being used, mainly as a tool to reduce water permeability of concrete, thus guaranteeing the tightness of structural elements, when required. This kind of additives contain substances which react with cement constituents and form calcium silicate hydrates. The reaction propagates through the concrete mass because of osmosis, Brownian motion and progressive involvement of anhydrous cement particles. The reaction products tend to fill the capillary voids, thus resulting in a system impervious to water and other environment born aggressive substances. The reaction consumes the moisture inside the concrete but can also undergo a delayed activation, whenever the material comes back into contact with water and/or environment moisture. This, as a matter of fact, can happen upon crack formation even at later ages. The effects of this kind of additives on triggering the self healing capacity of cracked concrete have not been so far investigated and hence deserve being assessed, in the sight of the aforementioned potential applications.

In order to quantify this self healing capacity and its effects on the recovery of mechanical properties a methodology has been developed and will be presented in this paper. It consisted in pre-cracking up to different crack opening levels (a three point bending scheme with COD control was employed) prismatic beam specimens, made with both concrete added or not with the aforementioned additive. Specimens were then submitted to different exposure conditions (natural winter or summer environment, underwater, accelerated temperature and humidity cycles respectively representative of winter or summer exposure conditions) for different times. Finally, end three point bending tests were performed on either uncracked or pre-cracked specimens and results, in terms of load-crack opening curves, were compared with those obtained from virgin specimens before any “conditioning”. This allowed recovery to be evaluated in terms of effective crack opening and “self healing” indices to be defined and quantified. It is worth remarking that the results presented in this study will only deal with accelerated climate chamber conditioning representative of winter exposure, which actually represents the first step of a wider on-going experimental project.

2 EXPERIMENTAL PROGRAM

This study focused on the assessment of the self healing capacity of cementitious composites and the reliability of aero-crystallizing additives to trigger and enhance it, quantifying its effects on the mechanical properties of the materials To this purpose two normal strength concretes were mixed (Table 1). The aero-crystallizing additive was dosed according to the prescriptions of the manufacturing company.

Table 1. Mix design of investigated concretes.

Constituent	without additive (kg/m^3)	with additive (kg/m^3)
Cement type II 42.5	300	300
Fine aggregate		
0-8 mm	975	975
Coarse aggregate		
8-16 mm	975	975
Water	165	165
(w/c)	0.55	0.55
Superplasticizer	3	3
Aero-Crystallizing Additive	=	3

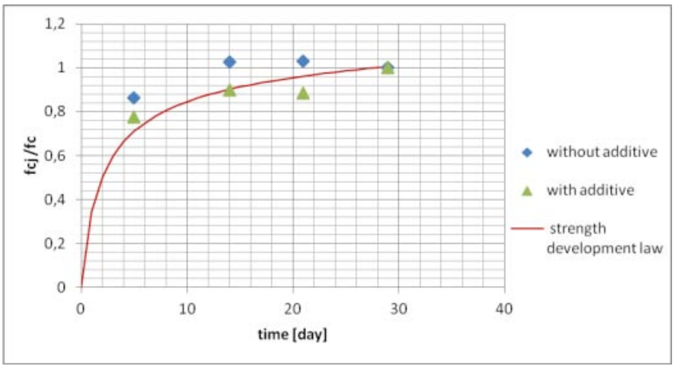


Figure 1: strength development of concrete with and without aero-crystallizing admixture and comparison with strength development rule of Eurocode 2.

Figure 2: 3-point bending test set-up

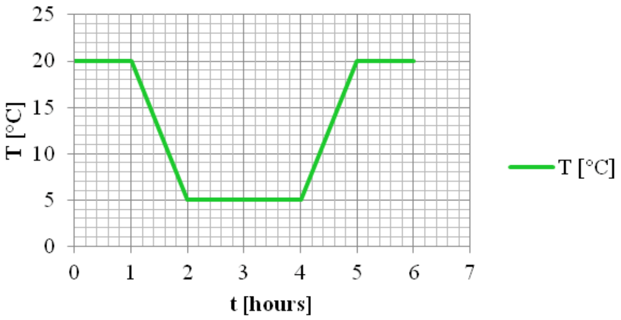


Figure 3: hygrothermal cycles

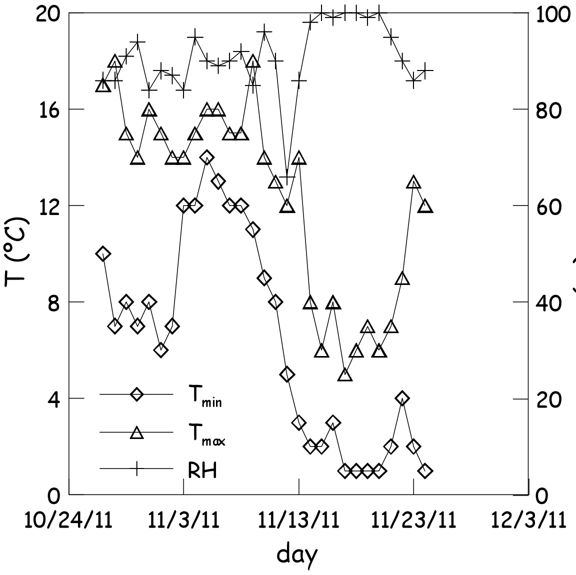
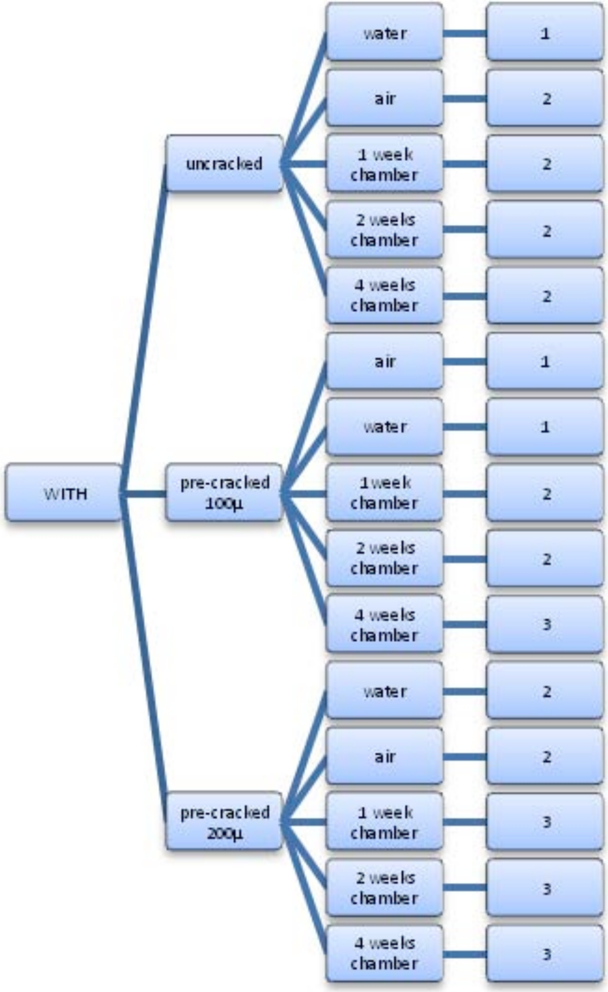


Figure 4: T and RH recorded during November 2011 in Milan

31 beam specimens, 50 mm thick, 500 mm long and 100 wide, were cast with each of the mixed concretes; the specimens, after 72h curing in lab conditions under quilts kept continuously wet, were stored in a moist room at 20°C and 95%RH for 35 days. Strength development was continuously monitored along this period, through compressive strength tests on companion 100 mm side cube specimens, showing no significant difference between concrete containing or not the crystalline additive (Figure 1).

At the end of the curing period, specimens made with each type of concrete were divided into three groups; specimens of two groups, for each concrete, were precracked, according to the 3-point bending test set-up shown in Figure 2, up to (residual) crack openings equal to about 130 and 270 μm respectively, whereas specimens belonging to the third group were left uncracked. It is worth remarking that tests were obviously performed assuming as feedback control variable the Crack Opening Displacement (COD), measured at the mid-span section by means of a clip-gauge.

Specimens were then put into a climate chamber and subjected to the temperature and humidity cycles sketched in Figure 3. Each six-hour cycle was meant to simulate, in an accelerated way, an average autumn day in northern Italy (see Figure 4 for records of temperature and humidity during the month of November in Milan). Specimens were kept into the climate chamber for four weeks, thus approximately simulating four months of real exposure. At the end of the first and second week, one third of each group of specimens (uncracked, pre-cracked at both 130 and 270 μm, and both containing or not the additive) was taken out of the chamber and subjected to three point bending tests, up to failure, still employing the same set.-up shown in Figure 1. Figure 5 shows a synopsis of the experimental program, including air exposure and water immersion conditions which will be not dealt with in this paper.



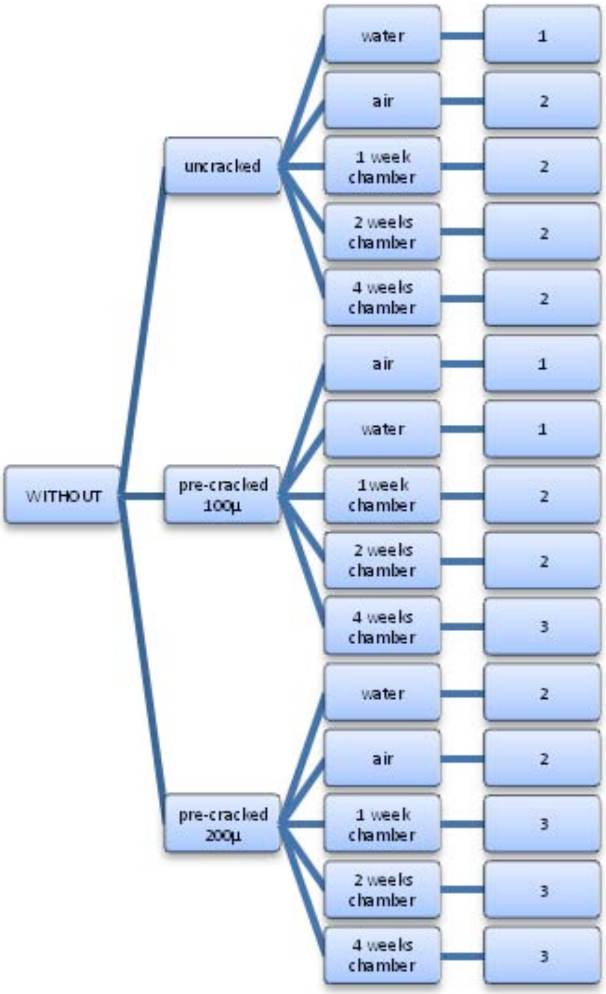
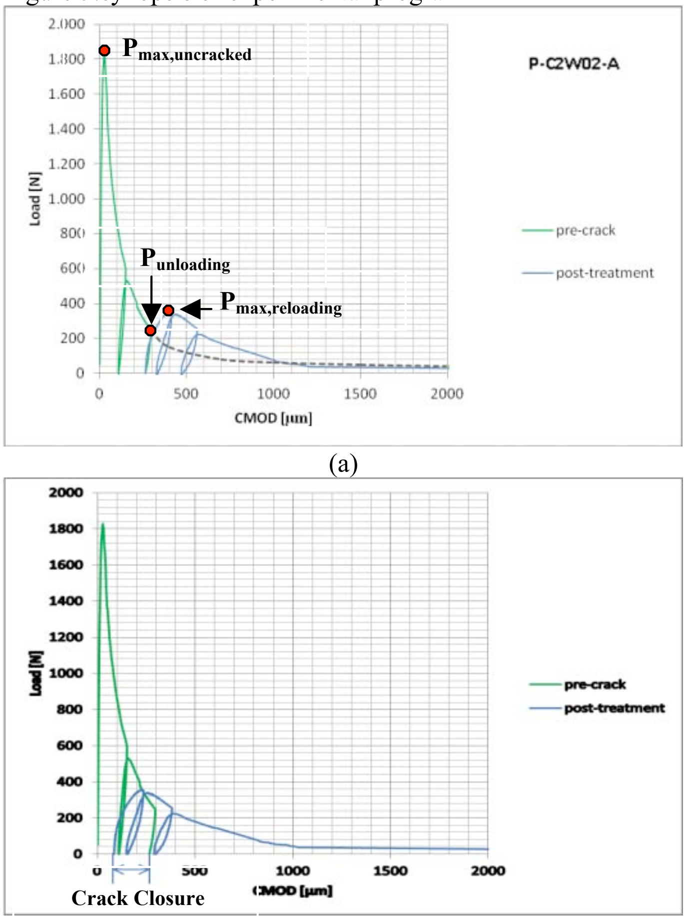


Figure 5:synopsis of experimental program



(a)

(b)

Figure 6: example of load-COD curve obtained from 3pb tests on the same specimen before and after hygrothermal conditioning showing strength recovery (a) and proposal of a procedure to evaluate crack closure (b)

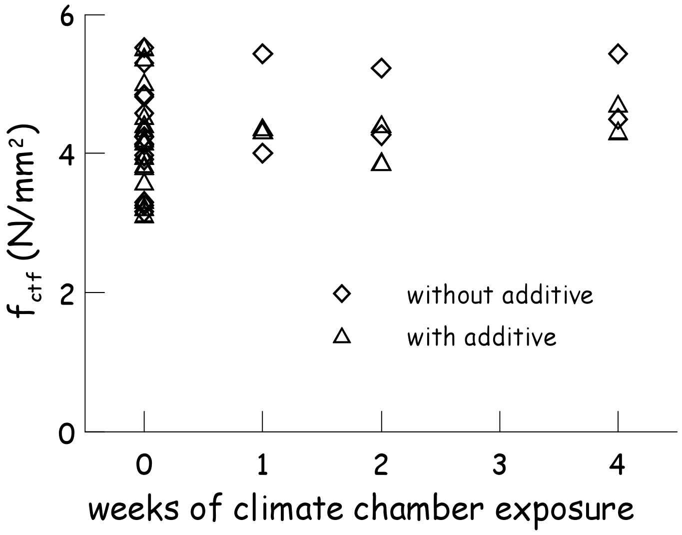
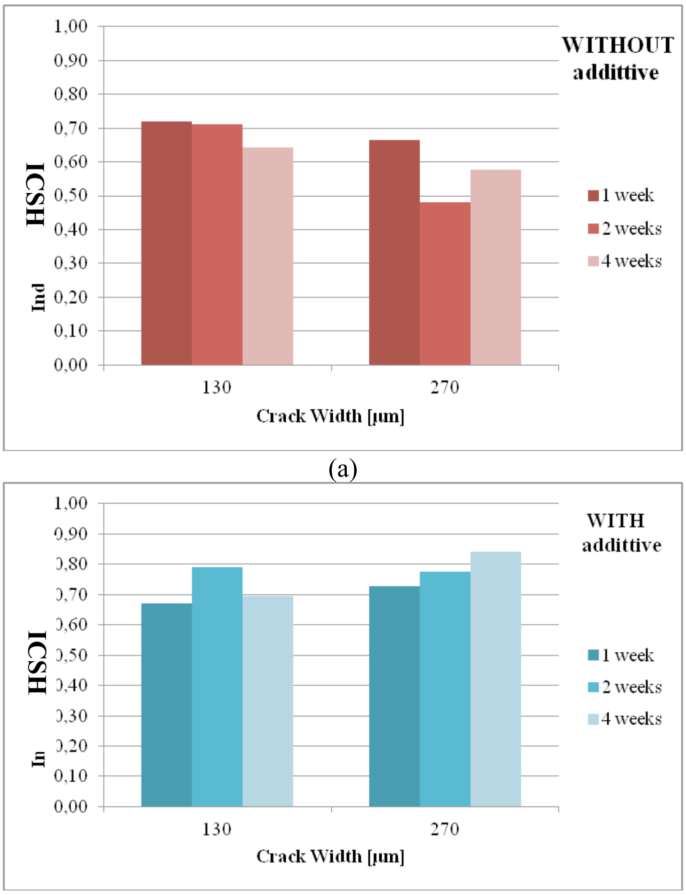


Figure 7: influence of climate chamber exposure on bending strength of unckracked beam specimens

3 EXPERIMENTAL RESULTS

Figure 6a shows an example of Load vs. COD curve, as recorded from the same specimen tested in 3-point bending before and after the exposure to hygrothermal cycles in the climate chamber. Consistently with the rationale of the testing program, the curve obtained after the climate chamber exposure has to be interpreted as a reloading of the specimen, following a previous unloading at a prescribed crack opening and the hygrothermal conditioning. An evident strength recovery capacity has been exhibited by the specimen, which, upon reloading, would have otherwise attained a strength level equal to the one at which is was previously unloaded. It is worth here remarking that all tested specimens featured the aforementioned strength recovery, obviously as a function of presence of the additive, duration of exposure to hygrothermal conditioning and width of the pre-induced crack.

It can be reliably hypothesized that the strength recovery occurred right because of the self healing, which led to a partial closure of the previously created crack. The comparison (Figure 7), in terms of flexural strength, between specimens tested at the end of the curing period, *i.e.* before any kind of exposure or hygrothermal conditioning, and uncracked specimens tested after it, supports this assumption, showing no significant occurrence of continuing hydration for uncracked specimens and hence for the bulk material. On the contrary it can be reliably hypothesized that because of the cracking, some unhydrated material inside the specimens was exposed to environment moisture, which activated, in case also through the aid of the additive, the chemical reactions featuring the self healing phenomena.



(a)

(b)

Figure 8: Index of Crack Self Healing (ICSH), evaluated for concretes without (a) or with (b) crystalline admixture, as a function of crack opening and exposure duration.

In order to quantify the crack-strength recovery and the effects on it of the variables recalled above, the following procedure has been adopted as hereafter proposed. The post-conditioning load-COD curve has been rigidly shifted backward along the axis of abscissae (Figure 6b), until its peak load point intersected the softening branch of the virgin load-COD curve. The reasonable matching of softening branches after this shifting may be called to confirm the reliability of the proposed procedure. It is furthermore worth remarking that what has been shown in Figure 6b with reference to one experimental case has been significantly systematically obtained for all the tested specimens. The aforementioned shifting led to a new position the origin of the post-conditioning curve, originally assumed equal to the residual crack-opening upon unloading the virgin specimen after pre-cracking tests. The amount of this shifting could hence been assumed to quantify the crack closure, and its ratio to the previous residual crack opening was defined as Recovery Index or Index of Crack Self-Healing (ICSH). This has been plotted, in Figure 8a-b, for concretes both containing or not the additive, as a function of the previous crack width and of the duration of exposure.

The following statements hold:

- even normal strength concrete, mixed with medium to high water/cement ratios, is likely to exhibit, after conventional aging time (> 28 days), a not negligible capacity to self-heal cracks which may be created by applied loads; this is most likely due to continuing hydration of anhydrous cement particles present on cracked interfaces and exposed to water or even to environment moisture upon cracking. This capacity anyway appears to be randomly scattered and not affected by the duration of the exposure to high humidity;

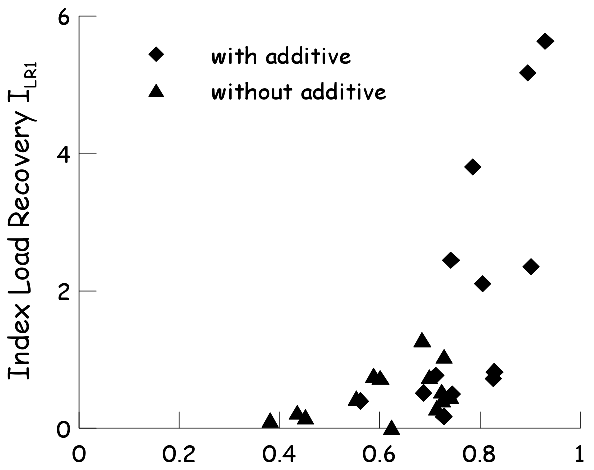
- the addition of aero-crystallizing admixture enhances the aforementioned self-healing capacity, which appears to increase with the time of exposure to high moisture and, most of all, is significant even for higher crack opening.

The consistency and significance of the ICSH defined as above clearly appear if correlated to other parameters which can be regarded as representative of the recovery of the mechanical performance of the material. In Figure 9 it has been assumed as the variable governing the load recovery capacity, referred to either the material virgin or post-cracking residual strength, and quantified through the following indices of load recovery (I_{LR} – see notation in Figure 6a):

$$I_{LR1} = \frac{P_{max,reloading} - P_{unloading}}{P_{unloading}} \qquad (1a)$$

$$I_{LR2} = \frac{P_{max,reloading} - P_{unloading}}{P_{max,uncracked}} \qquad (1b)$$

In both cases the improvements, even remarkable, which can be achieved thanks to the additive clearly appear. They can be most likely attributed to the capacity of the additive itself to react with environment moisture and concrete hydration products forming self healing compounds.



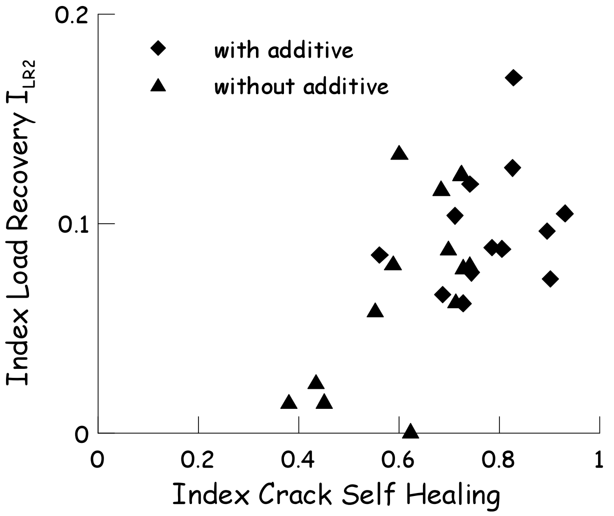


Figure 9: Indices of Load Recovery I_{LR1} and I_{LR2} vs. ICSH

4 CONCLUSIONS AND FURTHER WORK

In this study a methodology has been proposed to measure and quantify the effects of self-healing on the mechanical properties of cement based materials. The methodology is based on pre-cracking beam specimens to prescribed crack-widths, exposing them to suitable real or artificial environment conditions, and, after that, testing them again until failure according to the same set-up employed for pre-cracking. Self-healing capacity has been evaluated by seeking suitable matching between the load-crack opening curves obtained for the virgin specimen and for the conditioned one.

In this paper only artificial exposure conditions, corresponding to autumn Northern Italy climate, have been considered, as a start-up of a more comprehensive research program.

It has been shown that cementitious materials inherently possess, within an acceptable range, some self-healing capacity, most likely due to continuing hydration favored by suitable environment conditions, which is anyway randomly scattered.

The inclusion in the concrete mix of aero-crystallizing admixtures not only enhances the aforementioned self-healing capacity, even up to more than 80% recovery of the crack opening, but also makes it more reliable and consistent.

The proposed methodology, as well as the previous statements referring to the effects of self-healing, needs to be assessed and confirmed with reference to a much wider variability of natural and artificial exposure conditions (different hygrothermal cycles, natural exposure, water immersion, wet-and-dry cycles even in marine-like environment etc.). Characterization of self-healed cracked interfaces through microscopy observation is also needed and currently ongoing. This will be surely instrumental to gain a stronger confidence in the self-healing phenomenon and its effects on mechanical properties of cementitious composites, which is of the utmost importance in order to consistently take them into account in the framework of durability-based design approaches.

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