POLITECNICO DI TORINO

Master's Degree in Civil Engineering

Master's Degree Thesis

Study of the performance of waterproofing additives capable of promoting the Self-Healing in Concrete

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To my mom, dad

and brother.

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Abstract

Over time, the world of Civil Engineering has turned its attention to create structures under the concepts of sustainability and durability by reducing the consumption of raw materials and avoiding the emission of toxic gases that harm the environment. In addition, the scientific research community has focused on the study of resilient and intelligent materials capable of promoting multiple benefits, both economic and ecological, promoting sustainability.

One of the most used materials in the construction world is concrete due to its multiple benefits, versatility in its use, excellent mechanical properties. However, with the pass of time, the works carried out with concrete require maintenance to ensure the superb condition of its design; this means using time and resources. Therefore, if one could guarantee that concrete works could heal themselves when required, not only would large amounts of resources be saved, but it would also change the way construction has been perceived so far.

Self-healing concrete is a mechanism that is naturally or artificially induced. For example, concrete with damage can activate these mechanisms and initiate a self-healing process, the cracks will close, and mechanical properties lost are partially recovered.

This work proposes the study of the influence of two crystallizing additive and treatment in promoting self-healing concrete, such as Admixplus and Multiseal, products of the company Supershield Srl. This experimental campaign has three phases which can be summarized as: pre-damage, where the specimens to be studied are created, the control specimens are distinguished from those where the respective products are added and are kept in different conditions of exposure to the samples, submerged in water or exposed to air; damage, where the damage is created employing a compressive strength test, in displacement controlled mode; post-damage, whereafter the procedure of making the cracks, the specimens are kept for a certain

period in different exposure conditions (submerged in water, exposed to air or with sprayed water).

At each stage, measurements are made using the ultrasonic pulse velocity test, which provides us with knowledge regarding cracked specimens in each campaign phase. The compressive strength test results, the influence of the test setups, the exposure conditions, the admixture used, and the visual evaluation of self-healing are analyzed and discussed.

The present study results show, regarding the initial exposure conditions, more significant percentage increases in the samples compressive strength exposed in air, the specimens immersed in water show higher values of resistance to compression. Therefore, Admixplus is more beneficial in terms of the increase in compression resistance values. Likewise, the force-controlled test setup influences the results, incrementing compressive strength values compared with the specimens under displacement-controlled setup.

As part of the UPV results obtained, it is evidenced the presence of water is essential to promote self-healing, the more water the specimens are exposed, the better the results obtained from the self-healing, it is also observed humidity of the environment it is not enough to activate the mechanisms of the crystallizing additive and treatment.

Sommario

Nel tempo, il mondo dell'Ingegneria Civile ha rivolto la propria attenzione alla realizzazione di strutture all'insegna della sostenibilità e della durabilità riducendo il consumo di materie prime ed evitando l'emissione di gas tossici dannosi per l'ambiente. Inoltre, la comunità di ricerca scientifica si è concentrata sullo studio di materiali resilienti e intelligenti in grado di promuovere molteplici benefici, sia economici che ecologici, favorendo la sostenibilità.

Uno dei materiali più utilizzati nel mondo delle costruzioni è il cemento per i suoi molteplici vantaggi, versatilità nel suo utilizzo, ottime proprietà meccaniche. Tuttavia, con il passare del tempo, le opere realizzate con il calcestruzzo necessitano di manutenzione per garantire la superba condizione del suo progetto; questo significa impiegare tempo e risorse. Pertanto, se si potesse garantire che le opere concrete possano autoguarirsi quando necessario, non solo si risparmierebbero grandi quantità di risorse, ma cambierebbe anche il modo in cui la costruzione è stata finora percepita.

Il calcestruzzo autorigenerante è un meccanismo indotto naturalmente o artificialmente. Ad esempio, il calcestruzzo danneggiato può attivare questi meccanismi e avviare un processo di autoriparazione, le crepe si chiuderanno e le proprietà meccaniche perse verranno parzialmente recuperate.

Questo lavoro propone lo studio dell'influenza del additivo e trattamento cristallizzanti nella promozione del calcestruzzo autorigenerante, come Admixplus e Multiseal, prodotti dell'azienda Supershield Srl. Questa campagna sperimentale prevede tre fasi che possono essere riassunte come: pre-danno, dove vengono creati i campioni da studiare, si distinguono i campioni di controllo da quelli in cui vengono aggiunti i rispettivi additivi e vengono mantenuti in diverse condizioni di esposizione ai campioni, immerso in acqua o esposto all'aria; danno, in cui il danno viene creato impiegando una prova di resistenza alla compressione, in modalità a spostamento controllato; dopo il danneggiamento, dopo la procedura di realizzazione delle

fessurazioni, i campioni vengono conservati per un certo periodo in diverse condizioni di esposizione (immersi in acqua, esposti all'aria o con acqua nebulizzata).

In ogni fase, le misurazioni vengono effettuate utilizzando il test della velocità dell'impulso ultrasonico, che ci fornisce le conoscenze sui campioni incrinati in ogni fase della campagna. Vengono analizzati e discussi i risultati del test di resistenza alla compressione, l'influenza delle impostazioni del test, le condizioni di esposizione, gli additivi utilizzati e la valutazione visiva dell'auto-riparazione.

I risultati del presente studio mostrano, rispetto alle condizioni di esposizione iniziale, incrementi percentuali più significativi della resistenza a compressione dei provini esposti in aria, i provini immersi in acqua mostrano valori di resistenza alla compressione più elevati. Pertanto, Admixplus è più vantaggioso in termini di aumento dei valori di resistenza alla compressione. Allo stesso modo, la configurazione del test a forza controllata influenza i risultati, aumentando i valori di resistenza alla compressione rispetto ai provini con configurazione a spostamento controllato.

Nell'ambito dei risultati UPV ottenuti si evidenzia la presenza di acqua indispensabile per favorire l'Autoguarigione, più acqua sono esposti i campioni, migliori sono i risultati ottenuti dall'Autoguarigione, si osserva anche l'umidità dell'ambiente non è sufficiente attivare i meccanismi degli additivi cristallizzanti.

Resumen

Con el tiempo, el mundo de la Ingeniería Civil ha centrado su atención en crear estructuras bajo los conceptos de sostenibilidad y durabilidad reduciendo el consumo de materias primas y evitando la emisión de gases tóxicos que dañan el medio ambiente. Además, la comunidad de investigación científica se ha centrado en el estudio de materiales resilientes e inteligentes capaces de promover múltiples beneficios, tanto económicos como ecológicos, promoviendo la sostenibilidad.

Uno de los materiales más utilizados en el mundo de la construcción es el hormigón por sus múltiples beneficios, versatilidad en su uso, excelentes propiedades mecánicas. Sin embargo, con el paso del tiempo, los trabajos realizados con hormigón requieren de un mantenimiento para asegurar el inmejorable estado de su diseño; esto significa usar tiempo y recursos. Por tanto, si se pudiera garantizar que las obras de hormigón se curan solas cuando sea necesario, no solo se ahorrarían grandes cantidades de recursos, sino que también se cambiaría la forma en que se ha percibido la construcción hasta ahora.

El hormigón autocurativo es un mecanismo que se induce de forma natural o artificial. Por ejemplo, el concreto dañado puede activar estos mecanismos e iniciar un proceso de autocuración, las grietas se cerrarán y las propiedades mecánicas perdidas se recuperan parcialmente.

Este trabajo propone el estudio de la influencia del aditivo y tratamiento cristalizante en la promoción del hormigón autorreparador, como lo son Admixplus y Multiseal, productos de la empresa Supershield Srl. Esta campaña experimental tiene tres fases las cuales se pueden resumir en: pre-daño, donde se crean las probetas a estudiar, las probetas de control se distinguen de aquellas donde se agregan los respectivos aditivos y se mantienen en diferentes condiciones de exposición a las muestras, sumergido en agua o expuesto al aire; daño, donde el daño se crea empleando una prueba de resistencia a la compresión, en modo de desplazamiento controlado; post-daño,

después del procedimiento de hacer las grietas, las muestras se mantienen durante un cierto período en diferentes condiciones de exposición (sumergidas en agua, expuestas al aire o con agua pulverizada).

En cada etapa, las mediciones se realizan mediante la prueba de velocidad de pulso ultrasónico, que nos proporciona conocimientos sobre las muestras agrietadas en cada fase de la campaña. Se analizan y discuten los resultados de la prueba de resistencia a la compresión, la influencia de las configuraciones de prueba, las condiciones de exposición, los aditivos utilizados y la evaluación visual de la autocuración.

Los resultados del presente estudio muestran, con respecto a las condiciones de exposición inicial, incrementos porcentuales más significativos en la resistencia a la compresión de las muestras expuestas al aire, las muestras sumergidas en agua muestran valores más altos de resistencia a la compresión. Por lo tanto, Admixplus es más beneficioso en términos de aumento de los valores de resistencia a la compresión. Del mismo modo, la configuración de prueba controlada por fuerza influye en los resultados, aumentando los valores de resistencia a la compresión en comparación con las muestras en la configuración controlada por desplazamiento.

Como parte de los resultados de la UPV obtenidos, se evidencia que la presencia de agua es fundamental para promover la Autocuración, a más agua se exponen los ejemplares, mejores son los resultados obtenidos de la Autocuración, también se observa la humedad del ambiente. no basta con activar los mecanismos de los aditivos cristalizantes.

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Chapter 1: Introduction

1.1 Engineering motivation

The cities development measures the evolution of countries over time; one of the main variables commonly used to quantify it is structure's constructions such as buildings, houses, hospitals, and infrastructure. Thus, the direct relationship between economic development and construction in the world allows us to evaluate the economic and territorial evolution of the world's cities.

The durability of the constructions represents a fundamental characteristic when planning any civil engineering work, which translates into preserving lives, safety, and the economic benefit of knowing that the structures will last over time. Different factors play a fundamental role in the durability and sustainability of structures. Construction materials certainly play an essential role. Concrete is part of the most used construction materials in the world and one of its principal components is cement. The U.S consumption of cement in 2020 was about 102.000 metric tons as reported in Figure 1. There are different reasons why this phenomenon occurs, among them the capacity concrete has to resist compressive forces, its versatility since it is capable of adopt an endless number of forms, its resistance to fire. However, concrete is characterized by a low resistance to tensile stresses, which is the reason reinforcing steels are used to counter this characteristic, thus forming what is known as reinforced concrete.

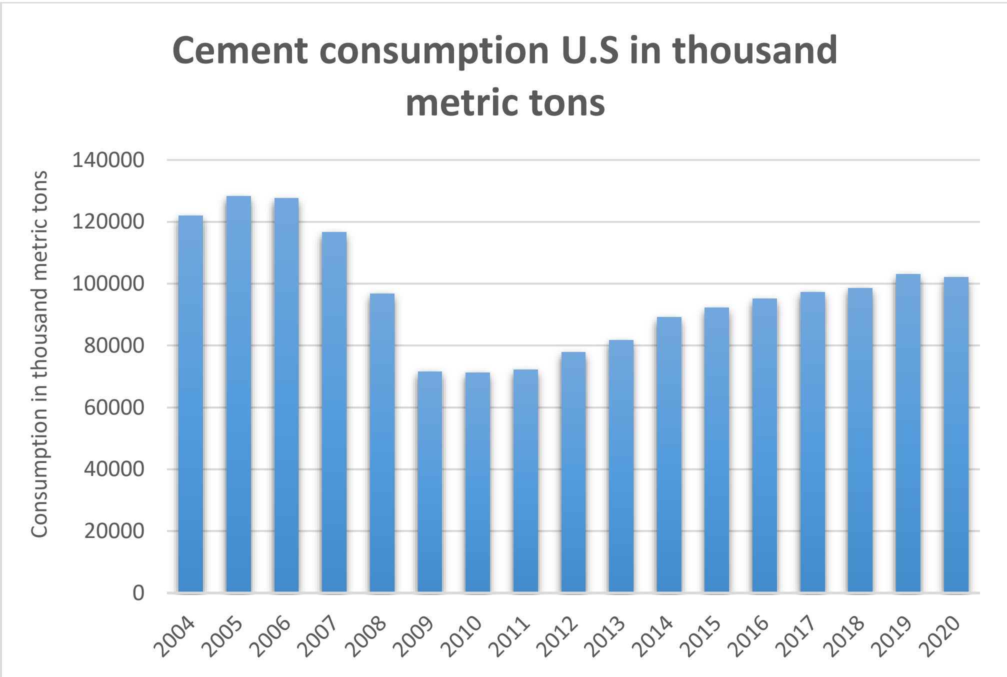

Figure 1: Cement consumption U.S in thousand metric tons

As said before, the durability of the materials used in construction is essential. Moreover, over time structural design requires materials with excellent mechanical properties, which allows creating better structures.

Formation of cracks, even small cracks (100 – 300 μm), favors the entry of unwanted agents to the concrete matrix, which represents a threat to the dynamics that exist between the concrete compounds, creating problems that can weaken structures in the long term and cause significant stability problems and therefore safety problems in buildings.

Everyday science aims to create materials that are smart and provide an ecological benefit for the sustainability of our planet. The French academy presents the self-healing concrete definition in 1836, which explains the capacity that concrete has to heal itself under certain conditions. The implementation of self-healing provides excellent benefits for the structures and infrastructures in concrete. Integrate this technology in future constructions translates into new paradigms for the creation of resilient structures.

Furthermore, concrete can self-heal or activate intrinsic mechanisms to start the self-healing process, and this affects the maintenance of structures as it is known today. With the use of self-healing concrete it is possible to obtain durable constructions, where the expense produced in their constant maintenance is reduced. This not only means economic savings, but also less use of material, less consumption, less damage to the environment (Ferrara et al., 2018).

Self-healing of concrete can occur in two ways: autogenous approach, which is a natural process produced by continuous hydration or carbonation, and autonomous approach, which implies the use of specific agents to stimulate self-healing. These agents can be introduced in the concrete matrix in different ways that will be discussed in the subsequent chapters (de Rooij et al., 2013).

Implementing the self-healing process in the world construction industry represents an innovation in the use of concrete; therefore, a new way to create sustainable and long-lasting structures is possible, it is the future.

1.2 Research objectives

This work aims to evaluate the phenomenon of self-healing in concrete promoted by waterproof crystallizing additive and treatment through an experimental campaign where different scenarios are compared before and after the damage.

Specific objectives include:

- To develop a literature review among the most recent publications related to self-healing and the use of crystallizing additives.
- To propose a methodology for the evaluation of self-healing oriented to the use of the ultrasonic pulse velocity test and the visual identification of the closure of cracks.
- To compare the setups implemented in the different phases of the self-healing evaluation process and evaluate how it affects the expected results.
- To evaluate the effect of different types of curing conditions and the use of crystallizing admixtures on the compressive strength of concrete.
- To study the influence of the specimen conditioning environment after the damage phase and the use of crystallizing additives and treatments in the self-healing phenomenon after a prolonged period.

1.3 Manuscript Organization.

This work is organized into five chapters, each one composed as follows:

- The first chapter is the present introduction to this study. Then, the motivation to carry out this dissertation is explained, and the objectives are proposed and a brief description of each chapter.

- The second chapter includes a literature review, where the concepts and definitions necessary to understand the self-healing process in concrete and its types are introduced and explained, making particular reference to self-healing with crystallizing additives.

- The third chapter explains the experimental campaign, starting with the materials and equipment used, a description of the specimen preparation process, and its name. Next, the methods used to evaluate the self-healing of concrete are explained from the evaluation of the initial concrete properties, pre-cracking process, curing conditions and time, and evaluation after conditioning.

- The fourth chapter shows the results obtained in the experimental campaign and their analysis. Furthermore, a broad perspective is given of how the crystallizing additive or treatment and other variables influence the self-healing of concrete, evidenced, and evaluated.

- The fifth and final chapter compiles the conclusions obtained from the analysis carried out in the previous chapter and the recommendations and future perspectives for the study of self-healing of concrete.

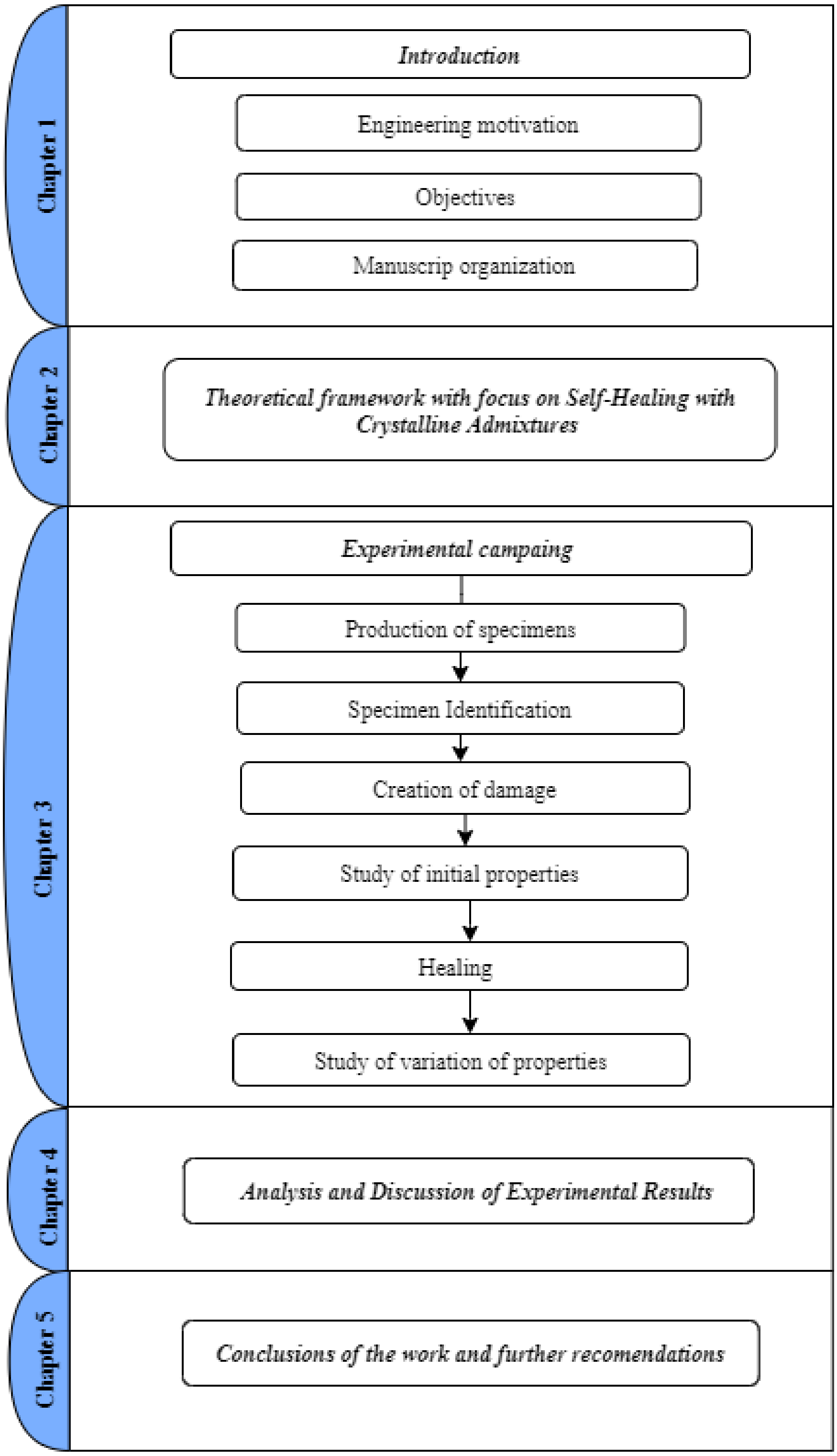

Figure 2: Manuscript organization.

Chapter 2:

Theoretical framework

2.1 Introduction

Self-healing approach has been inspired in how our body can heal itself, after falling and breaking a bone, a muscle tear or wound the skin, our body begins a natural self-healing process promoted by cells (collagen protein) that act to restore the initial condition before the damage, the recovery of its initial properties (Wallace et al., 2021). When a wound is made in the skin, it opens the possibility to allow bacteria get in, the body itself make a coordinate process to seal up the wound, the time is an important factor, as much time passes with this gap bigger the possibility to have worse consequences, likewise similarity can be made to the self-healing process in concrete.

The cracks found in the first stages of concrete are normal due to different shrinkage processes (Day, 2021) also to stresses that it experiences, and does not affect its structural functioning, furthermore and depending on the size of the cracks, these can compromise the integrity of concrete properties, its durability, being an influencing factor in the possible entry of unwanted agents into the interior of our structural elements, such as beams, columns, slabs, these agents can trigger processes such as carbonation, corrosion of reinforcing elements in the case of reinforced concrete a representation is shown in figure 3 which should be avoided at all costs (Roig-Flores et al., 2021).

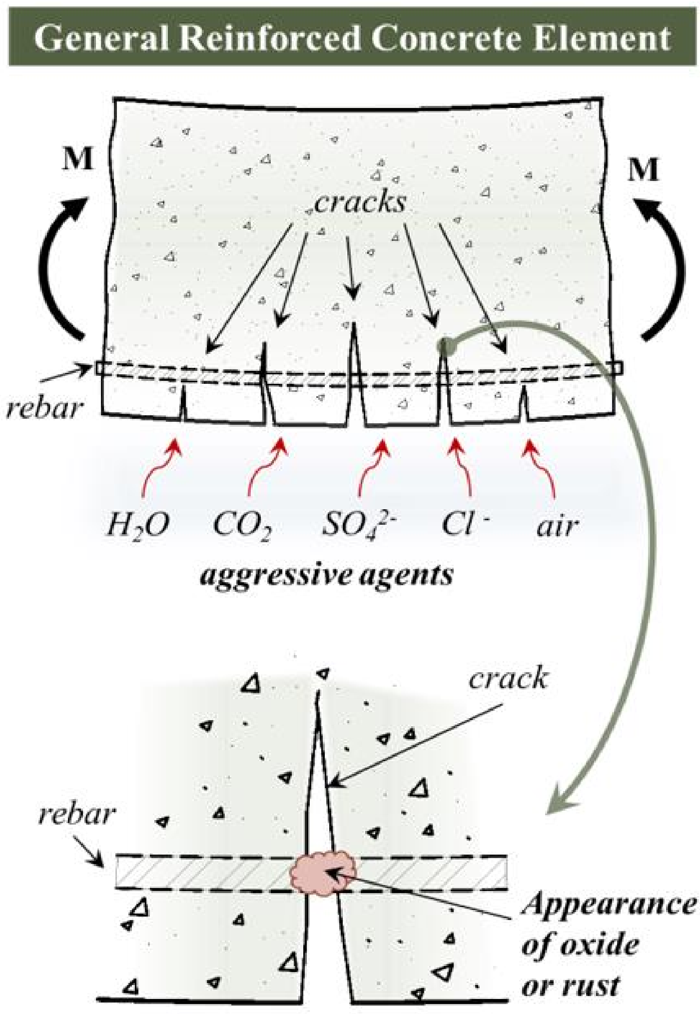

Figure 3: General diagram of a reinforced concrete element.

Concrete gives way to its implementation in most structures such as bridges, viaducts, tunnels, roads, buildings, houses, etc., the production of cement, one of the main components of concrete, in 2020 was about 4.1 billion tons as can be seen in figure 4, the importance of concrete's good condition over time translates into the safety of the people who make lives in these structures, so it is essential to ensure not only that it complies with the estimated requirements in the structural design, that is to say with its mechanical properties but also with their durability over time (Garside M., 2021) .

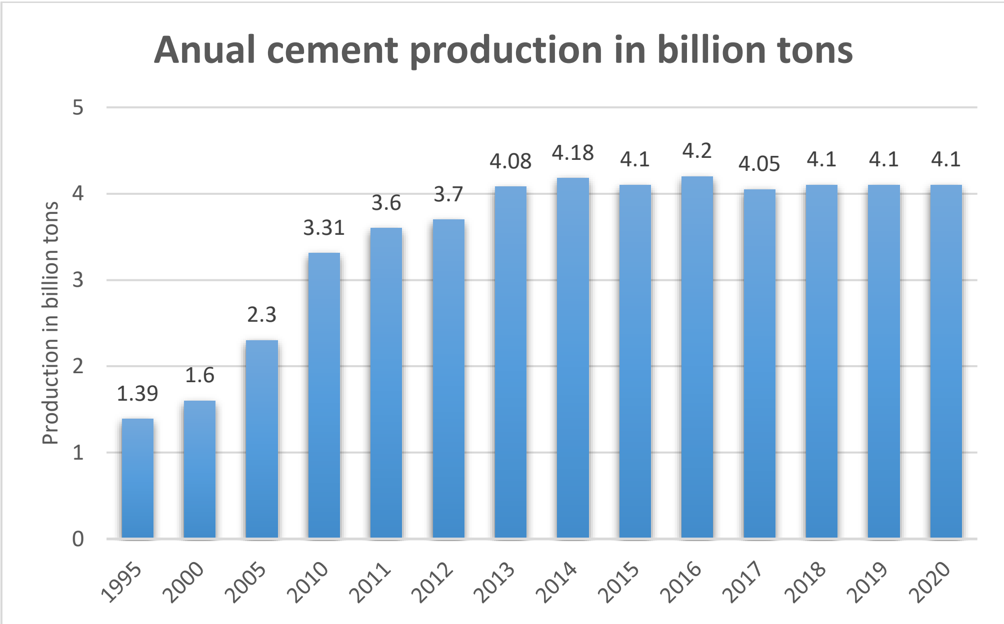

Figure 4: Cement production worldwide from 1995 to 2020 (in billions tons).

This chapter presents the most relevant definitions and concepts necessary to understand this work, contributions from different authors to this line of research, as well as the most recent studies regarding self-healing concrete with crystalline admixture.

2.2 Self-healing phenomenon

The first evidence of self-healing was found by the French Academy of Sciences in 1836, they found this phenomenon in fractured hydraulic structures, Hyde and Smith, studied the permeability of cements and cement mortars, in their specimens and in structures such as tunnels and aqueducts, noticing the evidence of self-healing (Hyde & Smith, 1889).

K.R Lauer and F. O Slate, evaluate the influence of water on the self-healing phenomenon, where they found that the presence of water was essential to find the largest closed of cracks, in environments with less water, the resistance obtained were minor, furthermore, they found that in order to seal the cracks it was necessary that the concrete was wet, identified that there is a proportionality between the time the sample spent in water and the amount of surface of the crack sealed with crystals, which the longer the period, the larger the crystals formed (Lauer & Slate, 1957).

Hearn and Morley (1997) evaluated the flow of water through saturated concrete, stating that permeability can be used as a measure of the concrete's immune system, evidencing the importance of water to activate self-sealing mechanisms in cementitious materials, specifying also the different mechanism promoting self-healing concrete.

Over the decades, the interest of the scientific community in self-healing concrete has grown, so it has emerged the need to make a self-healing of concrete and reinforced concrete definition, with the pursuit of creating a theoretical framework in which further research can be sustained; JCI (Japanese Concrete Institute) TC-075B began with the process of creating concepts (Igarashi et al., 2009), which then RILEM (Reunion Internationale des Laboratoires et Experts des Materiaux, Systemes de Construction et Ouvrages) adopt, this latter has played an essential role in the unification of the terminology, from where an internationally accepted definition for self-healing and its relative concepts have been created (de Rooij et al., 2013).

Introducing self-Healing in concrete concept, it is a phenomenon in which the material itself, through different processes, natural or artificial, recovers and, in some cases, improves its initial properties, repairing its cracks after an action that altered the expected material's state (de Rooij et al., 2013).

The process of self-healing in concrete has two different scenarios as illustrated in figure 5 which can be experienced or implemented, it will depend on the approach followed to activated self-healing, which are mainly natural also called Autogenous or artificial also known as Autonomous, both are explained in detail in the following sections.

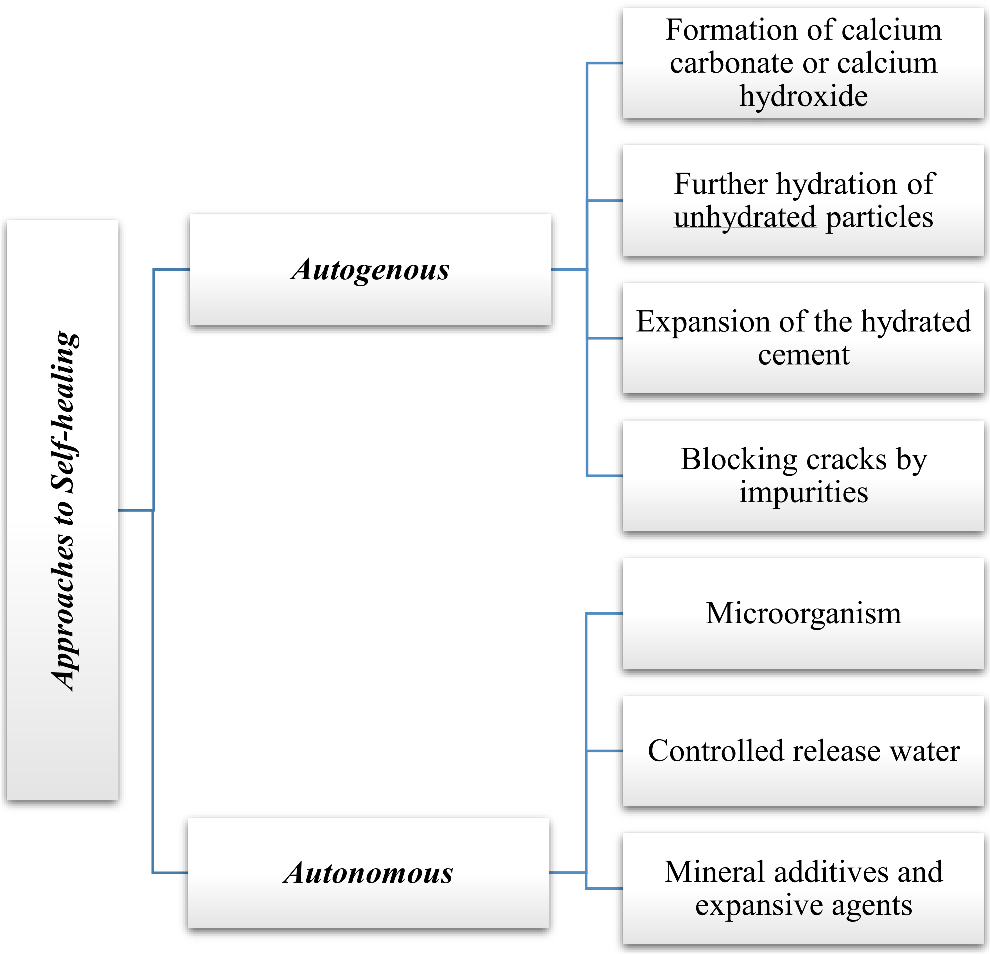

Figure 5: Approaches to self-healing (Coppola et al., 2018)

2.2.1 Autogenous Self-Healing

The process known as ***Autogenous self-healing***, some authors called it natural healing (Mihashi & Nishiwaki, 2012), is an intrinsic activity of the materials composing the initial matrix of the concrete, whose even when are not meant to be added for propitiating self-healing, has been observed that naturally the mechanism is activated, this is a process that not requires any external intervention but it is generated by the hydration of un-hydrated particles in the cementitious components, also can take place as a result of the precipitation of calcium carbonate (CaCO3), carrying out total or partial closure of small cracks between 10- 100 µm (De Belie et al., 2018) also the recovery of properties as a result .

Although, over time the cause of producing self-healing has been attributed to different mechanisms, at present these have been studied and defined, explained in RILEM state of the art (de Rooij et al., 2013), they have been classified according to its causes as shown below Figure 7.

- ***Physical causes:***

Matrix swelling:
Due to a saturation in the matrix, an increase in volume take place, as a consequence of the water path in the cement matrix causing also shrinkage, as previously said even when shrinkage plays an important role in terms of durability and with time can compromise the structural function of the concrete structures (Van Tittelboom, K.; Snoeck, D.; Wang, J.; De Belie, 2013).

- ***Chemical causes:***

Continued hydration:
Concrete in an early age start the hydration process, in which the cement/water ratio is the principal variable also the humidity influence this process, furthermore, during this process an among the components of concrete, some particles do not hydrate, then

these are hydrated when they encounter water, which produces derivatives that fill the cracks, Hearn and Morley studied this phenomenon in 26 years old concrete, they stated that did not find any un-hydrated particles in this specimens due to age (Hearn & Morley, 1997).

Calcium carbonate formation:

Calcium carbonate is formed when the portlandite and carbon in dioxide contact with water react and fill the crack, the quantity of calcium carbonate produced will depend on the amount of CO_2 present.

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \qquad (1)$$

When a crack is found in a concrete element, the equation (1) shown above presents the reaction of calcium ions Ca^{2+} of concrete matrix and carbonate ions CO_3^{2-} that are present in water or in carbon dioxide CO_2 from the incoming air which produce calcium carbonate $CaCO_3$.

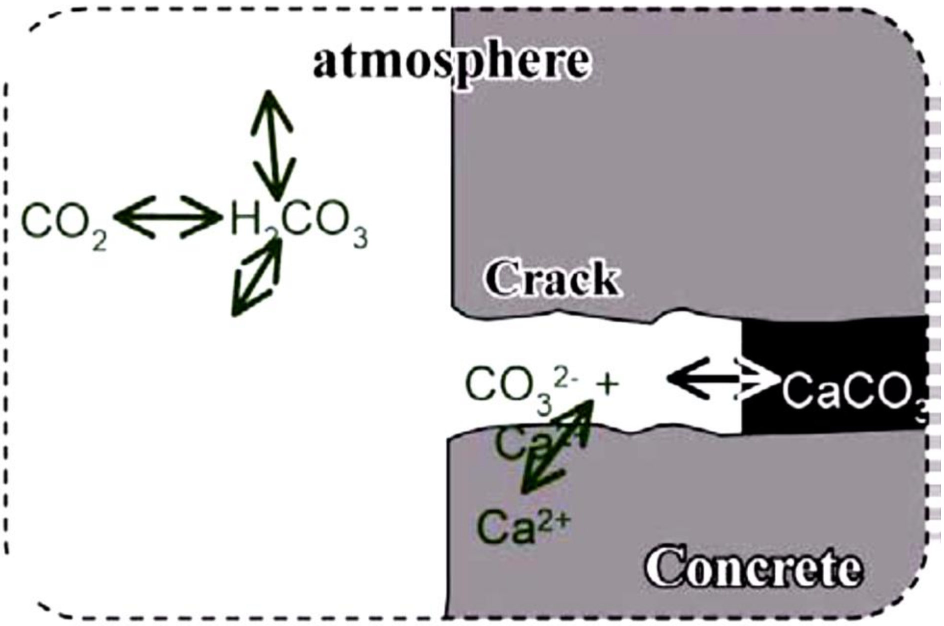

Figure 6: Example of natural healing in hydraulic structures.

Edvardsen found that growtg ratio of CaCo3 is directly depended on two main variables, water pressure and the width of the cracks present in the specimens, discarding the influence of cement and water hardeness (Edvardsen, 1999)

- ***Mechanical causes:***

Sedimentation of fine particles:

In this case two possibilities can fill the crack, when a fracture occurs in the surface or coming with the external water, many authors have study what happens with the particles coming from a failure, Hearn and Morley cite the study made by Glanville in which he state that the variable influencing the increment in the permeability taking place after some flow cycles, was the sandstone and not the particle movement (Hearn & Morley, 1997).

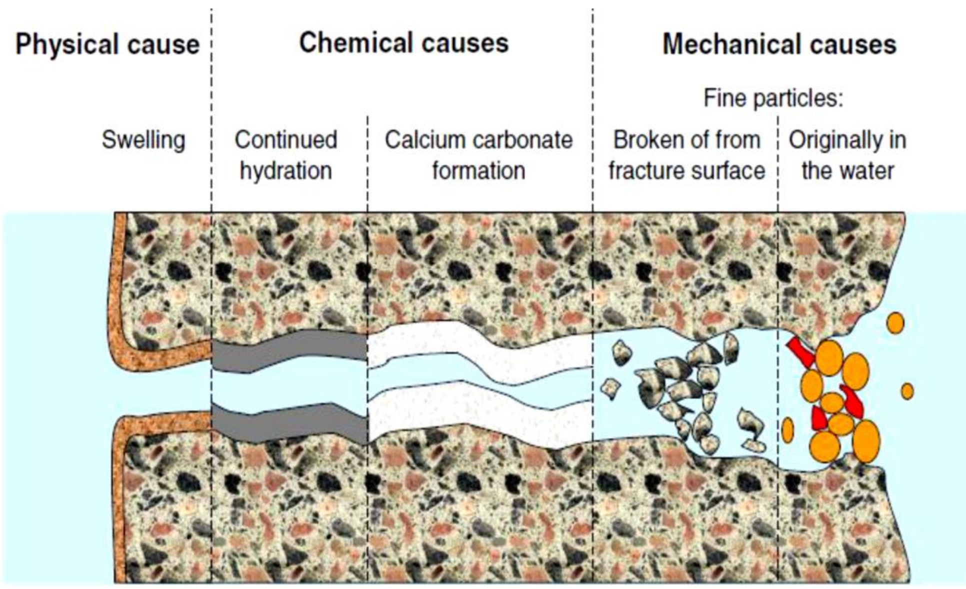

Figure 7: Causes for autogenous healing (de Rooij et al., 2013)

2.2.2 Autonomous Self-Healing

The second approach also called ***Autonomic self-healing or Engineered self-healing,*** self-healing is promoted or activated because of intentionally adding an agent in the concrete matrix components, which can be include directly to the matrix or encapsulated, altering the commonly use mix design to produce an improved self-healing action, different agents can be used to activate autonomous self-healing in concrete, an important fact is the way these mechanisms are activated, can be when the crack it is contact with air or water, or also by others mechanisms in the matrix that act as a catalyst (Roig Flores, 2018).

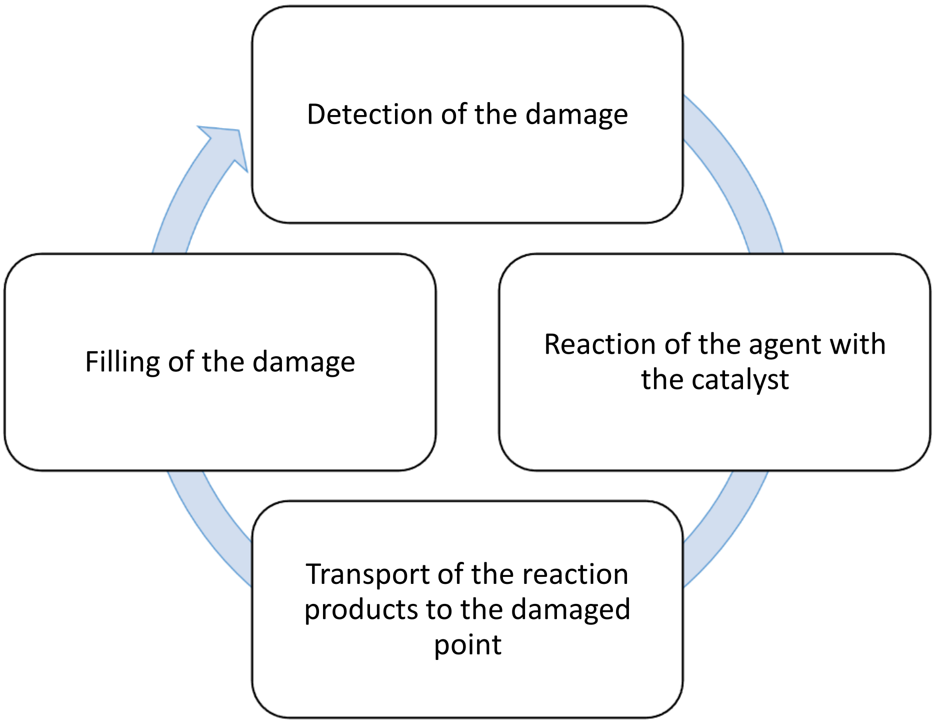

Figure 8: Process of Autonomous self-healing.

Through the years, different methods have been studied to promote a reliable Autonomous self-healing, the methods most currently implemented are explained below.

2.2.2.1 **Microorganism**

The use of microorganisms as an option to implement self-healing has been of interest to the scientific community, also known as Bio-concrete, it has been created inspired by nature, using one of its main components, bacteria.

The bacteria that promote self-healing in concrete grow in alkaline environments such as concrete, they can survive for years, these are added to the traditional concrete mix, as well as the appropriate nutrients for bacteria, urea, calcium lactate, and other components that become food, when the bacteria are released, they feed and thus produce CaCO3 limestone (Vijay et al., 2017) ,this being the main component that closes the cracks, this process is known as Microbially-induced calcite precipitation (MICP)

There are two processes by which S-H can be implemented in concrete by MICP (Li et al., 2019): Urea Hydrolysis by ureolytic bacteria or the respiration process.

> First, ureolytic bacteria produce urease enzyme, which by a hydrolysis process converts urea into ammonia and CO2, which increases Ph and CaCO3 production. Among the best known we can name, Bacillus megaterium, Sporosarcina pasteurii, Sporosarcina ureae (Vijay et al., 2017).
>
> Sencond, in the case of respiration process, non-ureolytic bacteria, such as those of the Bacillus family (De Belie, 2016), favor the precipitation of limestone, this mechanism is activated when a scream occurs in the concrete elements and from the exterior enters water to the matrix of these.

The speed of the efficiency of the methods when bacteria are implemented will depend on their introduction to the concrete matrix. As explained above, the bacteria are added in the mixing stage in plastic capsules that degrade, these open when they encounter water. Bacteria can be added directly to the mix as embedded in porous particles, in cellulose or encapsulated microfibers (Roig-Flores et al., 2021).

2.2.2.2 **Controlled Release of water**

The continuous hydration of cement produces Autogenous self-healing, this fact produced the interest of the research community on implementing a controlled mechanism for the release of water, this is achieve using absorbent materials which can contain sort amount of water.

The most implemented as water reservoirs to promote self-healing are Superabsorbent polymers (SPAs), these are polymers made of polyacrylic acid cross-linked, this kind of polymers have great affinity with water, they have the characteristic of absorb. more amount of water than normal polymers (de Rooij et al., 2013), Superabsorbent polymers can store large amounts of water, with the peculiarity that the water should not contain significant amounts of ions (He et al., 2019).

The implementation of polymers in self-healing is carried out in the mixing stage, 1% SAPs by cement weight requires adding to the water cement ratio from 0.35 to 0.43 (He et al., 2019), adding more water to this ratio produces the formation of pores and compressive strength is reduced; However, in this stage it does not perform its absorption function due to the high pH values, when a crack appears in the concrete element, and it comes into contact with the water present in the atmosphere, the water that is absorbed by the polymers, is released and helps to fill the pores and parts of the crack, thus preventing the entry of unwanted materials.

Superabsorbent polymers have two fundamental characteristics for self-healing, firstly, thanks to their expansion property, they can fill the cracks that may occur in concrete, and as explained above, due to their ability to reserve water, they help the process by Autogenous self-Healing.

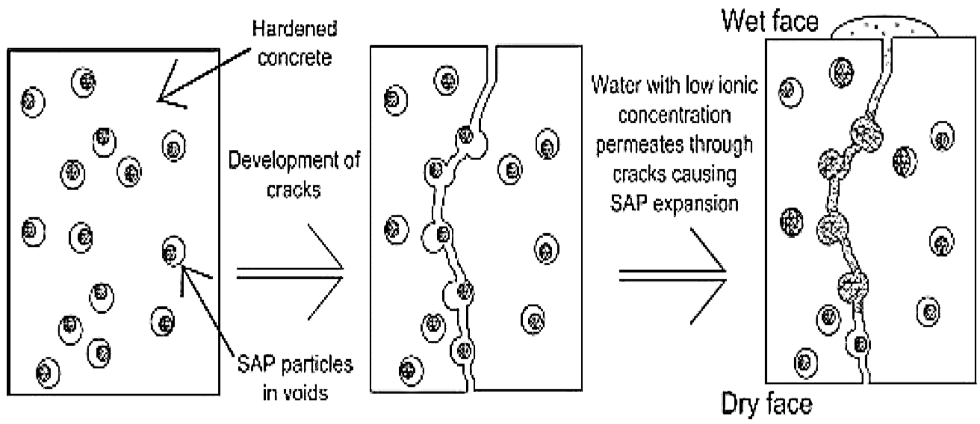

Figure 9: Schematic showing the mechanism of self-sealing using SAP (Lee et al., 2016).

2.2.2.3 **Inorganic Chemical Agents**

As explained above, different types of agents can be added in the mixing stage to promote self-healing, when necessary, among these agents are different types of additives, which can be added encapsulated, or as one more component of the mix design without any type of container, according to the requirements in the design of the mixture carried out, the one that best suits the needs of the final product should be chosen.

Expansive Agents

As part of the inorganic chemical agents added to promote self-healing concrete expanding additives are presented, usually composed of calcium sulfoaluminates (CSA), are implemented in the concrete mix during its production, with the purpose to counteract the contractions produced during the setting and hardening stage of the concrete, these additives are compatible with the other components of concrete, due to their expansive nature helps to close pores that may occur, thus achieving better permeability and durability of the structural elements in concrete (Roig-Flores et al., 2021).

Different authors have been interested in its application in the field of self-healing, as an agent capable of filling the cracks that may occur in the useful life of structures, Sisomphon studied the results obtained by replace 10% of the cement content with CSA- base expansive agents, among the most relevant conclusions are that in cracks not greater than 0.3mm improvement in terms of visual closing, permeability, in terms of mechanical properties, no great improvements were observed (Sisomphon et al., 2012).

Crystallizing additives

Nowadays, the companies that produce additives for concrete have turned their interest in the qualities of the so-called crystallizing additives and their property of promoting self-healing, for which there are a great variety of products with this characteristic. Crystallizing additives (CAs), also known as permeability reducers, are included in this section as their main function is to promote the formation of crystals in the concrete matrix, they are hydrophilic, it means they are activated in the presence of water.

The CAs are added in the concrete mixing phase as one more component, its presentation is dry and in powder, it should be noted that its use is regulated, it is usually added in small quantities (1% by the weight of cement), likewise it provides not only the property of concrete to be resistant to water but in some cases its influence on the compressive strength of concrete has been observed when added in 3, 5, and 7% by weight of cement (Weng & Cheng, 2014).

The process in which the Crystallizing additives act is simple, in the presence of water, crystals are created forming a kind of barrier that prevents the entry of water, these crystals grow and fill the pores that can be created in the concrete matrix if it suffers some damage or is in the presence of cracks, the process is repeated whenever the CAs get contact with water, this latter being the catalyst element. Once the crystal formation mechanism is activated, it makes the concrete itself a barrier against water coming from the outside in case this experience the appearing of cracks, allowing autogenous self-healing phenomenon.

Among recent studies carried out in self-healing concrete where inorganic chemical agents are implemented we can find the studies carried out by Sisomphon, he studied the self-healing that occurred in mortar specimens, which were cracked after 28 days, cracks created between 100 and 400 microns, and to which expansive additives and crystallizing additives were added, among the conclusions are favorable results for the specimens that contain these self-healing promoters, as well as higher pH values, which helps the precipitation of calcium carbonate (Sisomphon et al., 2012)

Another experimental campaign proposed by Sisomphon, in which was implemented 4 different mix designs, including control design, 10% CSA, 1.5% CS and 10% CSA + 1.5% CA mix, the specimens were expose to different environmental conditions, as conclusions they found in the specimens with expansive additives and in which expansive additive and crystallizing additives were combined that the mechanical properties were recovered, it was also found that among other factors the quality of the water played a fundamental role, as well as the exposure conditions and the type of cement implemented (Sisomphon et al., 2013).

This work studies the performance of a crystallizing additive and treatment to promote self-healing, for which section 2.3 recaps the latest research made in self-healing in concrete implementing Crystallizing Admixtures as essential background for the present work, these research not only are of great relevance for this line of research but also have apport invaluable knowledge in the use of CAs as self-healing promoters.

The chemical components of each crystallizing additive and treatment are kept confidential by each manufacturer, in this dissertation the products of *SUPERSHIELD ITALIA SRL*, Admixplus and Multiseal have been implemented, both will be described in a forthcoming section.

2.3 Researches conducted in Self-Healing by using Crystalline Admixture in concrete.

The implementation of the crystallizing additives to promote S-H has taken great relevance in the scientific community, in this section the most recent research where crystallizing additives are used are presented, these investigations have been used as references to define the methodology implemented in this dissertation.

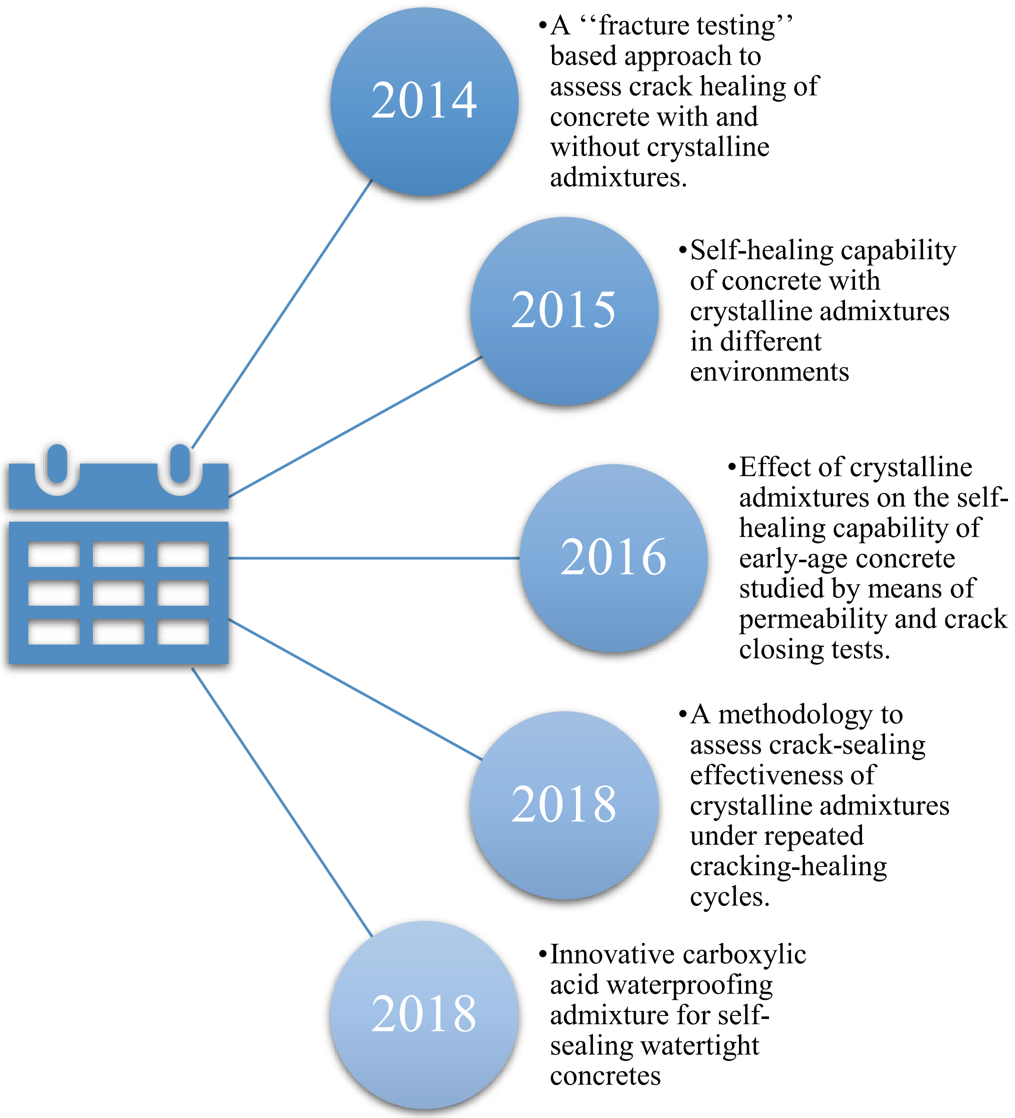

Figure 10: Timeline of Researches conducted in self-healing concrete with crystalline admixtures.

2.3.1 Research N° 1

A "fracture testing" based approach to assess crack healing of concrete with and without crystalline admixtures (Ferrara et al., 2014).

Who.

Liberato Ferrara, Visar Krelani, Maddalena Carsana.

Where.

Department of Civil and Environmental Engineering, Politecnico di Milano, piazza Leonardo da Vinci 32, 20133 Milan, Italy. Department of Chemistry, Material and Chemical Engineering, Politecnico di Milano, via Mancinelli 7, 20133 Milan, Italy.

When.

2014

Why.

In order to assess the proposed methodology of characterization of self-healing, both autogenic and engineered self-healing this methodology has been implemented on ordinary concrete, with or without a crystalline admixture.

How.

Implementing 3-point bending tests, performed up to controlled crack opening and up to failure. Among the exposure conditions considered are water immersion, air exposure and accelerated temperature cycles. Then, Ultrasonic Pulse Velocity tests and microstructural observations have been carried out.

Results.

Under water immersion, the presence of crystalline additive sped up the crack healing process as evaluated by visual observation and the recovery of mechanical properties evaluated through 3-point bending test. Meanwhile in the case of air exposure, lower results were obtained but highly effective.

2.3.2 Research N° 2

Self-healing capability of concrete with crystalline admixtures in different environments (Roig-Flores et al., 2015).

Who.

M. Roig-Flores, S. Moscato, P. Serna a, L. Ferrara.

Where.

ICITECH-Institute of Concrete Science and Technology, Universitat Politècnica de València, Valencia, Spain Politecnico di Milano, Milano, Italy.

When

2015.

Why

This paper analyzes the self-healing effect of a crystalline admixture in four types of environmental exposure comparing with a reference concrete.

How

Self-healing was studied by means of permeability tests performed on cracked specimens, furthermore physical closing of the crack was observed by optic microscope.

Results

It was demonstrated the importance of the presence of water, hence, is necessary for the healing reactions. Regarding the exposure and the presence of the crystalline admixture, different healing behaviors were obtained.

2.3.3 Research N° 3

Effect of crystalline admixtures on the self-healing capability of early-age concrete studied by means of permeability and crack closing tests (Roig-Flores et al., 2016).

Who

M. Roig-Flores a, F. Pirritano b, P. Serna a, L. Ferrara b.

Where.

ICITECH-Institute of Concrete Science and Technology, Universitat Politècnica de València, Valencia, Spain Politecnico di Milano, Milano, Italy.

When

2016.

Why

This paper analyzes the self-healing properties of early-age concretes, engineered using a crystalline admixture (4% by the weight of cement),

How

This paper implemented measuring the permeability of cracked specimens and their crack width, Two concrete classes (C30/37 and C45/55) in three different healing exposure conditions, respectively water immersion at 15 C, at 30 C and wet/dry cycles.

Results

It was observed an Almost perfect healing capability for specimens healed under water at 30 C, meanwhile for specimens healed under water at 15° C lower results were obtained, while insufficient for the wet/dry exposure.

2.3.4 Research N° 4

A methodology to assess crack-sealing effectiveness of crystalline admixtures under repeated cracking-healing cycles (Cuenca et al., 2018).

Who

Estefanía Cuenca, Antonio Tejedor, Liberato Ferrara.

Where.

Department of Civil and Environmental Engineering, Politecnico di Milano, Piazza Leonardo da Vinci, 32, 20133 Milan, Italy.

When.

2018

Why.

In order to analyze the autogenous and stimulated self-sealing capacity of steel fiber reinforced concretes, comparing the results of concrete with and without crystalline admixtures.

How.

The damage creation of the specimens by means of an indirect tensile test called Double Edge Wedge Splitting (DEWS) test, the crack opening up to 0.25mm. The exposure condition is set as repeated cracking and healing cycles for a period of 1, 3 and 6 months.

Results.

The specimens submerge in water reached the largest crack closures. In addition, it was observed that the crystalline admixture improves long-term self-sealing capacity in elements subjected to repeated cracking and healing events.

2.3.5 Research N° 5

Innovative carboxylic acid waterproofing admixture for self-sealing watertight concretes (Coppola et al., 2018).

Who.

L. Coppola, D. Coffetti, E. Crotti.

Where.

Department of Engineering and Applied Sciences, University of Bergamo, Italy Consorzio INSTM, UdR "Materials and Corrosion", Florence, Italy.

When.

2018.

Why.

With the aim to evaluate the performances of an innovative carboxylic acid-based admixture to promote concrete watertightness and self-sealing ability of the cement matrix.

How.

Were produce Six concrete mixtures using the innovative fumaric acid-based "waterproofing" admixture (WP) under study, the influences of the product were analyzed by means of the results obtained from SEM observations of crystals in the cracks.

Results.

The fumaric acid-based waterproofing admixture improves concrete watertightness. In a 7-day wet cured concrete, the addition of 1% by cement mass of the carboxylic polymer returned a result of a reduction in the water penetration under pressure of 50% compared to the values obtained of the corresponding reference concrete.

Chapter 3: Experimental Activity

3.1 Introduction

This chapter explains the materials, instruments, and methodology employed to evaluate the self-healing concrete. Furthermore, the curing and conditioning scenarios, as well as different periods, as variables to compare and assess the evolution of the cracks created on the various specimens, according to the additivities used, below is presented a detailed description of the different phases of the experimentation proposed in this thesis, as shown in Figure 11.

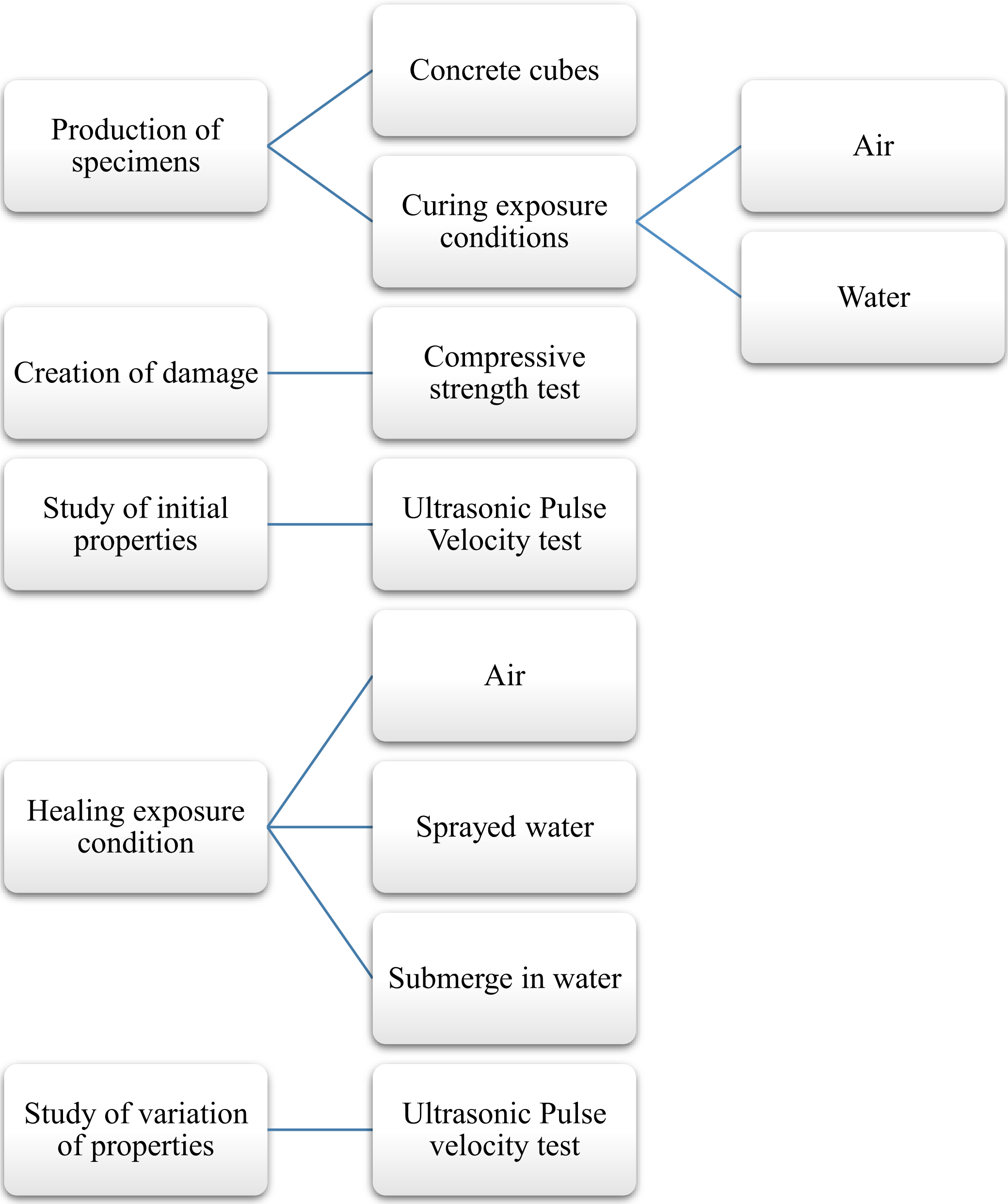

Figure 11: Proposed experimental methodology to evaluate self-healing

3.2 Production of specimens: Materials and manufacturing

This section presents the materials used for creating the studied specimens, which have been made to obtain a resistance of 30MPa. In addition, to evaluate crystallizing additive and treatment performance promoting self-healing, three types of samples have been created, in first place concrete cubes without additive, in case of Admixplus, or treatment in case of multiseal, ones to serve as a Reference, others to add the sprayed additive, and the last type are concrete cubes containing 1% by cement weight of Admixplus.

3.2.1 Concrete mix design

The implemented mixture is presented in table 1, where the mixture's components and quantities are shown in detail. The cement used is CEM II - 42.5R from COLACEM S.p.A, this type of cement is the most used in Italy, also known as Portland di miscella, constituted by Portland cement clinker in a bigger percentage and one or more minerals additions. The implemented superfluid is Dynamon SX 42, the dose adjusted to achieve the required fluency has been 1.1% by weight of cement.

The aggregates used have been Sand 0/8 at 58%, crushed stone of class 8/15 at 13%, and 15/25 at 29% from HOLCIM S.p.A.

Table 1: Mix Design

Code	Type	Description	Weights SSA	
Cem II 42,5 R	Cement	CEM II - 42.5R	kg/m3	319
Additive (1.1%)	Superplasticizer	Dynamon SX 42	l/m3	3.5
Well water	Water	Acqua di pozzo	kg/m3	185
Sand (58%)	Aggregate	Sabbia naturale 0/8	kg/m3	1058
Gravel (13%)	Aggregate	Pietrisco 8/15	kg/m3	237

Gravel (29%)	Aggregate	Pietrisco 15/25	kg/m3	527

3.2.2 Crystallizing additive and treatment implemented in the experimental campaign.

Multiseal created by Supershield Srl, is a liquid crystallizing treatment with various functions, one of which is to waterproof and protect concrete, as well as cement-based materials.

The protection generated by multiseal comes from two main crystal creation mechanisms. The first is hygroscopic crystals which are created and penetrate the concrete matrix, closing cracks and pores, which can be created in concrete elements for various reasons. The second corresponds to hydrated crystals that form just below the surface and create a repellent barrier to both chemical agents and water, thus creating protection against problems derived from the intrusion of water in concrete elements. Its application consists of being sprayed on the concrete elements, 1 liter of product is applied per 5 m2 of surface (*Multiseal - Products for the Protection of Infrastructures - Supershield*, n.d.).

Admixplus is a water-based additive, it is a waterproofing agent, which improves the durability of concrete by preventing the entry of water or any external chemical agent, promoting the formation of crystals capable of closing cracks inside the concrete mass.

Hence, admixplus is added during the concrete mix preparation cycle, 1 lt. every 100 kg of cement contained in a m3 of concrete. The creation of crystals is activated when it is required, being in the presence of water that for various reasons can enter the concrete elements. As part of the admixplus benefits, it can seal cracks of up to 0.4 mm. This product does not change the rheological properties of concrete (*Admixplus - Products - LCT Products Range - Supershield*, n.d.).

Both products are water-based and contain the characteristic of being ecofriendly, they not only provide benefits in terms of the durability of concrete structures but also ensure that their use does not harm the environment.

3.3 Specimen Identification

As mentioned before, 72 specimens compose the total amount of cubes analyzed in the present work. An identification code was created to recognize the specimens in which the variables influencing self-healing were mentioned to improve the time employed to organize the tested elements in the different stages of the methodology explained in this chapter, as they are conditioning, pre-cracking, and curing.

The variables that create the code are the conditioning environment and conditioning time in table 2, relative to the additive used, in the code is specified when it is applied the type of additive and the percentage added table 3, the cracking table 4 and finally the curing environment table 5

Table 2: Curing exposure and period.

Conditioning			
Environment		Time	
In Air	In water	28 days	6 months
AIR	*without words at the beggining*	*28g*	*6m*

Table 3: Additive and the specification of the stage in which it is implemented.

Additive			
Multiseal	ADMIXPLUS	%	applied post cracking (post fessurazione)
M	*A*	*1*	*pf*

Table 4: Type of cracking.

type of cracking	
fRc	Cracking with compressive strength

Table 5: Conditioning Environment.

Conditioning environment		
Air	Water	Water sprayed
a	*w*	*aw*

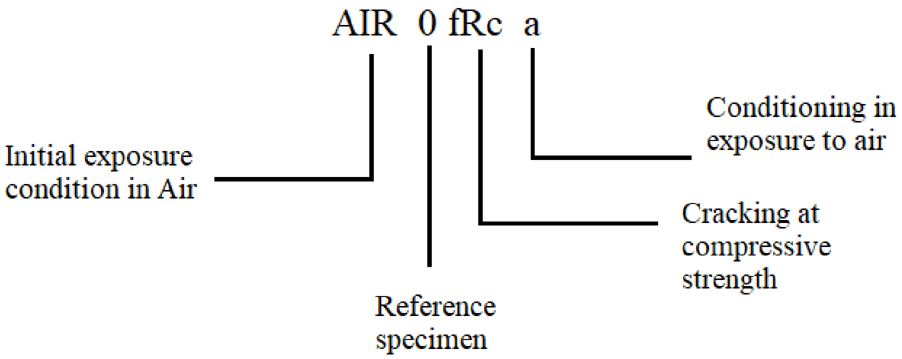

Figure 12: Code example of a reference specimen with initial exposure condition in air.

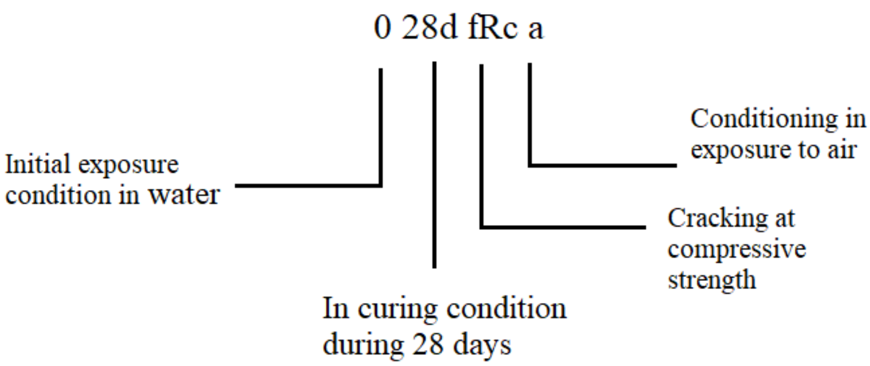

Figure 13: Code example of a reference specimen with initial exposure condition in water.

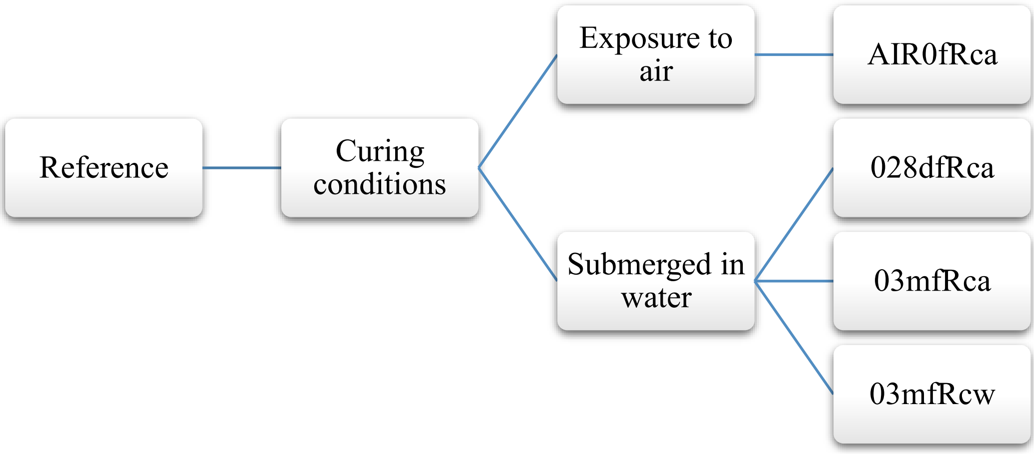

Figure 14: Schematic representation of reference specimens

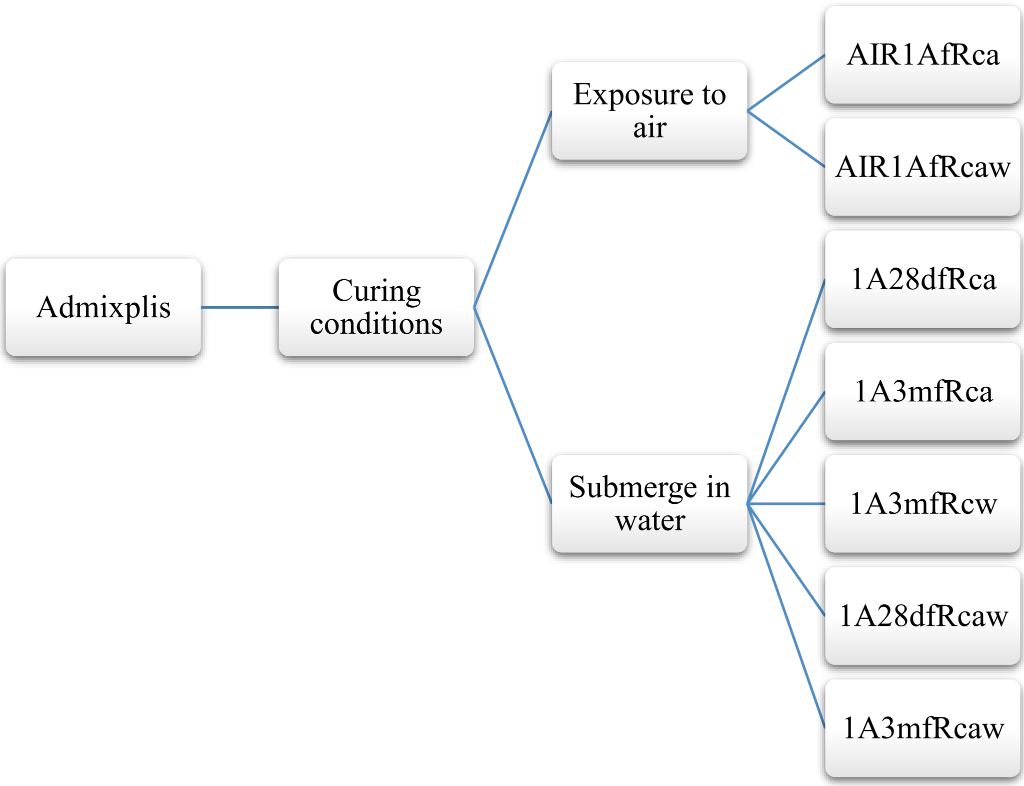

Figure 15: Schematic representation of specimens containing Admixplus.

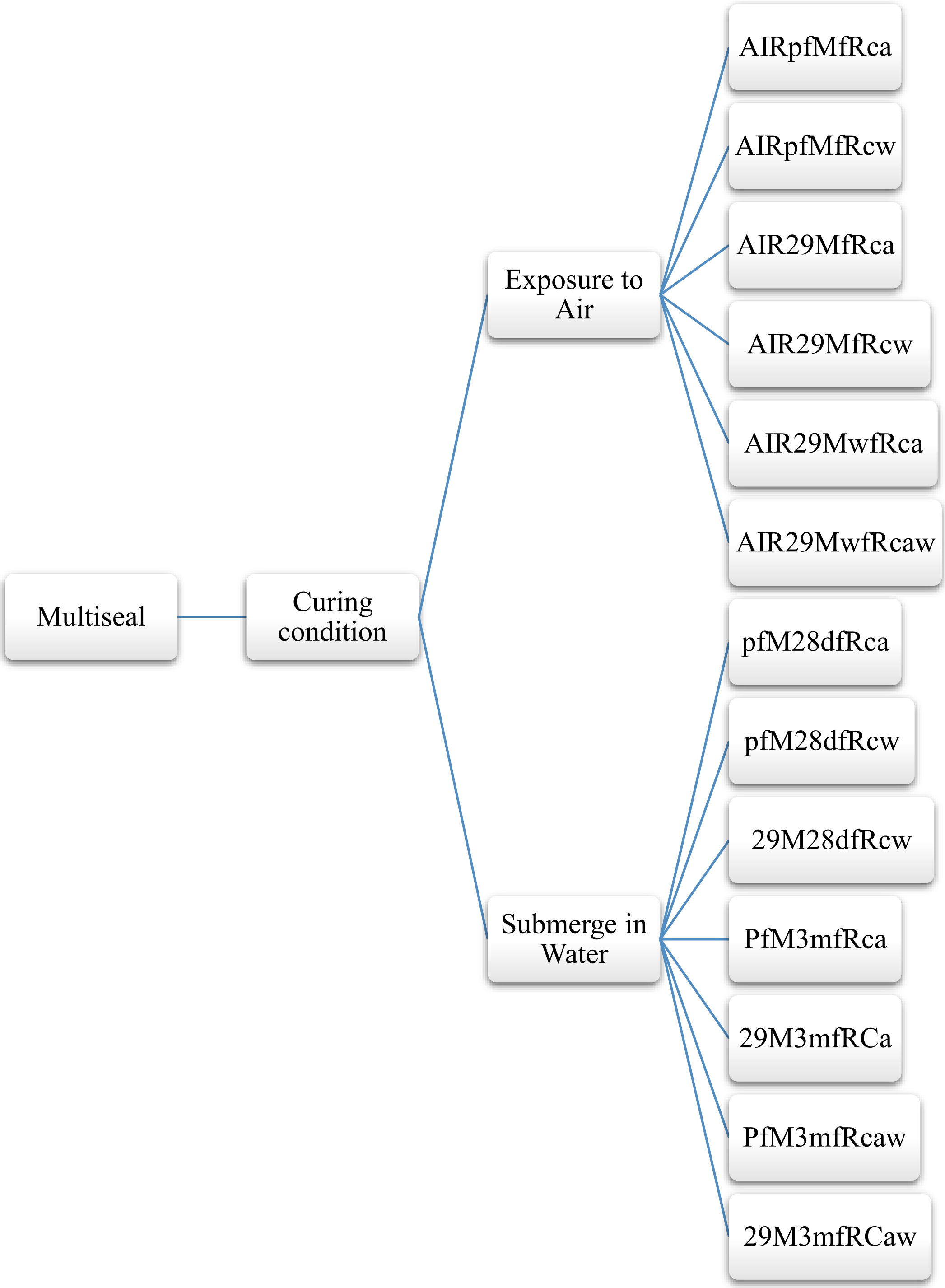

Figure 16: Schematic representation of specimens containing Multiseal.

3.4 Creation of damage

3.4.1 Pre-cracking technique

As part of the methodology proposed, compressive strength test define in the UNI EN 12390-3 is used as pre-cracking technique, its implementation allows not just to create the crack but also obtain the compressive strength of the different specimens under study, in order to evaluate how the Crystalline Admixtures and as explained in the section above, the different curing conditions used affects the compressive strength of concrete cubes, this analysis in presented in section 4.2, every sample has been triplicate to obtain a better statistic approximation in the results.

Compressive strength tests can be carried out in two different modalities, the first one where the force applied is controlled constantly, when the maximum applied load is exceeded, immediate failure of the sample occurs. The second type of test called displacement control test, small increases are made in the displacement applied to the sample, this makes it possible to have the load data after the maximum load has been reached, in this study it has been stablished a range of 5% after maximum load.

Hence, the two set up were established, a group of 30 specimens were cracked under a force-controlled condition, the application of the force at 0.6 MPa/s, while another 72 specimens were under a displacement controlled condition at 0.8 mm/min, the parameters established to perform the compressive strength test in each case are specified below in Table 6, this with the aim of compare the compressive strength resistance with the two setups and evaluate how can affects the results obtained.

Table 6: Compressive strength paramaters

Compressive strength test parameters		
Force controlled	0.6	MPa/s
Displacement controlled	0.8	mm/min
Standart force	30	MPa

Break sensitivity for force reduction	5	%Fmax
Force threshold for break investigation	3	%Fnom
Upper force limit	80	MPa

As specified in UNI EN 12390-3 the samples should be a cube or a cylinder, in this study 150 mm each side cubes have been created. It is known that concrete reaches its final compressive strength at 28 days of curing, therefore after an estimated time of 28 days or 6 months depending on the scenario studied, for the procedure of cracking the specimens, a compression press as indicated in figure 17 was used.

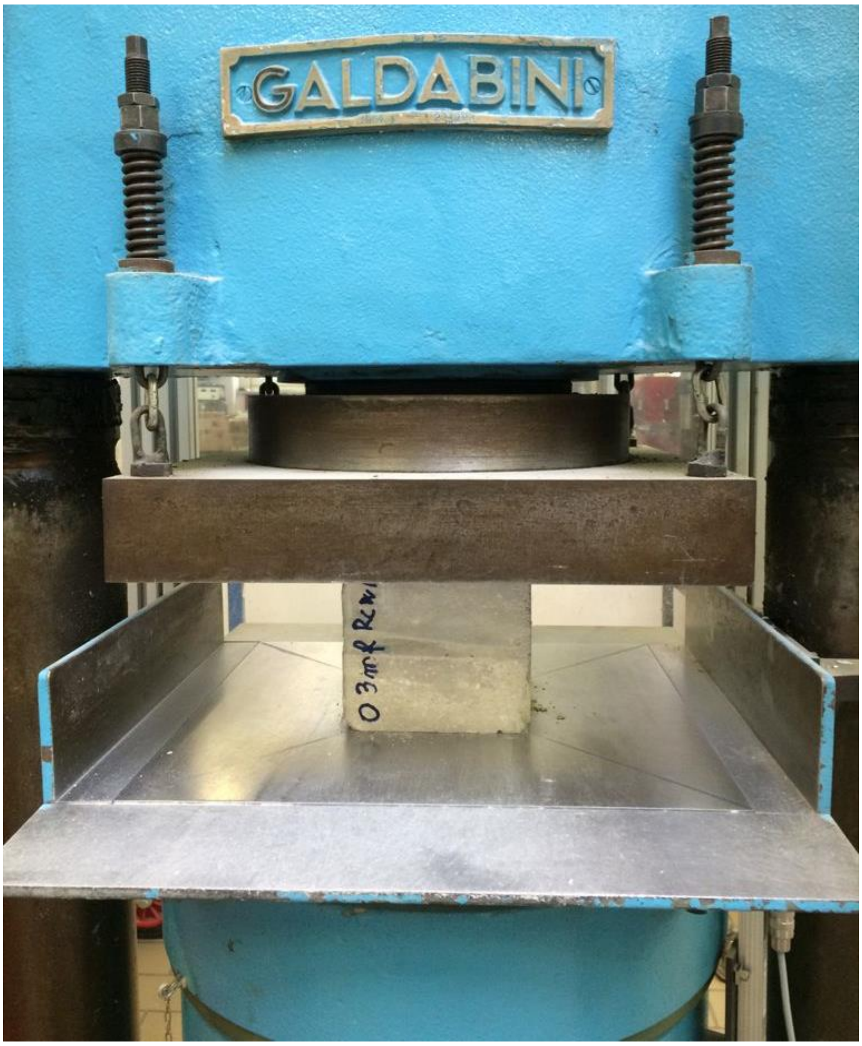

Figure 17: Compressive press implemented in the experimental campaign.

The cube's face directly in contact with the press corresponds to the Y direction, the remaining two has been called Z direction, and X direction.

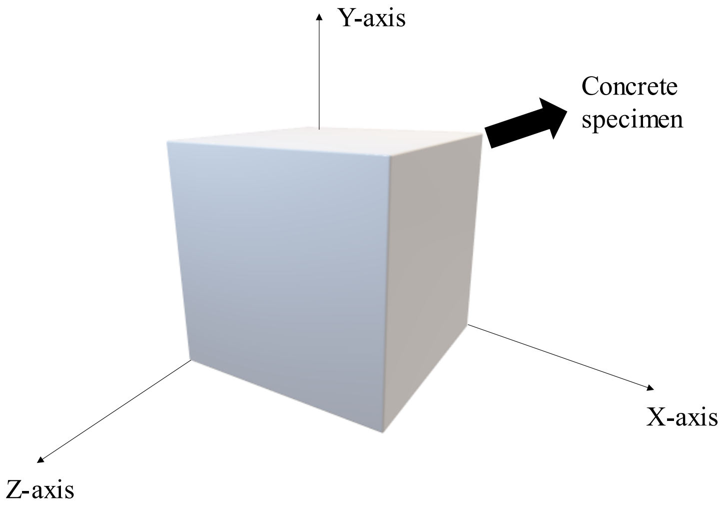

Figure 18: Coordinate's axis employed in concrete specimens for compressive test.

3.5 Study of initial properties

In this section the initial characteristics of the specimens, physical and mechanical, are defined, for which the pertinent measurements are made, these will be compared before and after the pre-cracking curing process or / and post-cracking conditioning to evaluate the self-healing of concrete.

3.5.1 Ultrasonic Pulse Velocity Test

One way to evaluate the self-healing of concrete is by comparing the conditions of the specimens before and after the cracking process, with the aim of quantify the damage, as well as after the conditioning period that in this study it is 3 months, in this section the existence of self-healing can be evidenced.

The cracks formed after the cracking process can be visible, however, inside the concrete cubes the damage can be evaluated in different ways, as defined in the scope of this study, it is employed the measurement of the propagation speed of the ultrasound pulses as specified in UNI EN 12504-4 in different three phases: pre-damage, after the curing exposure condition, post- damage, after the creation of damage took place and post-conditioning, after the exposure condition period, as shown in figure 19 and thus evaluate the homogeneity and integrity of the concrete.

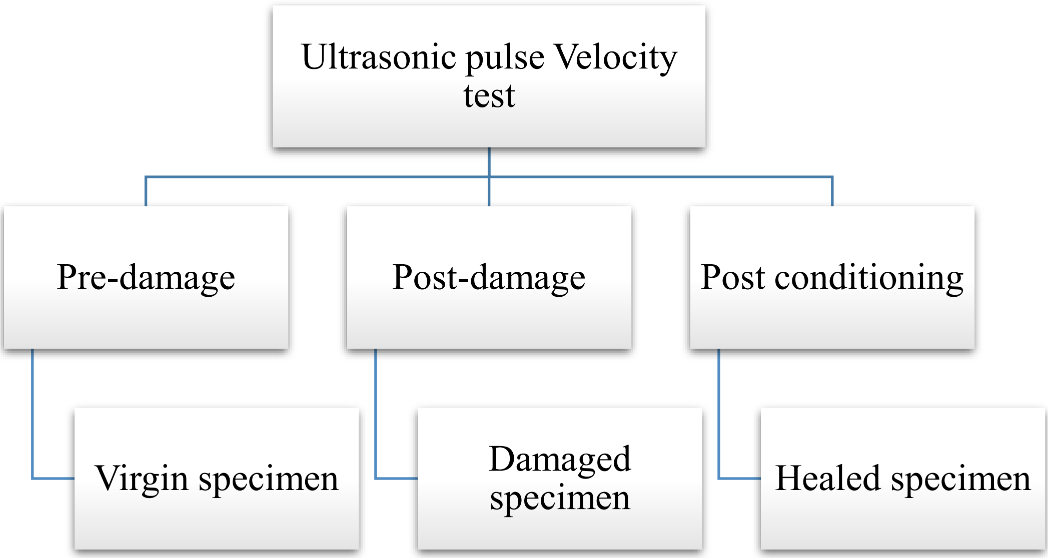

Figure 19: UPV stage measurements

For the measurements of the ultrasonic pulses, the Proceq Tico ultrasonic instrument is used, composed of a transducer, a receiver, both of 54kHz, twa cables BNC L=1,5 m, a calibration rod and an indicator to show the propagation time of the wave (IFM ELECTRONIC, 2010) as illustrated in figure 20, this time is converted to speed with the equation (2), these data allow to evaluate the presence of voids and cracks inside the specimens if an increase in transmission time is reflected compared to the same specimen prior to the cracking procedure, this means that due to existing disruptions in the waves path emitted by the transmitter, these waves take longer time to arrive to the receiver

Figure 20: Ultrasonic pulse velocity instrument.

The equation implemented to calculate from the data obtained in the UPV test is the following:

$$V_p = \frac{L}{\Delta t} \qquad (2)$$

Where:

- Vp is the ultrasonic pulse velocity (mm/s),
- L is the distance (mm) between the transmitter and the receiver.
- Δt is the transit time (s).

The following scheme (Bilgehan & Turgut, 2010) shows the circuit performed when the ultrasonic pulse velocity test is implemented, specifying the components and the internal procedures from where the final data, in this case, the transit time, is obtained.

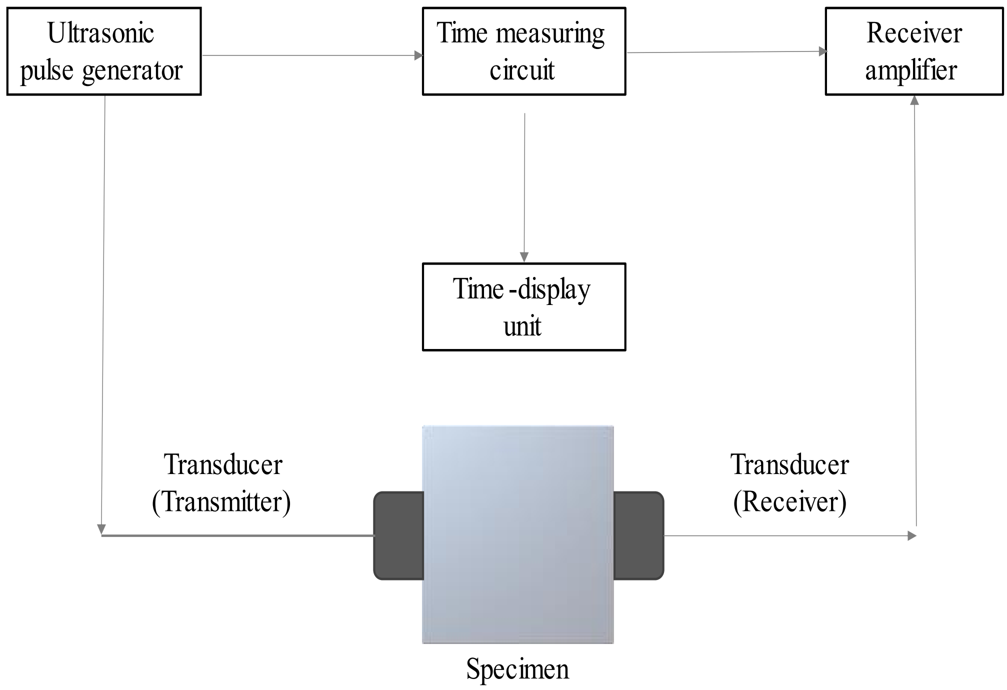

Figure 21: Schematic diagram of Pulse Velocity test circuit (Bilgehan & Turgut, 2010)

As part of the methodology used to evaluate self-healing, emphasis is placed on calculating the damage index, defined in equation (3), where the data obtained in the ultrasonic pulse velocity test performed before the damage and after the hurt (De Nardi et al., 2017)

$$D(\%) = \left(1 - \frac{Vd}{Vo}\right) \times 100 \qquad (3)$$

Where:

- Vd= UPV post-damage
- Vo= UPV pre-damage

In addition, quantifying damage in each specimen later allows us to understand the ability to close the cracks caused by the crystallizing additive and treatment under study and the influence of the conditions before and after the damage.

3.6 Healing

3.6.1 Exposure conditioning

In this section, the exposure conditions during the healing period are explained. Although exposure conditioning is a fundamental variable in the self-healing process (Roig-Flores et al., 2015), the influence of the concrete's exposure environments after being cracked has been studied by different authors whose conclusions affirm this is a vital phase in the process.

In the present study, to recreate different real exposure conditions, after the specimens have cracked, they go through a 3-month curing process in three different environments:

- In the first case, as mentioned in the codes section, the first environment is defined by exposure to natural air at room 20 °C temperature and 50% humidity, which represents concrete elements, not in contact with water at normal humidity levels.

Figure 22: Specimens in exposure to air conditioning.

– In the second case, the specimens are immersed in tap water at 20 °C temperature without removing the cubes from the immersion or changing the water; this condition simulates concrete elements underwater, like dams, bridge's columns.

Figure 23: Specimens submerged in water conditioning.

– In the third case, the specimens are sprayed with water on all four sides, and this constitutes exposure to sprayed water, this condition simulates when concrete elements are subjected to periods of rain.

3.7 Study of variation of properties

3.7.1 Post-curing conditions testing

As mentioned in the previous section, the conditioning period of the specimens after the pre-cracking process is three months, a considerable time to evaluate the self-healing process. Furthermore, as mentioned in the literature, there is a wide range of values implemented to study the phenomenon of self-healing concrete. However, the best results have been found after 35-50 days (Ferrara et al., 2018).

It is necessary to compare the initially measured conditions with those that occur after the conditioning period to evaluate self-healing in the different exposure conditions. The ultrasonic pulse velocity test measurements are performed on the specimens. The same instrument is specified before, placing the transmitter and the wave receiver in the same positions adopted in the first measurement stage.

As made in the pre-cracking and post- cracking phase, the measurement of the same characteristics allows obtaining the necessary data to corroborate self-healing in the deepest cracks that are not perceptible to the human eye. Furthermore, an increase in wave time record by the instrument means the wave path is short compared to the first stage of the study, and this affirms the closure of the existing internal cracks when self-healing had to occur.

Once the ultrasonic pulse velocity test measurements have been carried out after the conditioning period, a healing index is calculated with the equation (4) presented below (De Nardi et al., 2017).

$$H(\%) = \left(\frac{Vh-Vd}{Vd}\right) \times 100 \qquad (4)$$

Where:

- Vd= UPV post-damage
- Vh= UPV post-conditioning

The healing index allows studying, in the different configurations of test cubes made, the percentage achieved to close the cracks created.

A recovery of initial properties index is also calculated with the values obtained from the pre-damage and post conditioning UPV results, with the equation (5) presented below:

$$RI(\%) = 100 - \left[\left(\frac{Vh - Vo}{Vo}\right) \times 100\right] \qquad (4)$$

- Vo= UPV pre-damage
- Vh= UPV post-conditioning

These data allow to evaluate together with the damage index the influence of the crystallizing additive and treatment, as well as each exposure scenario, the results and corresponding analyzes are presented in detail Chapter 4.

Finally, as part of the study to demonstrate the presence of self-healing, the visual evaluation of the crack's closure on the cube's surfaces is shown in section 4.4. The qualitative analysis of the images is carried out to compare the states after the damage and after the conditioning period of three months in the different exposures, as well as with each configuration used according to the crystallizing additive or treatment, and to be able to compare their effectiveness.

Chapter 4: Analysis and Discussion of Experimental Results

4.1 Introduction

In this chapter the analyzes carried out in the experimental campaign explained in chapter 3 are presented, the results obtained, and their respective analysis are shown, to demonstrate the effectiveness of the methodology used in the evaluation of the influence of crystallizing admixtures in promoting self-healing in concrete.

The comparisons made between different scenarios are shown in detail, which allows us to have a broader idea of the influence of the initial conditions, as well as the effectiveness of the crystallizing additive or treatment used in each case, in increasing or decreasing resistance to compression of the studied specimens. Likewise, the influence of the set up used in the compressive strength tests on the results obtained is evaluated.

Later in section 4.3 the results obtained in the post-damage conditioning healing stage are presented, where it is shown by the results obtained in the Ultrasonic Pulse Velocity test carried out for the evaluation of self-healing, with special emphasis on the curing conditions and the admixture implemented in this stage. Then, the characteristics found in the visual evaluation of the closure of surface cracks in the specimens are mentioned.

4.2 Compressive Strength

Among the most important properties of concrete, the compressive strength is essential to evaluate the behavior of the material when receiving loads, which has a direct relationship with the safety and durability of concrete structures, in this section the results obtained from compression tests, carried out with the aim of evaluating different variables that may influence the compressive strength of the specimens, such as the influence of the test modality performed under the setup of force controlled and displacement controlled. Then, the effect of the additive and treatment on the compressive strength as well as the influence of the curing conditions, these results as well as their discussion are presented below.

Compressive strength resistance is calculated with the formula:

$$f_c = \frac{F}{A_c}$$

Where:

-f_c: Compressive strength in MPa (N/mm2)

-F: Maximum load at break

-A_c: Cross-section area of the specimen.

Once the specimens have been cracked, they are evaluated through ultrasound measurements, a phase that is explained in the next section.

4.2.1 Influence of the test setup in the compressive strength results.

In this section, the results obtained in two test setups are presented, as explained in chapter 3, first compression tests are used with the condition of force controlled and then displacement controlled, the values obtained in both cases are compared.

In force-controlled setup most of the specimens maintain an almost uniform trend, the values are in a range of 40-41 MPa as shown in figure 24, in detail the higher values are presented in the tested cubes called *29M6mfRc* and *1A6mfRc*, in which Multiseal and Admixplus have been added respectively, the latter being the one with the highest value, both having in common a curing time of six months.

The concrete cube that reports the highest Compressive Strength MPa is the one that contains the Admixplus additive *1A3mfRc* with a value of 45.3, the Admixplus crystallizing additive is added in 1% by cement weight directly in the mixing process, in the matrix of the specimens, unlike Multiseal which is sprayed.

The lowest value of compressive strength 39.3 MPa is reported on the specimen named AIR29MfRc as the code name, explained in Chapter 3, refers, Multiseal was added at 29 days and before damage, furthermore the influence of the additive and the exposure condition on the results obtained will be analyzed in detail.

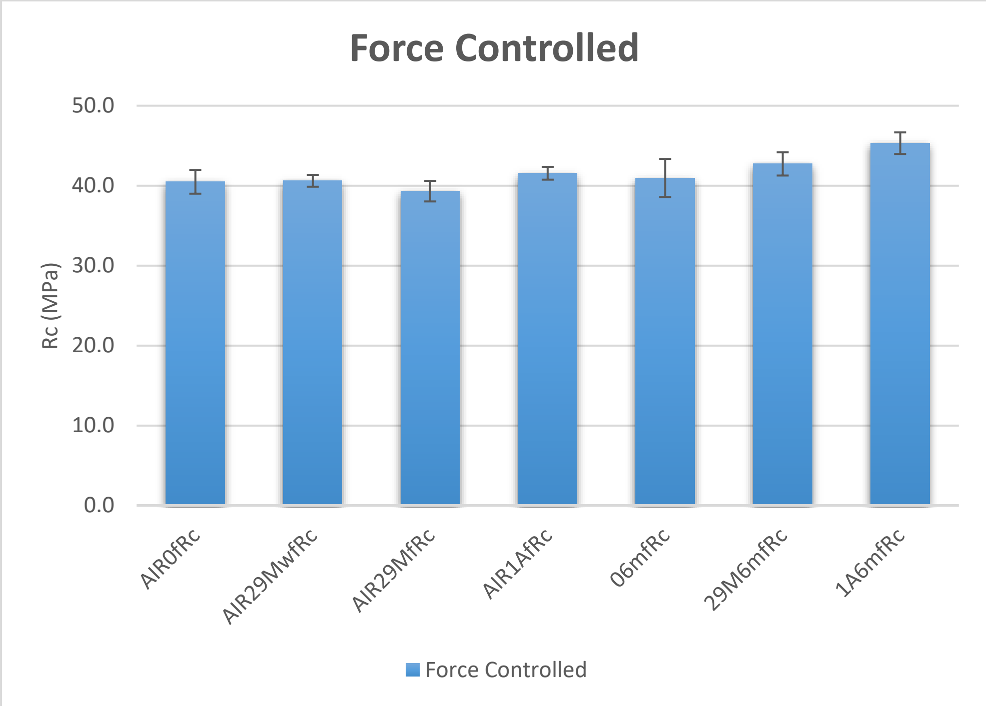

Figure 24: Compression test under Force controlled setup.

The specimens studied under displacement-controlled test setup show non-uniform values as shown in figure 25, in this case with a trend less than or equal to 40 MPa as is the case of the specimen *29M6mfRc* which has been cured for a period of six months and Multiseal has been added, except of the concrete cube named *1A3mfRc* to which as explained previously has been added Admixplus and cured for six months.

Even when the values in this test setup are lower than in force-controlled, the value of the *1A3mfRc* specimen continues to show a higher value than the previous ones and even similar in both test setups, in forced controlled equal to 45.3 MPa and in displacement controlled equal to 45.2 MPa.

The lower values are presented in the Reference specimens, as expected, these results support the theory that crystallizing products contribute to increasing the compressive strength of concrete, thus demonstrating not only the benefits in terms of self-healing that will be evaluated later in this chapter but also a contribution to the increase of mechanical properties of concrete.

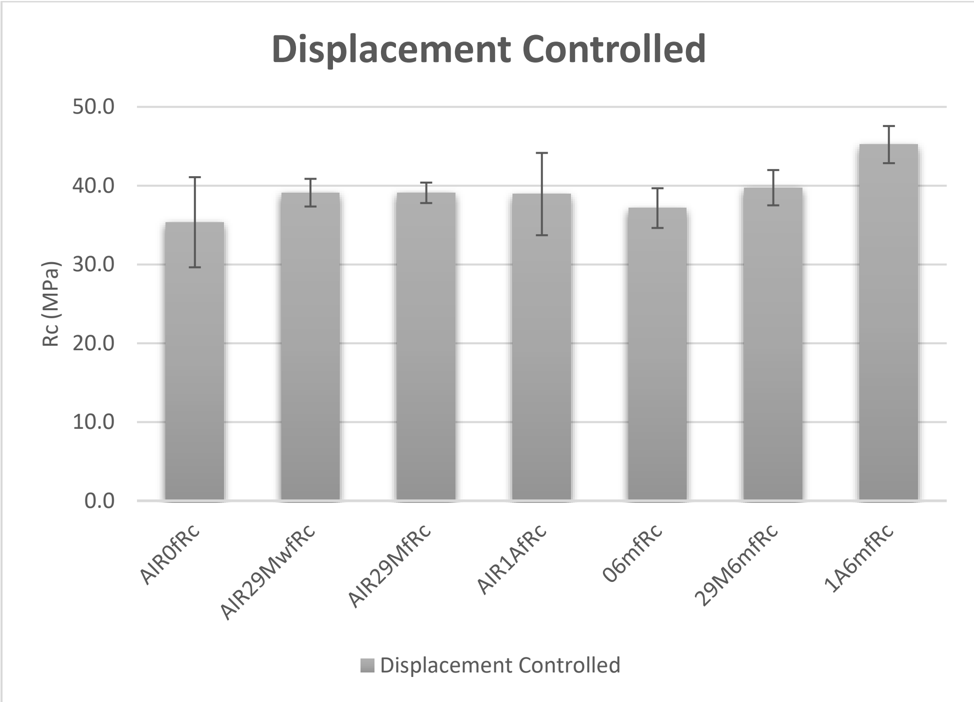

Figure 25: Compression test under Displacement controlled setup

As shown in table 7 an increase between 0.2 and 14.5% is obtained when comparing the results in Displacement-controlled and Forced-controlled setup, in this las one, a similar trend in the results between the different specimens even when Multiseal or Admixplus has been added is presented, this result was expected, as in the Forced-controlled setup a higher velocity is set to perform the test.

Table 7: Compressive Strength obtained with displacement controlled and force controlled setup.

Compressive Strength Rc (Mpa)							
Test setup	AIR0fRc	AIR29MwfRc	AIR29MfRc	AIR1AfRc	06mfRc	29M6mfRc	1A6mfRc
Displacement Controlled	35.4	39.1	39.1	38.9	37.1	39.7	45.2
Force Controlled	40.5	40.6	39.3	41.6	41.0	42.7	45.3
% Increase	14.5%	3.8%	0.6%	6.7%	10.3%	7.5%	0.2%

Although both test setups, force and displacement controlled, show similar results, in the specimen 1A6mfRc, in detail 45.3 MPa in the case of force controlled and 45.2

MPa in displacement-controlled test setup, hence proved when Admixplus is used in combination with curing exposure in water, there is no influence of the test setup on the results obtained, results are presented in figure 26.

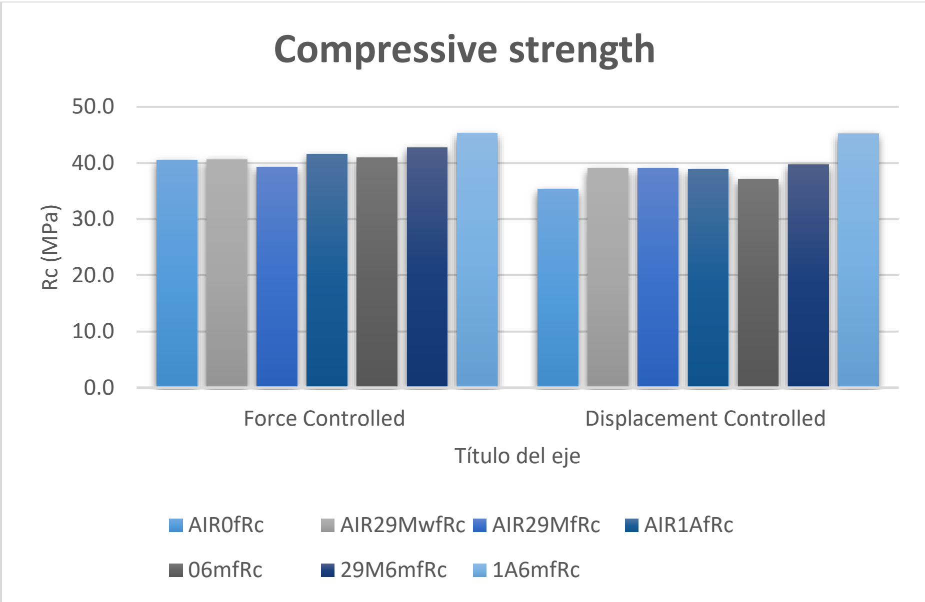

Figure 26: Comparison between compressive strength obtained in Force and Displacement controlled setup.

Another peculiarity is observed, the value of the cube named AIR29MwfRc, which contains Multiseal, and water was sprayed on it shows a value very close to the value found in the cube with Admixplus AIR1Afmc.

4.2.2 Influence of Admixplus additive and Multiseal treatment on compressive strength.

The evaluation of the effect of Multiseal treatment and Admixplus additive on compressive strength is presented, the results obtained in two test setups, forced-controlled and displacement-controlled, are shown with the aim to study the influence of the additive and treatment, the results are shown in two pre-damage curing conditions, air and water, the analysis and discussion of the results are presented below, the influence of both, Admixplus and Multiseal, is studied when making a comparison with the reference specimens, which as specified previously do not contain any additive, likewise the influence of additive or treatment, on the results obtained is contrasted, as a matter of fact, the effects in the specimens to which post-cracking Multiseal was added will be evaluated in the post-conditioning curing results in section 4.3.

4.2.2.1 **Air exposure**

As a result of the curing process with exposure to air figure 27, evaluating the reference value obtained the specimens show an increase in compressive strength when they contain some type of additive, specifically the specimens containing Multiseal show an increase of 10.6% in relation to the reference value, while the specimens containing Admixplus show an increase of 10.1%.

As can be seen there is a 0.5% difference between the increase in Compressive strength obtained with Multiseal and Admixplus, however, these results show a benefit from both products, Multiseal shows a better performance under this condition.

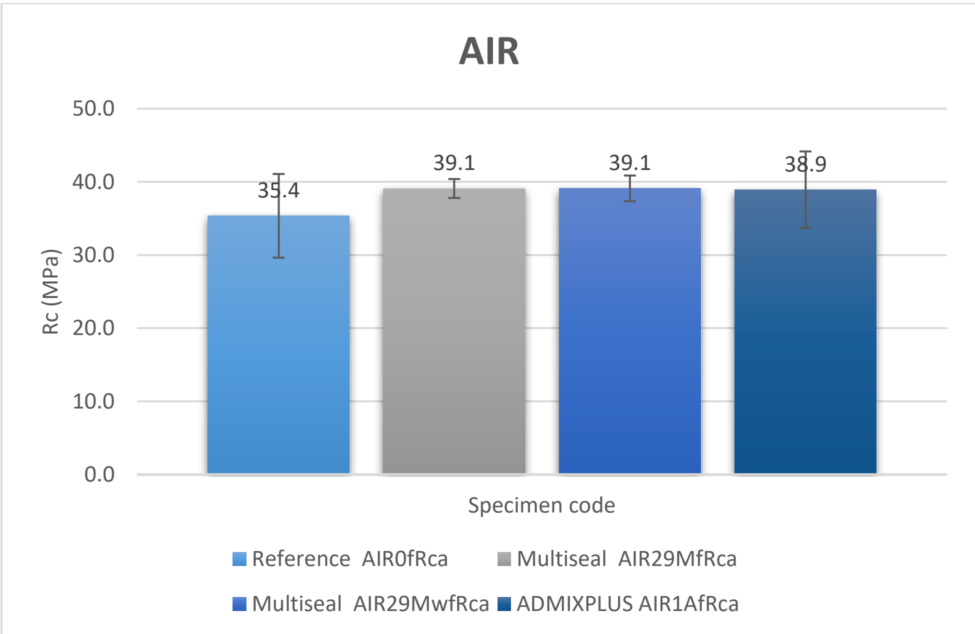

Figure 27: Specimens with exposure to air condition

Table 8: Compressive Strength obtained with displacement controlled under Air exposure condition.

Compressive Strength Rc (MpA)				
	AIR0fRca	AIR29MfRca	AIR29MwfRca	AIR1AfRca
Displacement Controlled	35.4	39.1	39.1	38.9
% Increase Displacement controlled		10.6%	10.6%	10.1%

4.2.2.2 **Water exposure**

When evaluating the influence of the additive on exposure to water, in contrast to what happened in exposure to air, in this case it is observed that the reference test cubes at 28 days in water reached a greater resistance than those that contain some type of additive, as for the test cubes with additive always in the same configuration of 28 days in water, those that have been added Admixplus present superior values of resistance to compression contrasted with the cubes that have Multiseal, 45.3 MPa and 45.0 Mpa respectively, these as can be seen in the figure 28 show lower values both when compared with the reference or with Admixplus values.

It is observed in the analysis of the influence of the Multiseal that in water the reference specimens present higher values of resistance to compression, this is since the Multiseal creates a layer that does not allow the entry of water into the matrix of the cube, for what the resistance that develops by the continuous hydration of the concrete stops.

Meanwhile, in the case where the specimens have been submerged in water for a period of 6 months with additive show an increase of 7% in the case of those containing Multiseal and of 21.7% in those containing Admixplus when comparing to the reference test cubes, in this case an increase in compressive strength was shown with both, Multiseal and Admixplus.

The highest value achieved is always present in the specimens containing Admixplus, 1A28dfRca and in 1A6mfRca, 45.3 MPa and 45.2 MPa respectively, while those containing Multiseal, although they show an increase, is not as significant as that obtained with Admixplus.

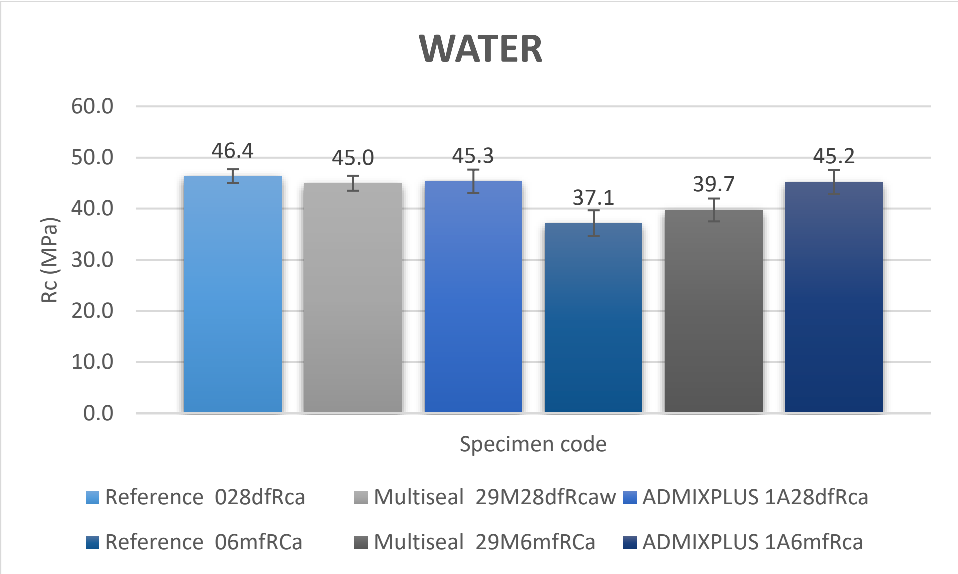

Figure 28: Specimens with submerged in water condition

The analyzed results demonstrate the effectiveness of crystallizing products to increase the compressive strength of concrete in periods after 28 days.

Table 9: Compressive Strength obtained with displacement controlled under submerged in water exposure condition.

Compressive Strength Rc (Mpa)			
	06mfRca	29M6mfRca	1A28dfRca
Displacement Controlled	37.1	39.7	45.2
% Increase Displacement controlled		7.0%	21.7%

4.2.3 Influence of curing condition.

The analysis of the data obtained in the cubes with Multiseal and Admixplus is presented, the specimens exposed to two curing conditions, air or submerge in water, in this study a total of 18 specimens were cured for a period of 28 days and 12 specimens for a period of six months, in this section emphasis is made on the analysis of how curing conditions influence the compressive strength of the specimens.

4.2.3.1 **Multiseal**

The compressive strength values of the specimens with Multiseal cured in air show values below 40MPa but percentage of increase in the compressive strength of 10.6%, while the specimens with the same additive but exposed to the condition of being submerged in water show values above 40 MPa, being the specimens with the highest values the reference one 028dfRca with 46.4 MPa and 29M28dfRcaw with 45.0 MPa, as mentioned before the reference show a higher value of compressive strength due to the fact Multiseal creates a barrier to water, a early age influence the continuous hydration of cement for this reason a lower value is obtained.

The positive influence of curing in water is presented in other studies (Roig-Flores et al., 2015), the curing process in water is the most conducive to activating the system of crystallizing additives to be resistant to water.

The specimens cured in water for six months and to which Multiseal was added at 29 days, show an increase in the compressive strength of 7.0% compared the values obtained in the reference specimens, as can be seen in figure 29. Even when there was an increase in compressive strength, the values obtained are lower than those compared with the specimens at 28 days with Multiseal, but greater than those exposed to air, which confirms that higher compressive strength results are obtained not necessarily higher increases when specimens are submerged in water in the case of Multiseal.

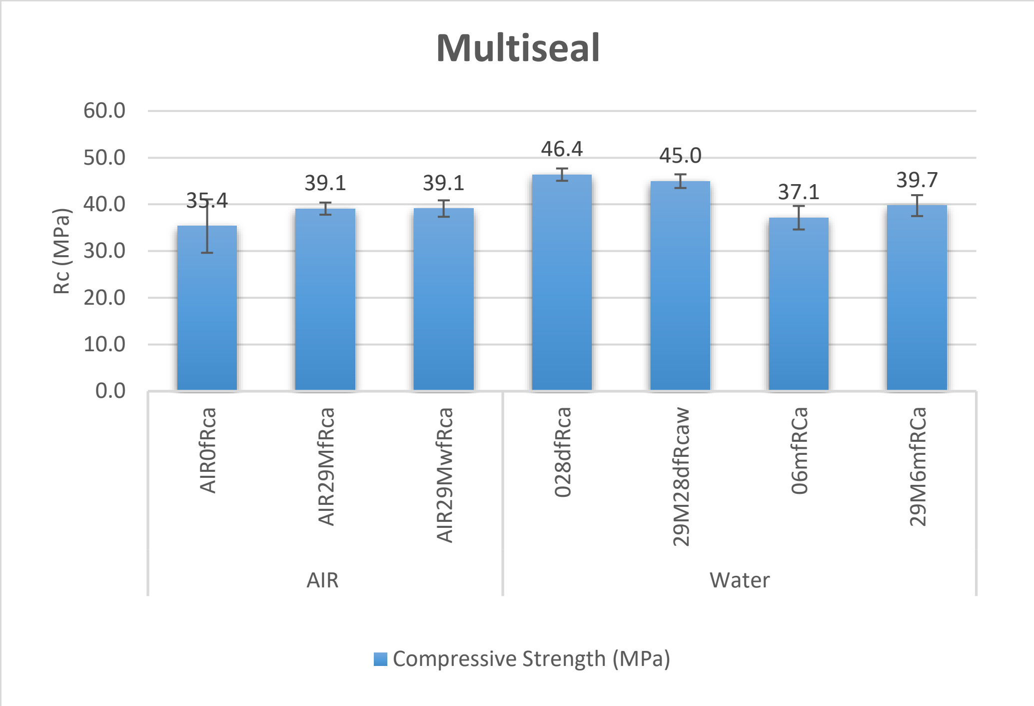

Figure 29: Specimens with multiseal in two exposure conditions.

Specimens containing Multiseal show a greater increase in compressive strength when cured in exposure to air. Although its resistance to compression increases, the value of those cured in water is still higher.

Table 10: Compression strength of specimens with multiseal in both initial exposure condition

	AIR			**Water**			
	AIR0fRc	AIR29MfRc	AIR29MwfRc	028dfRc	29M28dfRc	06mfRc	29M6mfRc
Rc (MPa)	35.4	39.1	39.1	46.4	45.0	37.1	39.7
% Increase		10.6%	10.6%		-3.0%		7.0%

4.2.3.2 **Admixplus**

The specimens that contain Admixplus cured in air show values lower than 40 MPa and a percentage increase of 10.1% in their compressive strength when compared to the reference, meanwhile, those cured in water for 28 days show values higher than

40 MPa and no increase in the compressive strength, even when no increase was obtained the values of those cured in water are still higher than those reported from the exposure to air.

Regarding the specimens cured in water for a period of 6 months, these present a significant increase of 21.7% when compared to the reference specimens, when the curing exposure is in water, the specimens containing Admixplus at 28 days and at 6 months period show very close values of compressive strength, 45.3 MPa and 45.2 MPa, a result that confirms the efficacy and performance of the crystallizing additive in the concrete matrix when the specimens are submerge in water.

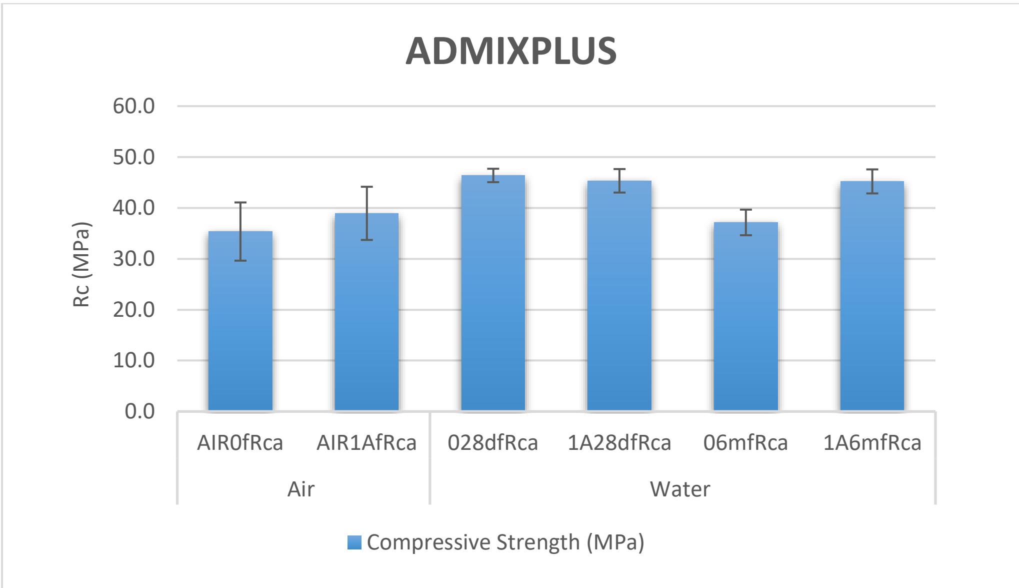

Figure 30: Specimens with Admixplus in two exposure conditions

The percentage increase values obtained with the Admixplus admixture are higher than those obtained with Multiseal, thus showing that the crystallizing additive applied in the matrix of the concrete mix gives more effective results in terms of increasing the compressive strength of the specimens.

Table 11: Compression strength of specimens with admixplus in both initial exposure condition

	Air		**Water**			
	AIR0fRc	AIR1AfRc	028dfRc	1A28dfRc	06mfRc	1A6mfRc
Compressive Strength (MPa)	35.4	38.9	46.4	45.3	37.1	45.2
% Increment	-	10.1%	-	-2.3%	-	21.7%

The specimens cured in water show a greater resistance to compression compared to those cured under the condition of exposure to air in both those containing Multiseal and those containing Admixplus.

As a general fact the values of the specimens with Multiseal or Admixplus show an increase in the compressive strength when compared with the values of the reference specimens, which do not contain any additive, this shows the influence of crystallizing products in improving concrete's mechanical properties, later in the post damage conditioning analysis section its influence on self-healing is shown.

4.3 Ultrasonic Pulse Velocity Test

The evaluation of the self-healing concrete has been evaluated employing the ultrasonic pulse velocity test as explained in chapter 3, section 3.5. Hence, using the measurement of the propagation time of the wave, the existence of internal cracks in the concrete cubes is evaluated. It also allows assessing the closure and healing of deep cracks.

Furthermore, to evaluate and demonstrate the existence of self-healing, the measurements are contrasted through the UPV test, these have been carried out in three stages of this study:

- First, in the specimens in a virgin state, that is, before being damaged.
- Second, in the concrete cubes after creating the crack and before the exposure condition, in this study are three, only in air, submerged in water and sprayed water.
- And finally, when the post damage exposure condition-stage is finished.

As can be seen, we have a total of three stages in which UPV measurements have been made. Therefore, making comparisons between the different stages allows evaluating self-healing and its effectiveness and how much it influences closing the cracks using crystallizing additive and treatment. Likewise, the exposure conditions are evaluated, which allows defining which ones have obtained more significant benefits.

The results of the comparison between the different stages are presented below and, depending on the case, the percentage decrease or increase in the speed obtained respectively from the UPV test, which have been defined as damage index and healing index, respectively.

The data obtained by performing an average between measurements of the speed of each specimen, a total of three for each class in each stage. Then it is calculated how much the decrease or increase was in terms of the values of each stage

4.3.1 Damage index obtained from pre-damage and post-damage UPV results.

In this section, the results obtained in the damage creation phase are evaluated by calculating the damage index as specified in equation (3), which allows quantifying the internal cracks created in the specimens. The creation of cracks is carried out by a compressive strength test, the ultrasonic pulse velocity test results are compared before and after damage process. Damage groups are made, with the aim to categorize de samples by the present damage index as shown in table 8. Three groups are defined in terms quantity of damage, group 1, group 2 and group 3 with light medium and severe damage, respectively. Furthermore, the distinction between different groups allows evaluating the percentage of damage cured by the crystallized additive and treatment, and the studied exposure conditions.

Table 12: Damage groups defined in terms of directions values.

Grupo 1	Grupo 2	Grupo 3
X< 25.00	25.00< X < 45.00	X > 45
Y < 25.00	25.00< X < 45.00	Y > 45
Z < 25.00	25.00< X < 45.00	Z > 45

The damage creation process is carried out employing the compressive strength test. The results obtained as shown in figure 31, present more significant damage in the X and Z directions, as these are the most affected by the configuration of the cube's position in the press, the Y direction is the least damaged.

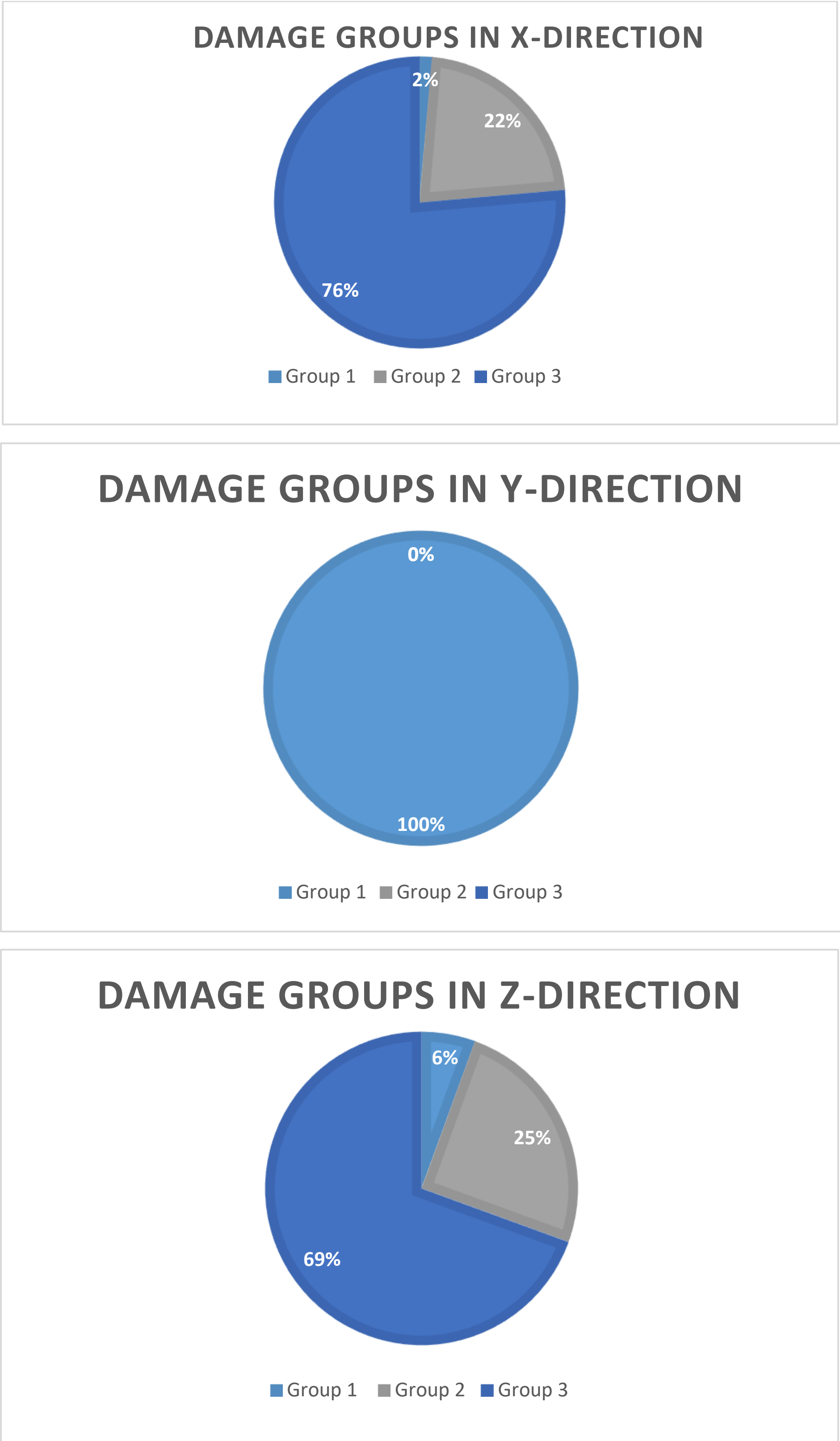

Figure 31: Damage groups defined in X, Y and Z direction.

The results presented below give us a reference of how much the specimens have been damaged, which will allow later in section 4.3 to study if a decrease in the cracks presented was obtained as well as the recovery of the initial properties of the cubes, that is, whether or not we have the presence of the self-healing phenomenon, promoted by the crystallizing additive used in this dissertation such as Admixplus and crystallizing treatment Multiseal, presented in detail in chapter two.

As can be seen in figure 32, the specimens containing Multiseal as well as the control samples, presented greater damage in the X direction those exposed to air during the curing phase, with damage between 55-80% being the highest damage value of 76.97% were multiseal was added after the damage, while the least damaged have been those that were submerged in water, both those containing Multiseal and the reference test cubes, with values between 30 - 65%, the highest damage value is 63.63%. While in the Z direction the trend is a little more varied, the highest damage values coincide with those defined in the X direction, except for 3 specimens submerged in water where the Multiseal was added after the damage.

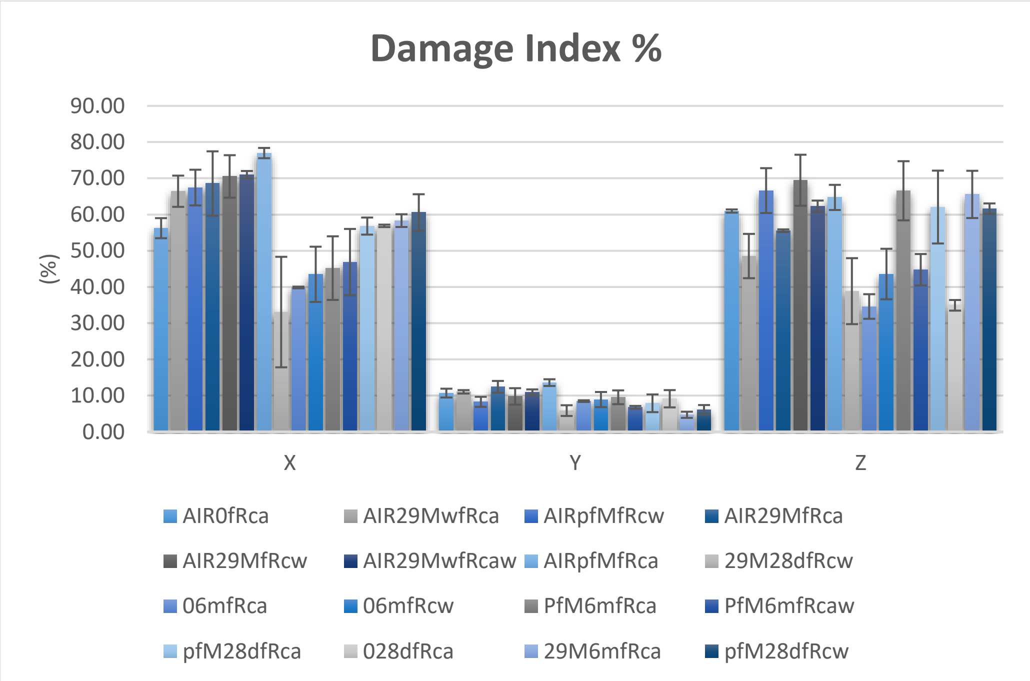

Figure 32: Damage index of multiseal specimens.

The results have been grouped in terms of the applied additive and its corresponding pre-damage exposure condition. Figure 33 shows the results obtained with Admixplus and the control test cubes have also been added. The samples that present more damage in this case, vary between those exposed in air and those submerged in water, the least damaged in a range between 30 - 45% and the most damaged between 55 - 80% in both directions.

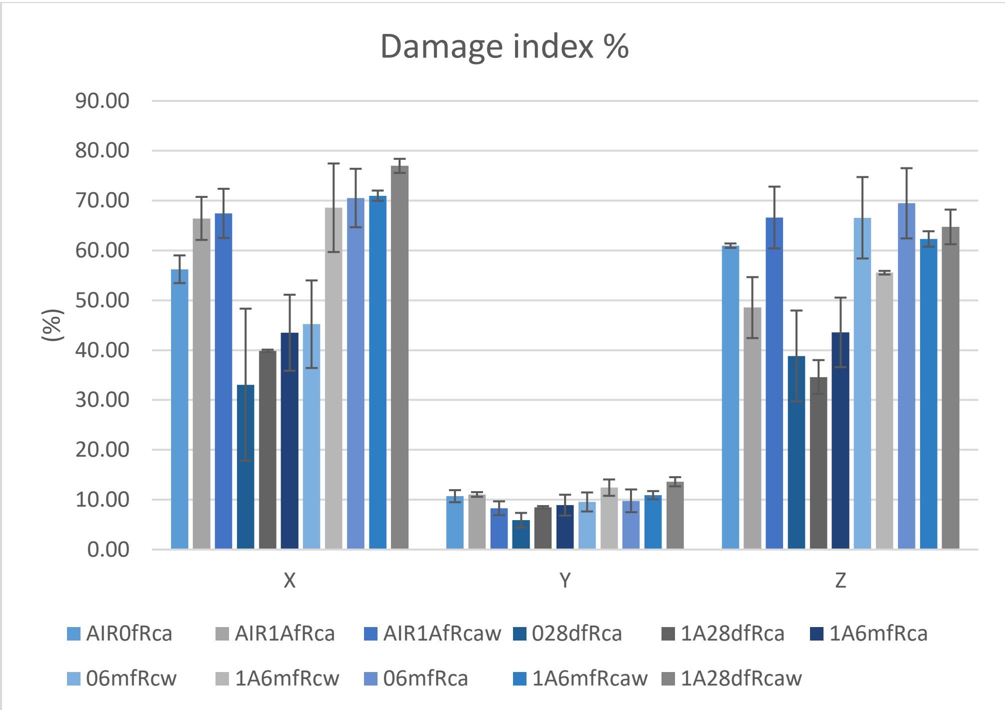

Figure 33: Damage index of admixplus specimens.

4.3.2 Influence of the post-damage exposure condition in the healing index

In this section, the influence on the self-healing phenomenon of crystallizing additive and treatment is evaluated in three different environmental exposures to which the specimens were subjected after being damaged. These conditions have been defined as:

- Exposure to air,
-Submerged in water,
- Sprayed water.

The samples studied in each condition are shown in Table 9, as part of the evaluation to contrast how self-healing is promoted in the different healing scenarios. The results of this section are defined as a healing index, representing the difference in the velocity obtained and compare with the previous stage as explained in Section 3.7.

Furthermore, the X, Y, and Z directions are grouped, from the Ultrasonic Pulse Velocity test, depending on the products added, multiseal or admixplus, thus allowing the only variable to be the different exposure conditions.

Table 13: Samples studied in each condition

Post- conditioning	Control	Multiseal	Admixplus
Water	06mfRcw	AIRpfMfRcw	1A6mfRcw
		AIR29MfRcw	
		pfM28dfRcw	
		29M28dfRcw	
Sprayed water		PfM6mfRcaw	AIR1AfRcaw
		AIR29MwfRcaw	1A28dfRcaw
			1A6mfRcaw
Air	AIR0fRca	AIRpfMfRca	AIR0fRca
		AIR29MfRca	
	028dfRca	AIR29MwfRca	AIR1AfRca
		pfM28dfRca	1A28dfRca
	06mfRca	PfM6mfRca	1A6mfRca
		29M6mfRCa	

4.3.2.1 **Multiseal additive and submerged in water exposure condition.**

The results of the specimens containing multiseal and with the exposure condition submerged in water are presented. The average results of three samples belonging to the exact composition allow a better statistic approximation, and the mentioned results are shown in figure 34.

The self-healing phenomenon is verified in all the samples, the smallest increase obtained is found in the control test cubes. The self-healing produced in this case is due to the influence of water in promoting autogenous self-healing. Hence, an 26.74 % increment in the x-direction, 45.39% in the Z direction, and 4.52% in the Y direction are obtained.

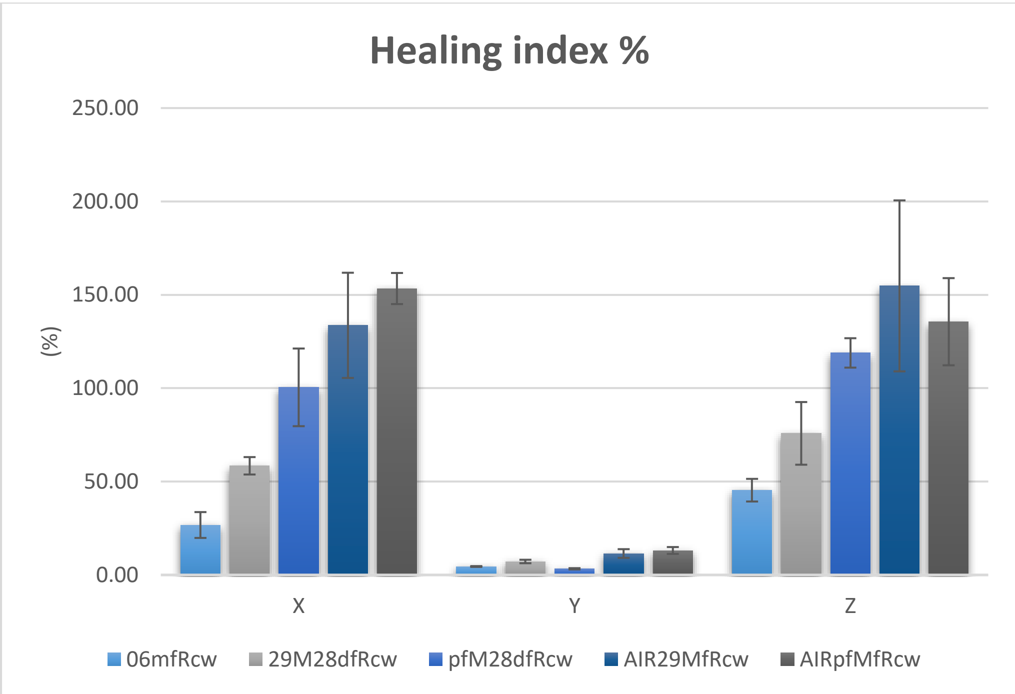

Figure 34: Healing index of specimens with Multiseal additive and submerged in water exposure condition

Regarding those containing multiseal in figure 29 can be seen there are organized from the lowest to the biggest healing index increment. The sample with the lowest values are two, which curing phase was submerged in water, in particular the named 29M28dfRcw in which the multiseal was added at 29 days shows the lowest increment, the second samples is pfM28dfRcw, in which multiseal was added after the cracking.

The reason the samples submerged in water in the curing phase are showing the lowest healing index increments, is because multiseal, as explained in section 3.2.2, has two main properties, promote self-healing with the creation of crystals and it also can make a waterproofing barrier, as these samples are in contact with water from the beginning, the property activated by multiseal is the waterproofing barrier, avoiding the path of the water to the interior of the sample.

Instead, the cubes whose initial curing exposure was to air, the values of healing index increment obtained are bigger when compare to the previous ones, for both samples, AIR29MfRcw and AIRpfMfRcw, being the latter the one with the biggest increase, 153.37% in X-direction, 13.10% in Y-direction and 135.60% in Z-direction. The presence of water during the healing phase is vital to activate the creation of crystals promoted by multiseal.

The difference between the X and Z directions concerning Y is because of the procedure to damage the samples, the Y-direction turns out to be the least cracked in the process.

4.3.2.2 **Multiseal additive with sprayed water exposure condition**

Regarding the results of the condition of sprayed water presented in figure 35, one of the two test samples evaluated showed the presence of self-healing. This is called AIR29MwfRcaw which curing condition was exposure to air and Multiseal was added at 29 days with water, the healing index obtained is 77.21%, 83.56%, and 6.89% in the X, Z, and Y directions, respectively, the latter being the lowest, as explained in the previous paragraph since the Y direction is less damaged, its increase also corresponds to the lowest.

On the other hand, the sample called pfM6mfRcaw which initial curing condition was submerged in water does not show any healing index, which means not self-healing have been experienced in this case. The fact the exposure in curing phase was submerged in water, as explained in the section before made Multiseal promote its waterproofing barrier function instead of the self-healing promotion.

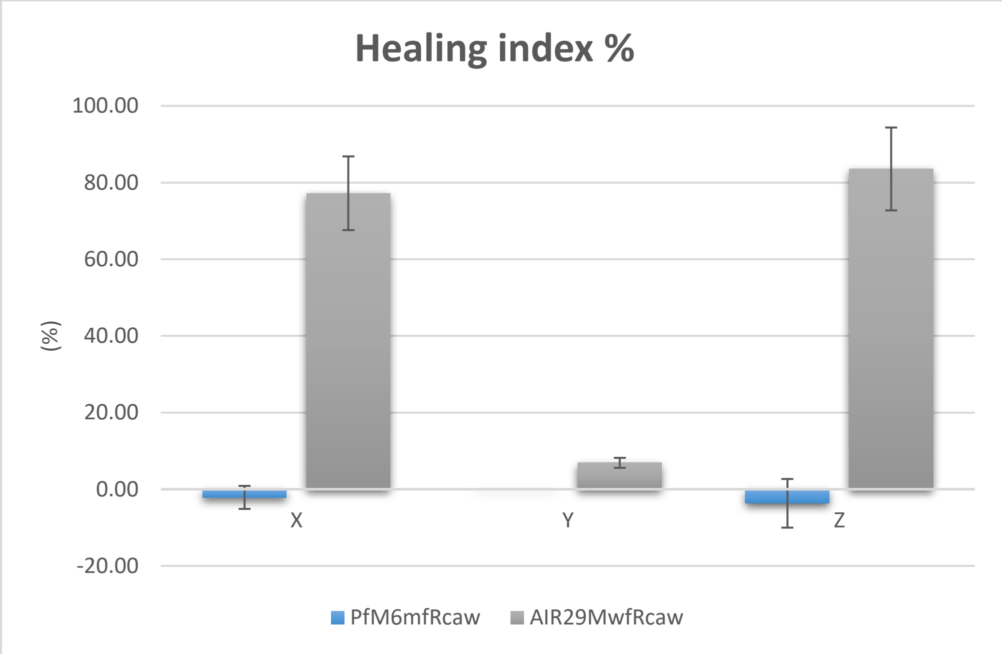

Figure 35: Healing index of specimens with Multiseal additive and sprayed water exposure condition

4.3.2.3 Multiseal additive with Air exposure condition

The specimens where Multiseal was added and exposed to air are evaluated. No results are obtained that demonstrate self-healing, since there is no significant percentage increase between the post-damage and post-conditioning velocities obtained from the Ultrasonic Pulse Velocity test. In addition, this exposure condition has also been studied by different authors, concluding that the humidity present in this exposure condition is not enough to promote self-healing. (Roig-Flores et al., 2015)

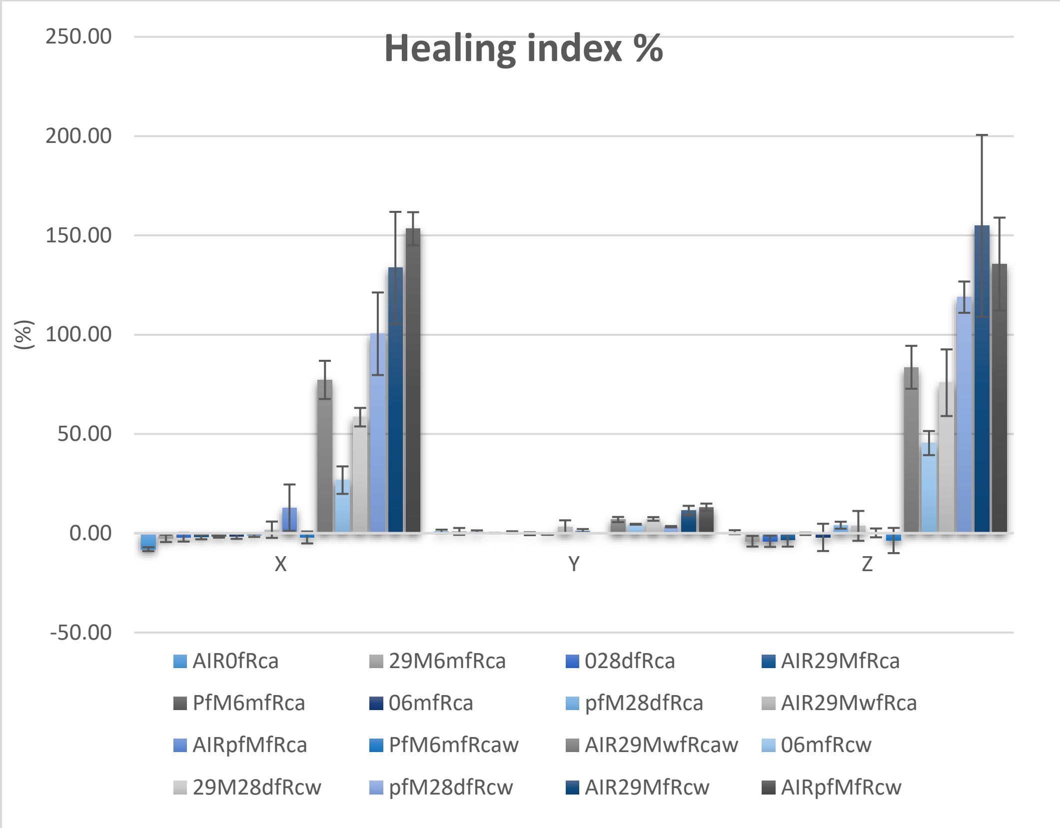

Figure 36: Healing index of specimens with Multiseal additive in the three exposure condition

As part of the results obtained, it is evidenced that the presence of water is essential to promote self-Healing, the more water the specimens are exposed to, the better the results obtained from the self-healing process will be, it is also observed humidity of the environment i.e. 50% it is not enough to activate the mechanisms of the crystallizing additive and treatment, so self-healing is not promoted.

Therefore, specimens with the most significant healing index were those in the curing pre-damage exposed to air. Moreover, there is a difference between 50-75% in the increase concerning the specimens immersed in water at the same experimental campaign phase.

4.3.2.4 Admixplus additive and submerged in water exposure condition.

The results obtained of the increase in the velocity of the ultrasonic pulse velocity test performed on the specimens containing Admixplus. The test cubes were exposed to the same three exposure conditions explained before for three months. The forthcoming figures show the values obtained in both the test cubes containing additive or treatment, and the control ones.

The specimens in contact with water reflect the presence of self-healing. Then, X and Z directions are where a more significant crack closure occurs. In the Y direction, an increase in wave velocity is also observed with lower values.

The samples called 1A6mfRcw show a percentage increase in their velocity of 39.74%, 3.61%, and 46.73% in X, Y and Z directions, respectively; when these results are compare with those obtained in the control test cubes whose present healing index increase values of 26.74% in X-direction 4.52 in Y-direction and 46.73% in Z-direction. It can be seen in the additive test cubes the increase was 13% in X and 1.34% in Z concerning the values obtained in the control specimens.

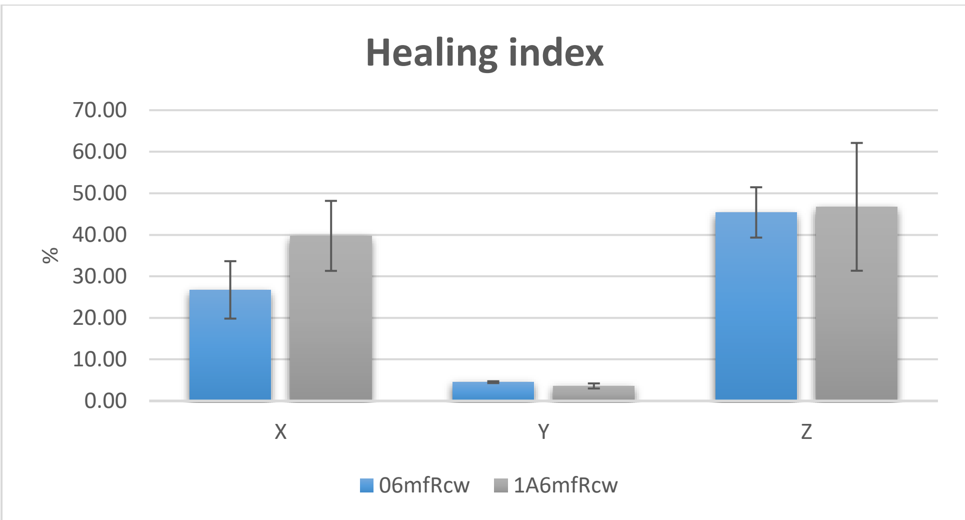

Figure 37: Healing index of specimens s with Admixplus additive and submerged in water exposure condition.

4.3.2.5 **Admixplus additive with sprayed water exposure condition**

In the case of sprayed water, a more significant increase is shown in the samples where in the pre-damage exposure condition were exposed to air, as is the case of the AIR1AfRcaw specimen, which offers an increase of 103.81%, 4.06%, and 65.37% in the X, Y and Z directions respectively. Meanwhile the specimens with lower values where those which curing exposure condition was submerged in water, values are lower when compare with the previous one, both 1A28dfRcaw and 1A6mfRcaw, this latter presenting the lowest increase in direction Z.

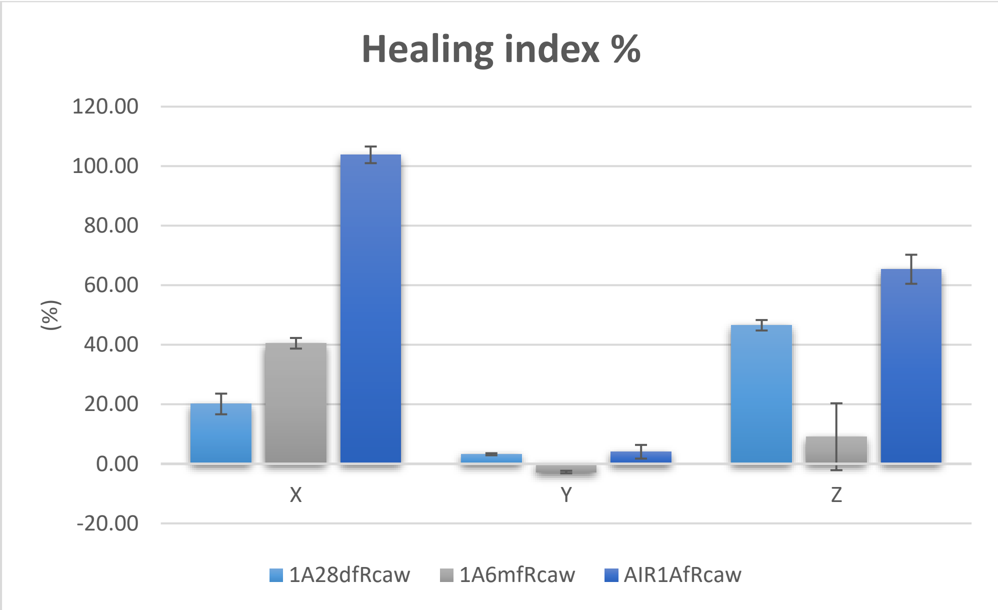

Figure 38: Healing index of specimens with Admixplus additive and sprayed water exposure condition

4.3.2.6 **Admixplus additive with Air exposure condition.**

The results, in the case of the control and Admixplus specimens, in the environmental condition of being exposed to air, do not show variations. Comparing the initial state from where self-healing begins to be studied, after the damage, as in the previous case, exposure to air does not promote self-healing. In the figure 39 all samples with admixplus discussed in this section are presented to evidence how self-healing is presented in the different exposure conditions.

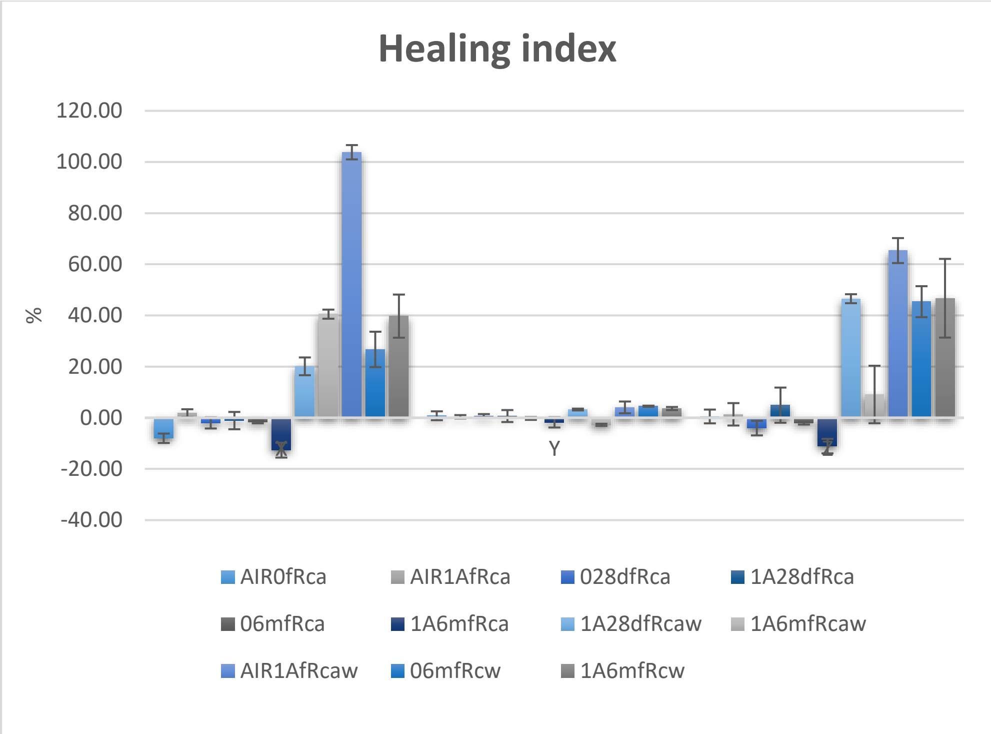

Figure 39: Healing index of specimens with Admixplus additive in the three-exposure condition

The evidence is consistent with the results found in the literature, where it is stated that contact with water in the conditioning or healing stage is essential to promote the self-healing phenomenon. The results obtained in this section of the experimental campaign show that it is important that the samples are in contact with water throughout the healing process, reaffirming water as one of the protagonists of this process. While sparked water also promotes self-healing to a lesser extent. Finally, exposure to air is not beneficial in terms of sealing cracks, the humidity present in the air is not enough.

The curing condition also plays an important role, the results show that in the specimens that were exposed to air in the initial condition, the healing index was higher, this is since the crystallizing additive creates a waterproofing barrier which avoid the entry of any moisture, when exposed in the condition submerged in water this barrier affects the capability of crystallizing when it is required latter, meanwhile when exposure to air this fact does not take place.

4.3.3 Influence of crystallizing additive and treatment in the healing index

In this part of the analysis, the influence of the multiseal and admixplus waterproofing treatment and additive, respectively, on promoting self-healing concrete is evaluated. The results obtained are grouped in terms of the same exposure condition after the damage, which allows contrasting the different additive configurations used in the specimens studied. In the case of Multiseal*,* it also varies in terms of application; it can be added in the pre-cracking or post-cracking phase.

4.3.3.1 Multiseal influence

Furthermore, when evaluating the behavior of both control specimens and the specimens containing additive, in the condition submerged in water, as evidenced in figure 40, there is a percentage increase in the speed of the UPV test. The multiseal shows better results in the AIRpfMfRcw specimens where the additive was added after cracking, and presents values of 153.37%, 13.10%, and 135.60% in the X, Y and Z directions, likewise the AIR29MfRcw specimen with 133.66%, 11.47%, and 154.79% healing index in X, Y and Z direction, in this case the Multiseal was added on day 29, both configurations have in common the pre-damage exposure to air, they show a relevant difference of almost 100% in X and Z direction.

Concerning the values of the control probe, the remaining cubes designs pfm28dfRcw and 29M28dfRcw present smaller increases as can be seen in the figure 40, both with initial exposure in water.

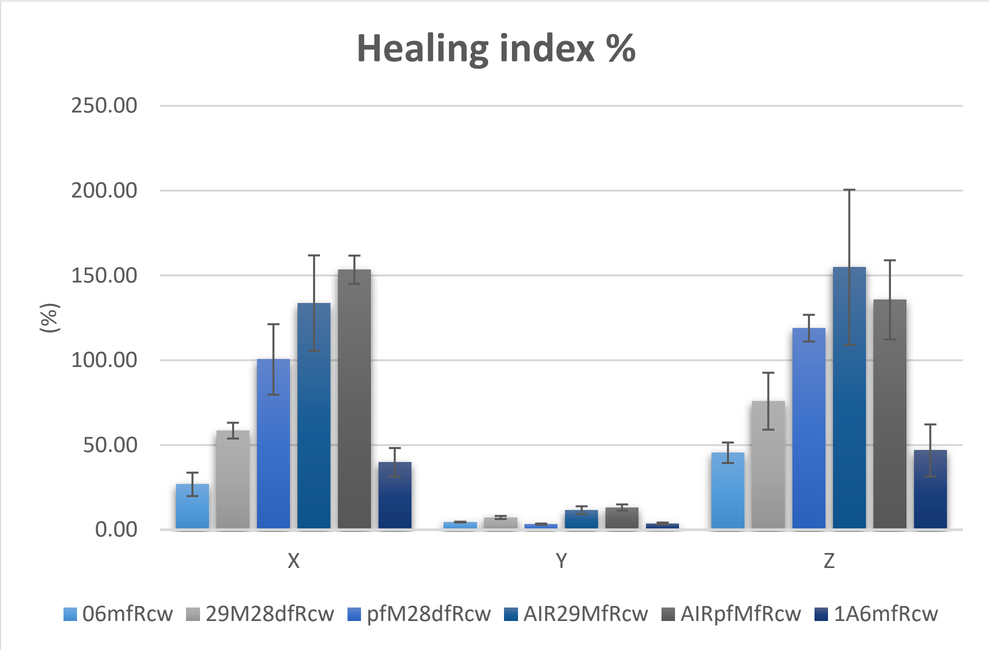

Figure 40: Healing index of specimens containing Multiseal and Admixplus under sumerged in water exposure condition

About the test cubes containing Admixplus, a percentage increase of 39.74%, 3.61%, 46.73% is presented, in the configuration 1A6mfRcw where the initial exposure was 6 months submerged in water, compared to the control test cube a percentage difference of 13%, 1% and 1.34% is obtained in the X, Y and Z directions.

Both for the test cubes with Multiseal and those that contain Admixplus, their performance while they are submerged in water, turns out to be the most suitable scenario to promote self-healing. For both products, their properties are evidenced as water proofing crystallizing additive and treatment able to promote self-healing.

Concerning the results obtained, in the specimens with multiseal, in the environmental condition of sprayed water, the best configuration is the one represented by

AIR29Mwfrcaw where in pre-damage exposure the specimens were exposed to air, multiseal was added on day 29 in combination with water, there is an increase in the velocity of the UPV test of xx in the x direction, xx in the y direction and xx in the z direction.

On the other hand, an increase, although less, was also found in the pfm6mfrcaw specimen, where the multiseal was added after the cracking, and whose pre-damage exposure was in water for a period of 6 months, for its part the 29m6mfrcaw configuration did not show signs of self-healing.

4.3.3.2 **Admixplus influence.**

Regarding Admixplus, figure 41 shows a positive healing index, which shows the presence of self-healing. Furthermore, in the three configurations evaluated, good results are shown. The specimens with the highest increase, AIR1AfRcaw where admixplus was added in 1% by cement weight, and its pre-damage exposure was in air, with 103.81%, 4.06% and 65.37% values in the X, Y and Z directions, respectively. Another positive configuration is the one called AIR29MwfRcaw with healing index of 77.21%, 6.89% and 83.56%, even presenting bigger value in Z direction than the previous one. In this last Multiseal was added before the damage, instead the cubes in which Multiseal was added after the damage does not show any positive value of healing index.

Meanwhile, the configurations that in the curing phase were exposed in water, the percentage of increase is lower, they were subjected to different periods of exposure, 28 days and 6 months, the latter being the one that obtained the lowest values of increase.

It is evidenced that both multiseal and admixplus under the sprayed water configuration generate optimal results by promoting self-healing. However, the conditions that show the best results are present where multiseal was added before the damage and in which the curing exposure was in air.

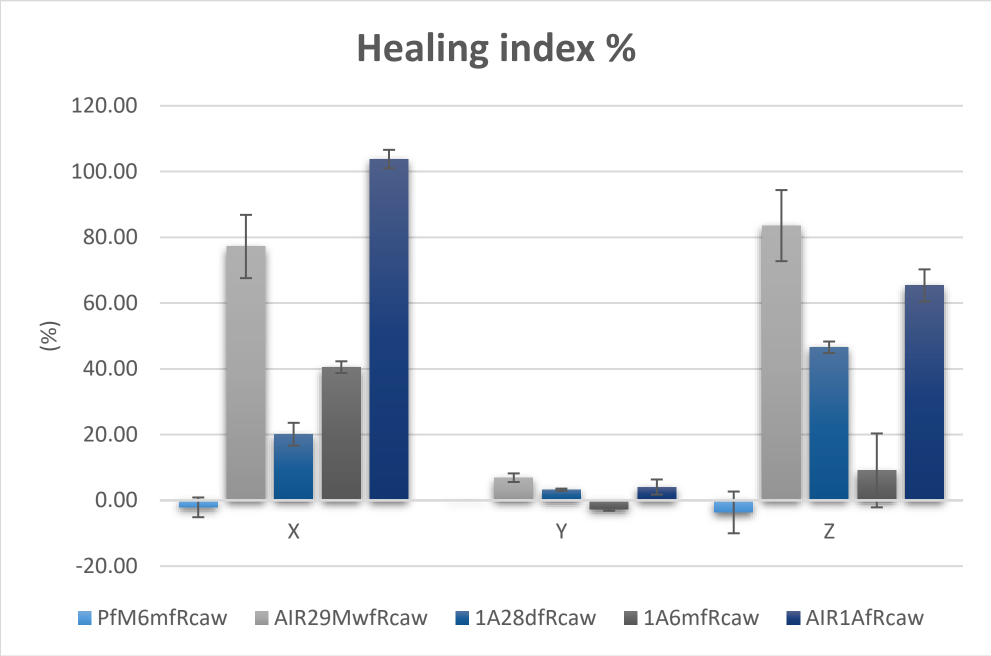

Figure 41: Healing index of specimens containing Multiseal and Admixplus under sprayed water exposure condition.

In the case of specimens containing multiseal and those containing Admixplus, both specimens exposed to air condition, did not obtain values that demonstrate the presence of self-healing concrete.

Furthermore, just two classes of samples present a positive healing index. The AIRpfMfRca configuration, although very low, there is a percentage increase in the UPV velocity of 12.86%, 1.28% and 0.17% in the X, Y and Z directions respectively, in this configuration as its name indicates, multiseal was added after the damage process, carried out under the displacement controlled compressive strength test mode, and in the configuration AIR29MwfRca with 1.77%, 3.22% and 3.70% values in the X, Y and Z directions, where the multiseal was added on day 29 in combination with water before the cracking process.

It is evident that combining either of the two crystallizing products and exposure to air does not promote self-healing. This result reaffirms the theory that the specimens must be in the presence of water totally or partially to activate the crystallizing additive mechanics; thus, self-healing can occur.

4.3.4 Relation between damage index and recovery of initial properties

This section shows the study carried out concerning the damage created and the recovery of the initial properties, in X, Y, and Z directions, making a distinction between the applied products and their exposure conditions during the healing period. The recovery of initial properties is defined as the difference between the velocity obtained in the pre-damage and the post-conditioning ultrasonic pulse velocity test measurements as explained in section 3.7.

Regarding multiseal samples, the greatest recovery of properties occurs in the X and Z directions, which were also the most damaged as explained in the previous sections. The specimens that register the highest recovery from the initial conditions in the X-direction have been the ones whose exposure during healing was submerged in water. Likewise, in the Z-direction, there is also a significant recovery for the specimens submerged in water and in which the water was sprayed, while the Y direction presents large recovery values, however, this direction has not been damaged enough to be considered in this analysis.

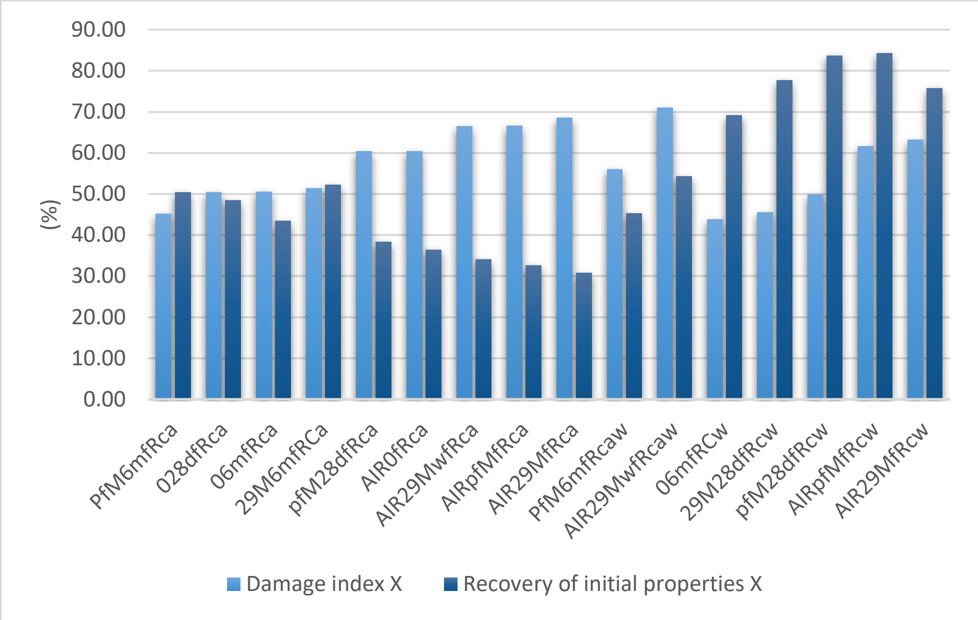

Figure 42: Comparison between damage index and recovery of initial properties index in X-direction of specimens containing Multiseal

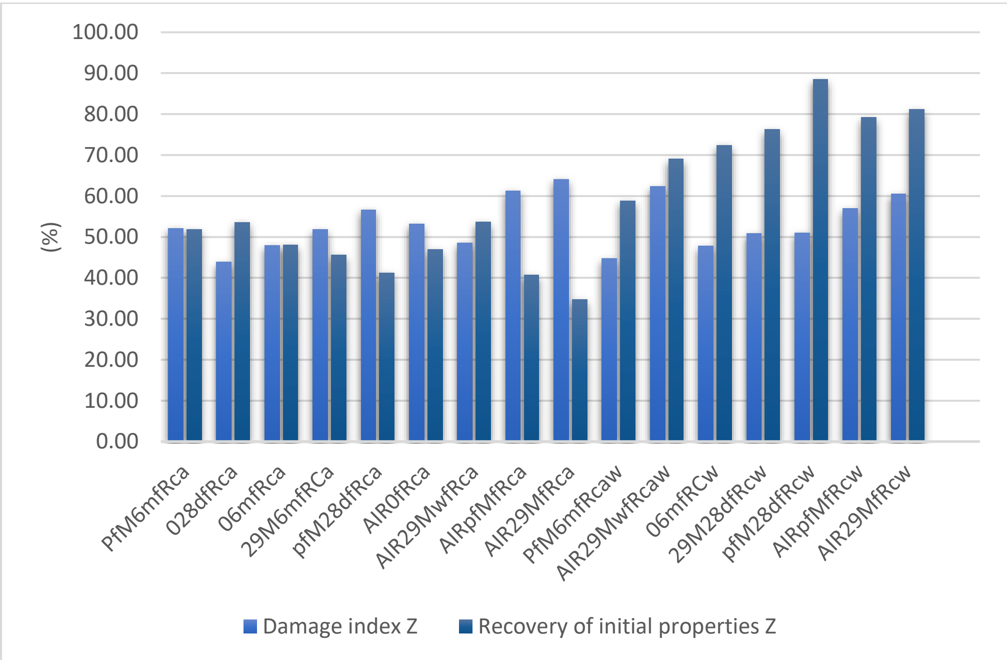

Figure 43: Comparison between damage index and recovery of initial properties index in Z-direction of specimens containing multiseal

In The other hand, admixplus has the highest recovery index in both the X and Z directions. As can be seen in Figure 44, the highest recovery value is evidenced in the specimens that have been submerged in water, for Z-direction also presents an important recovery where the water was sprayed.

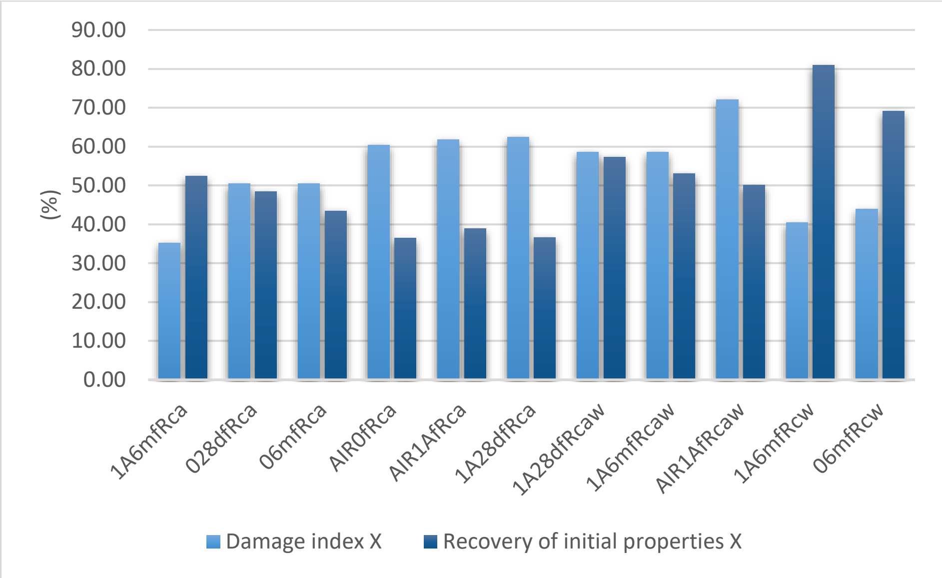

Figure 44: Comparison between damage index and recovery of initial properties index in X-direction of specimens containing admixplus

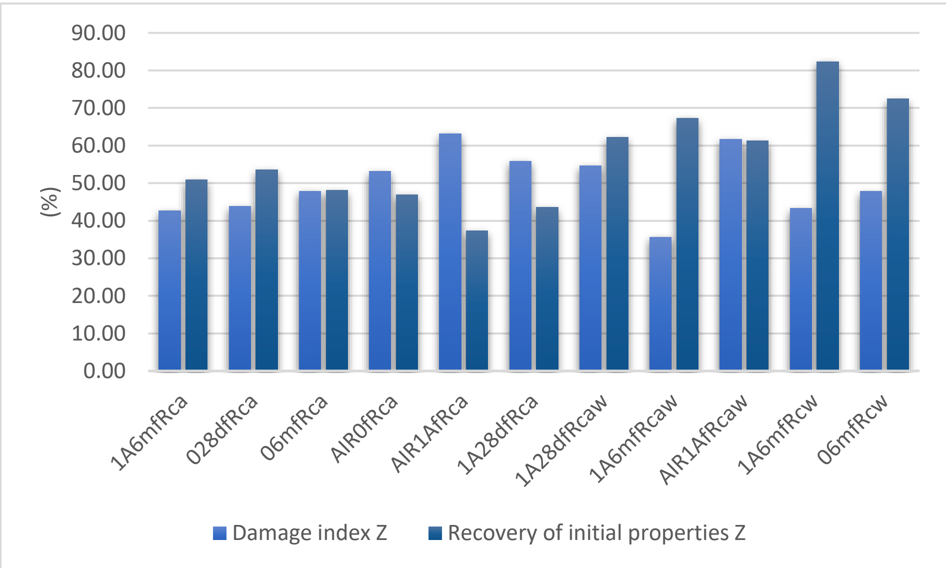

Figure 45: Comparison between damage index and recovery of initial properties index in Z-direction of specimens containing admixplus

As can be appreciated in Figures 46 and 47, the largest damage groups are concentrated in group 2 defined by values that are between 25.00% and 45.00% of damage index, and group three with values greater than 45.00%, in both directions. the largest number of specimens is concentrated in group three, that is, the samples present severe damage in terms of their initial condition.

Table 14: Damage groups.

Grupo 1	Grupo 2	Grupo 3
X< 25.00	25.00< X < 45.00	X > 45
Z < 25.00	25.00< Z < 45.00	Z > 45

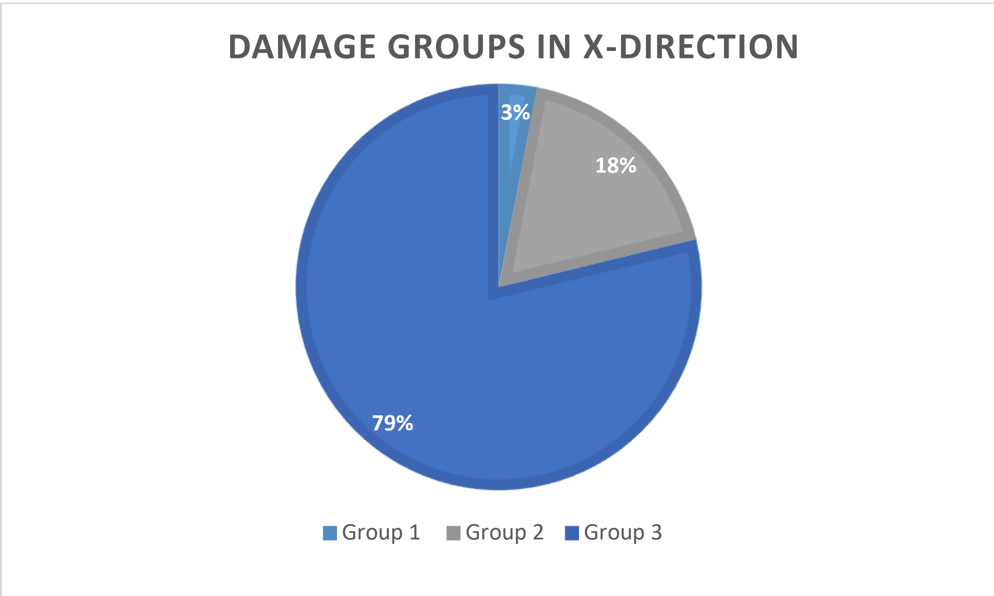

Figure 46: Damage groups in X- direction.

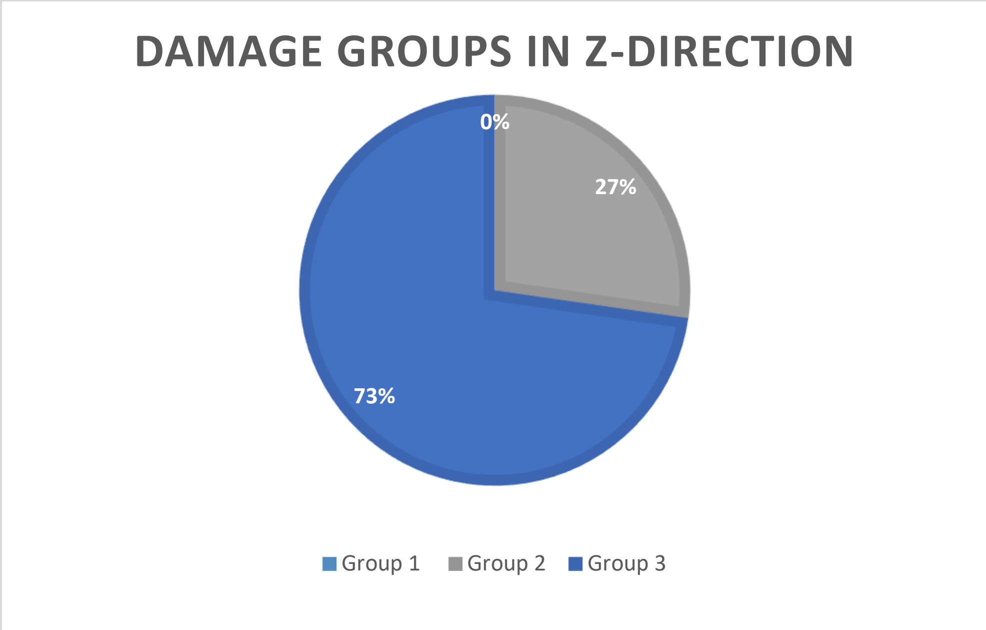

Figure 47: Damage groups in Y - direction.

The healing groups are concentrated between groups two and three as can be seen in figures 48 and 49, defined by the healing index between 5% and 40% and those greater than 40%, respectively. As occurred in the damaged section, the largest number of specimens are found in group three, this behavior affirms the relation stated the greater the damage, the higher the curing values.

Table 15: Healing groups.

Grupo 1	Grupo 2	Grupo 3
X< 5.00	5.00< X < 40.00	X > 40.00
Y < 5.00	5.00< Y < 40.00	Y > 40.00
Z < 5.00	5.00< Z < 40.00	Z > 40.00

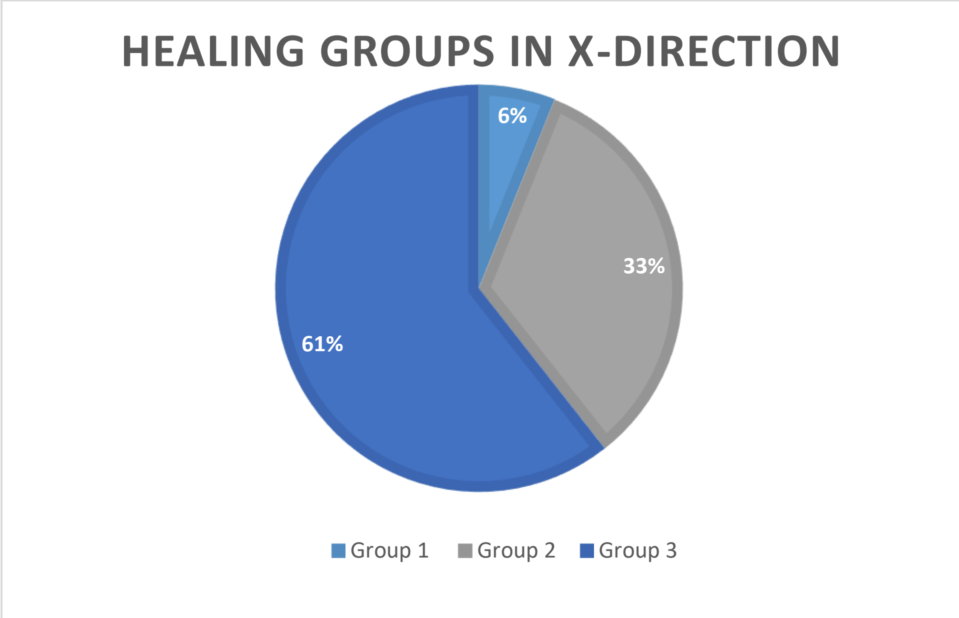

Figure 48: Healing groups in X-direction.

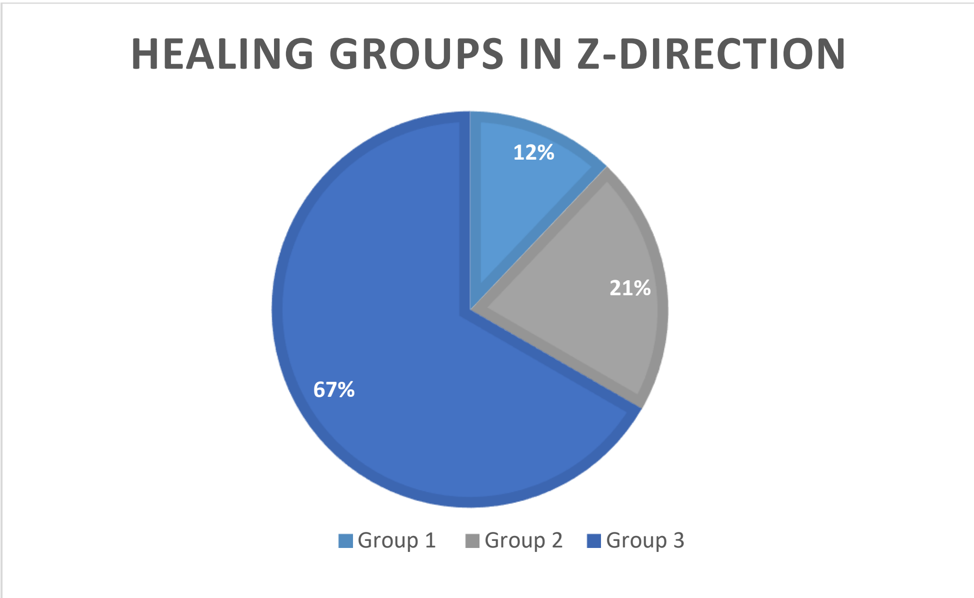

Figure 49: Healing groups in Z -direction.

As part of the results, it has been shown that the damage groups coincide with the groups defined to characterize the healing index in each direction, the specimens with damage recorded between 25% and 45% correspond to specimens that have been cured between 5 and 40%. Specimens whose exposure during the healing period has been exposed to air are excluded from this analysis, as the healing index is not considered remarkable.

It is evidenced that the specimens that suffered medium to severe damage also registered to heal higher than the minimum. There is a relationship between damage and the curing capacity of crystallizing additive and treatment.

4.4 Crack's closure visual qualitative evaluation

With the aim to demonstrating self-healing in the concrete cubes tested throughout the experimental campaign, photographs are taken in two phases, the first during the cracking process, before and after the compressive strength test, the second at the end of the 3-month conditioning period.

In correspondence with the results studied in the previous sections, in the cubes where the closure of the cracks has been more evidenced have been in the specimens whose exposure condition has been submerged in water, while the condition of sprayed water also found some samples of crystallization promoted by the studied products. On the contrary, in the samples exposed in air during the healing phase, they did not show signs of crystallization in the cracks.

The photographs selected among all the specimens that participated in the experimental campaign are presented below, likewise where it was found crystallization traits a millimeter zoom was performed.

Specimen code: AIR29MfRcw-1

Figure 50: Specimen in pre-cracking state

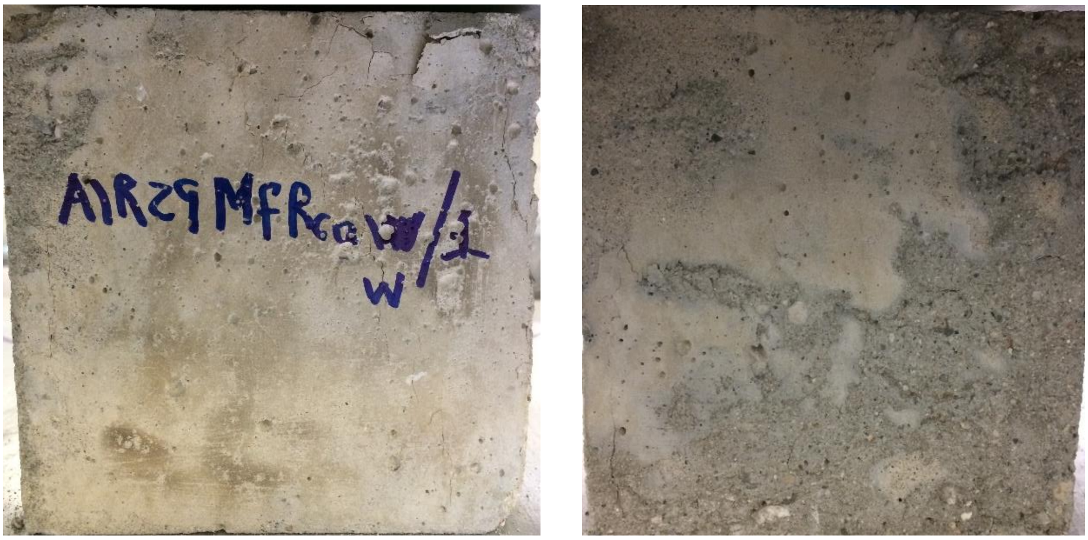

Figure 51: Specimen in post-cracking state

Figure 52: Specimen in post-conditioning state..

In this specimen the post-conditioning exposure condition was change after the cracking procedure, from sprayed water to submerged in water.

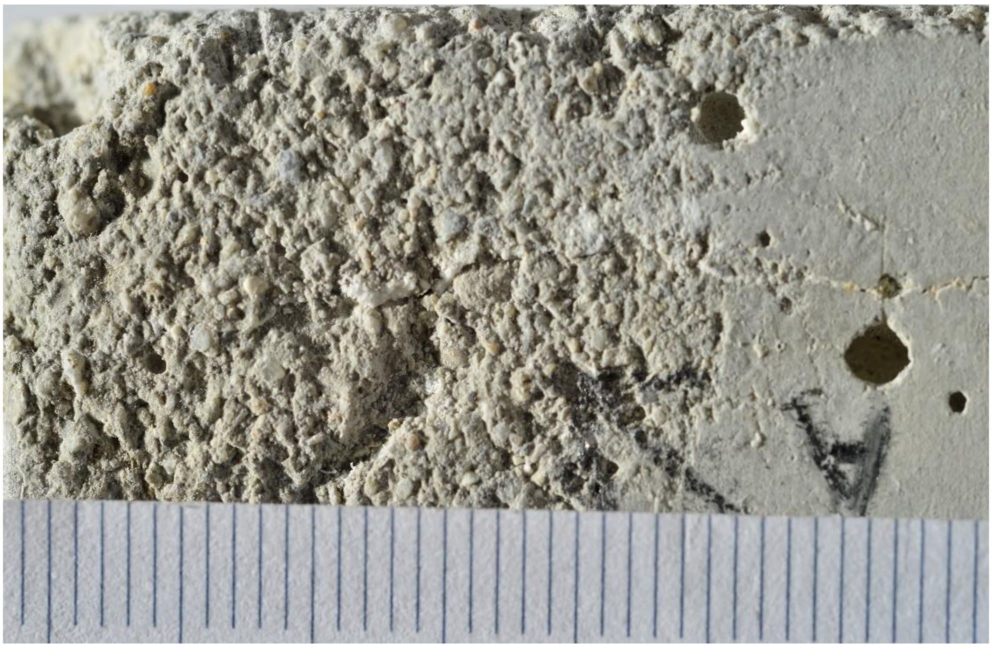

Figure 53: Evidence of crack closure.

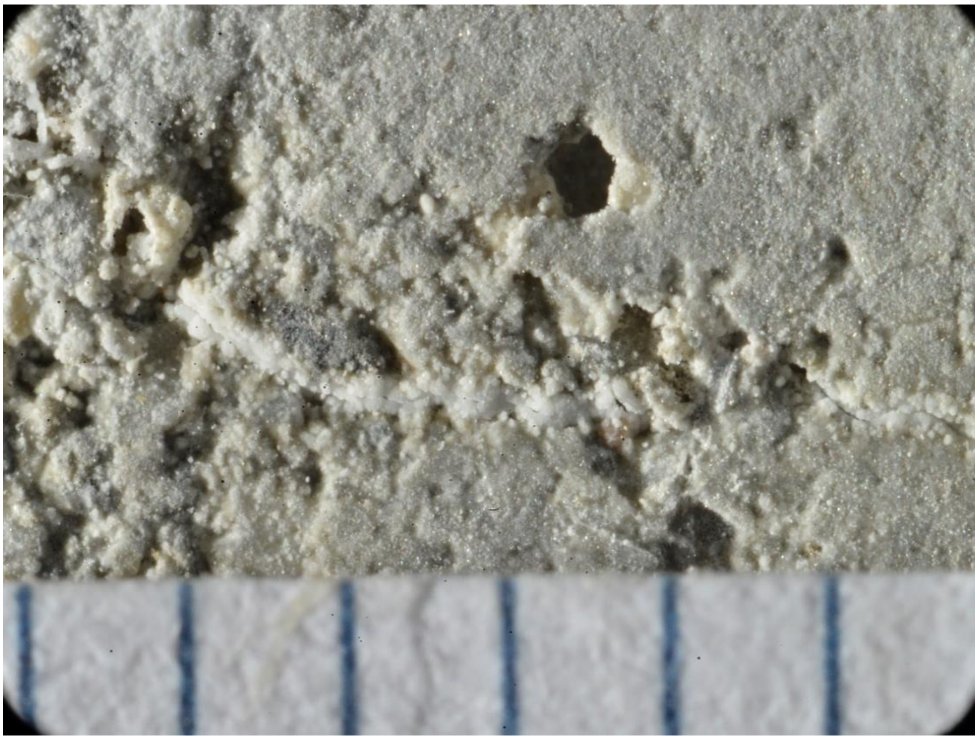

Figure 54: Evidence of crack closure and crystal formation

Specimen code: AIR29MfRcw-3

In this specimen the post-conditioning exposure condition was change after the cracking procedure, from sprayed water to submerged in water.

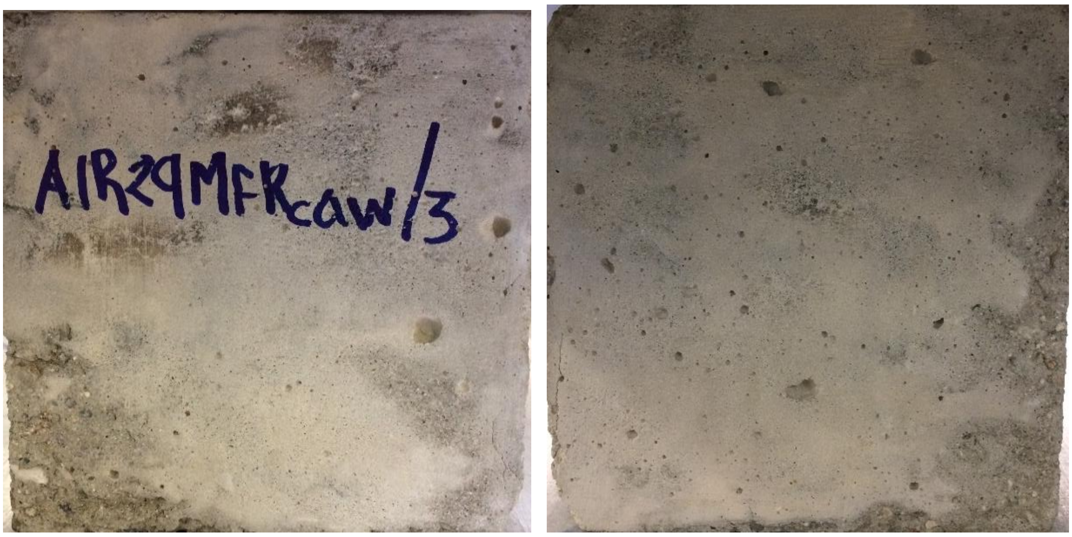

Figure 55: Specimen in pre-cracking state.

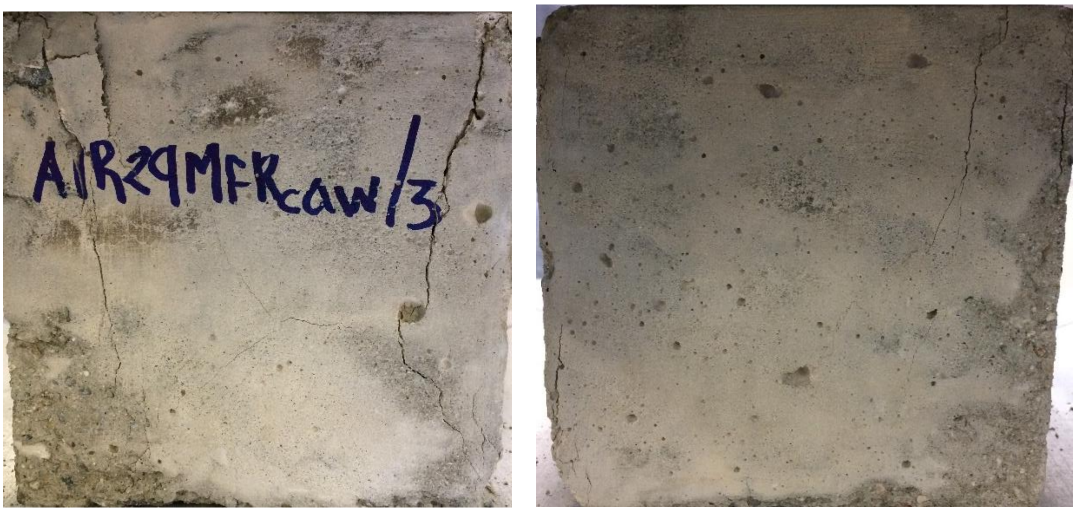

Figure 56: Specimen in post-cracking state.

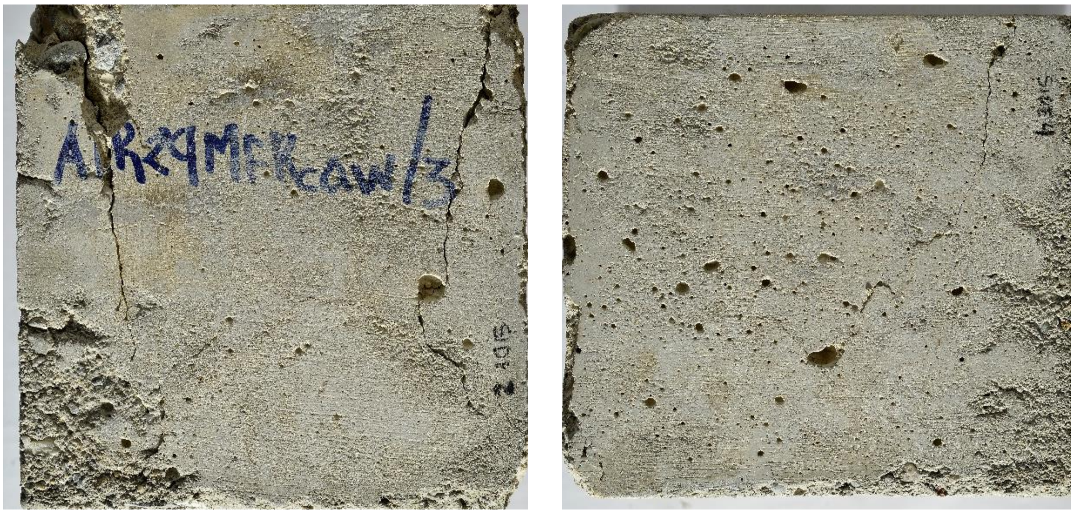

Figure 57: Specimen in post-conditioning state.

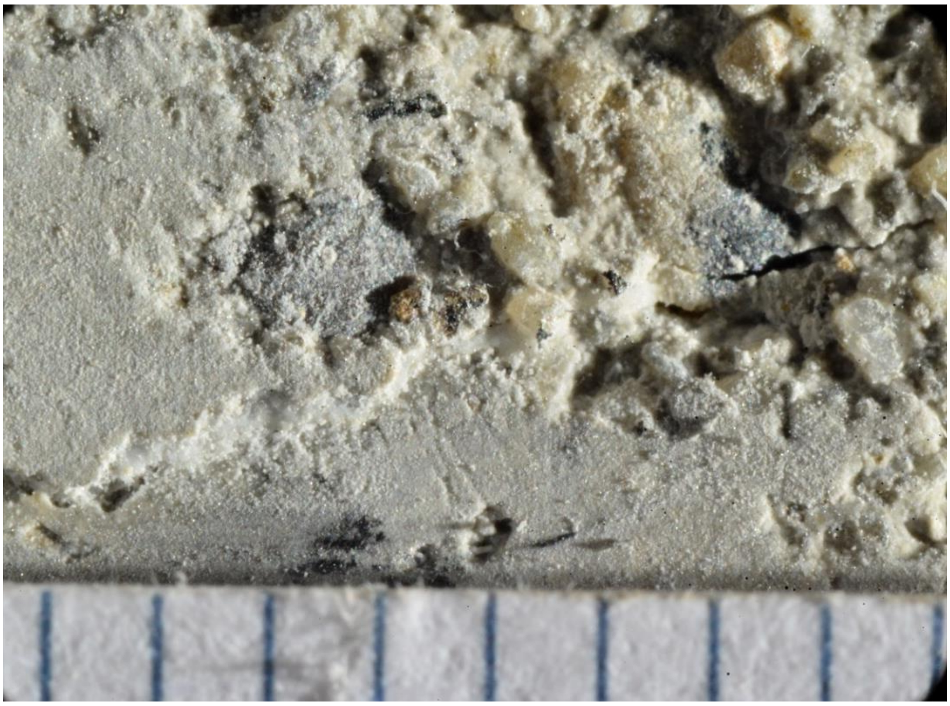

Figure 58: Evidence of crack closure.

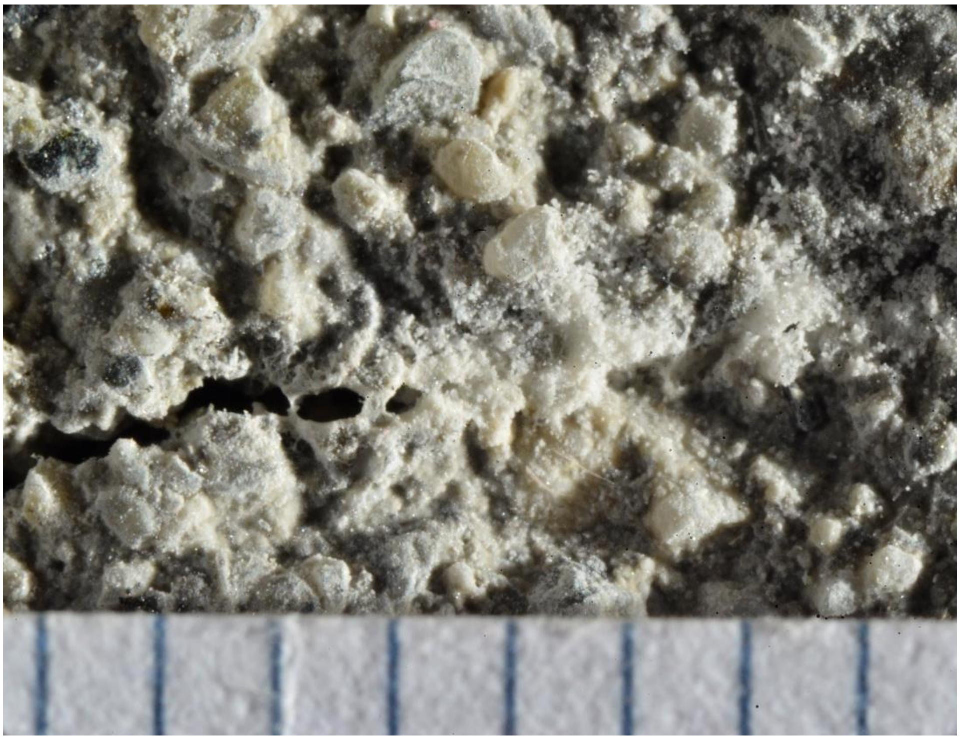

Figure 59: Evidence of crystals and crack in process to be sealed.

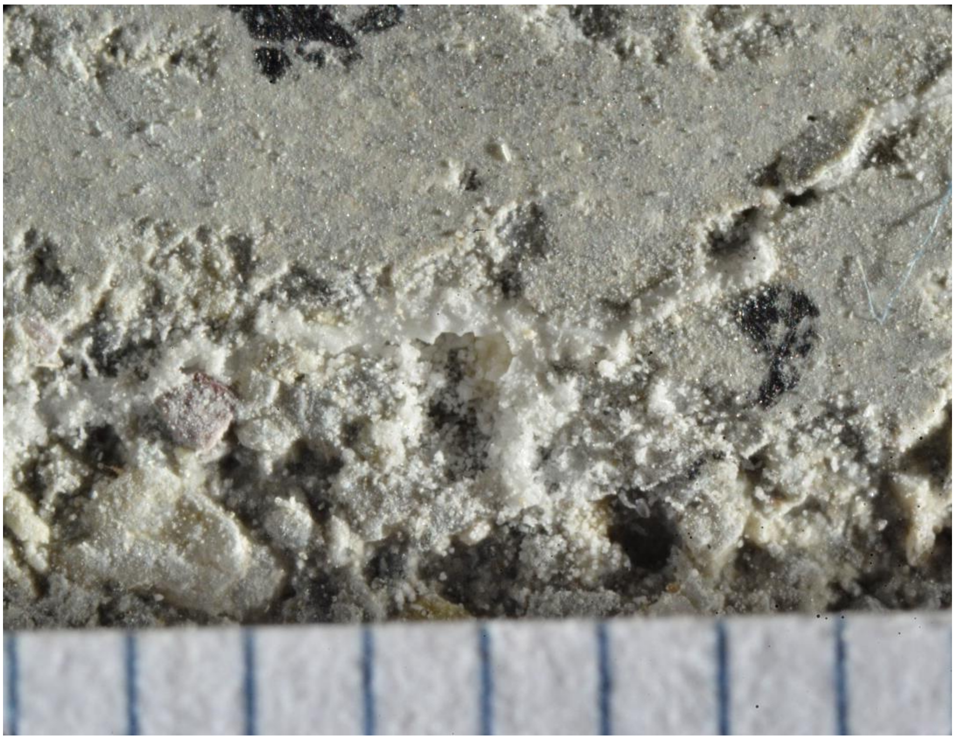

Figure 60: Evidence of crack closure.

Specimen code: AIR29MwfRcaw-3

Figure 61: Specimen in pre-cracking state.

Figure 62: Specimen in post-cracking state.

Figure 63: Specimen in post-conditioning state.

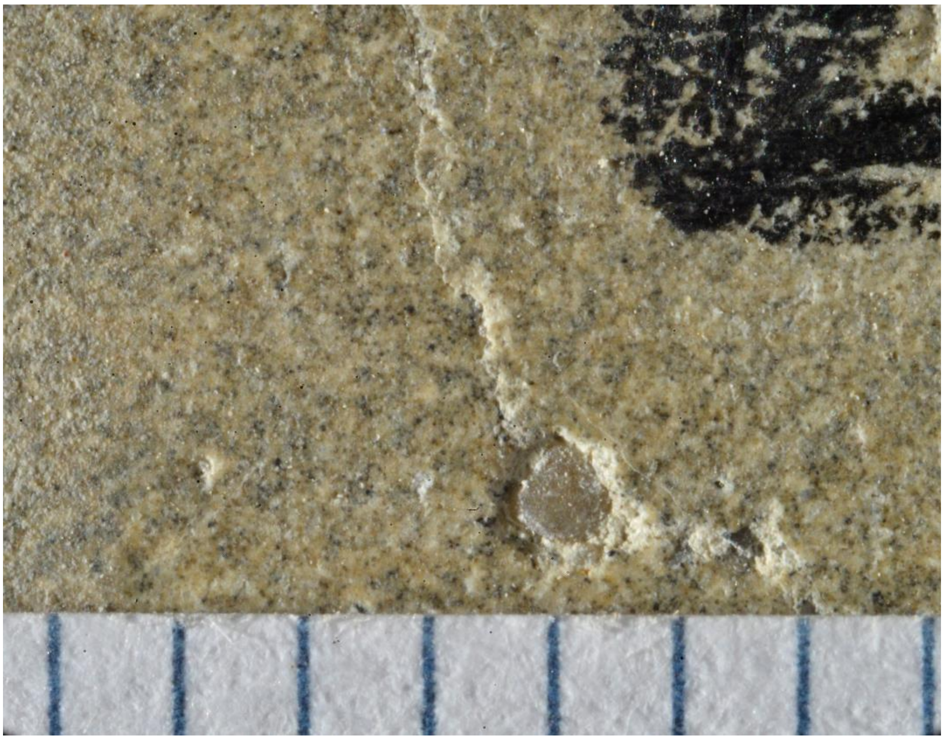

Figure 64: Evidence of crack closure.

Figure 65: Evidence of crystals and crack in process to be sealed.

Specimen code: PfM3mfRcaw-1

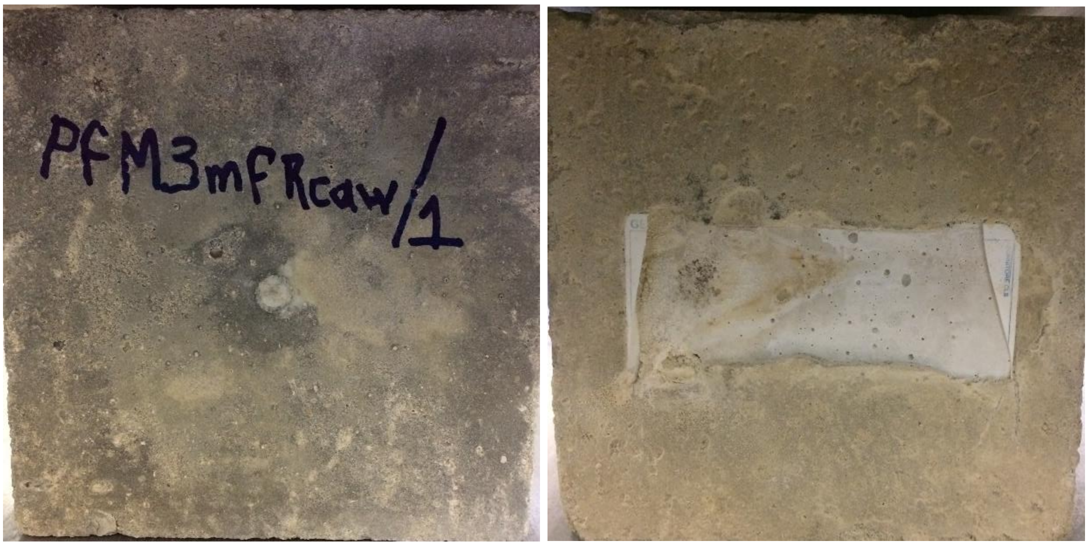

Figure 66: Specimen in pre-cracking state.

Figure 67: Specimen in post -cracking state.

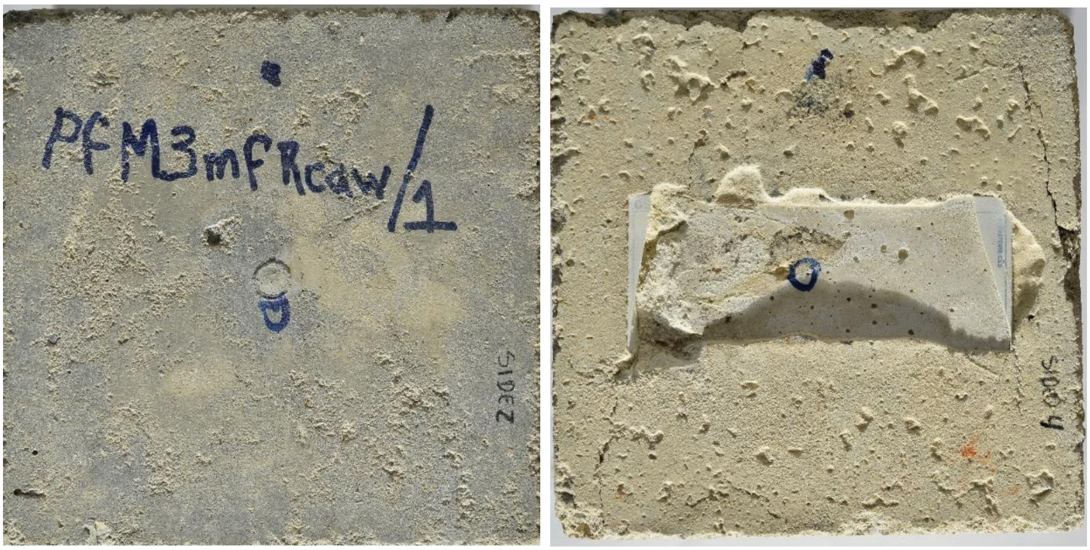

Figure 68: Specimen in post – conditioning state.

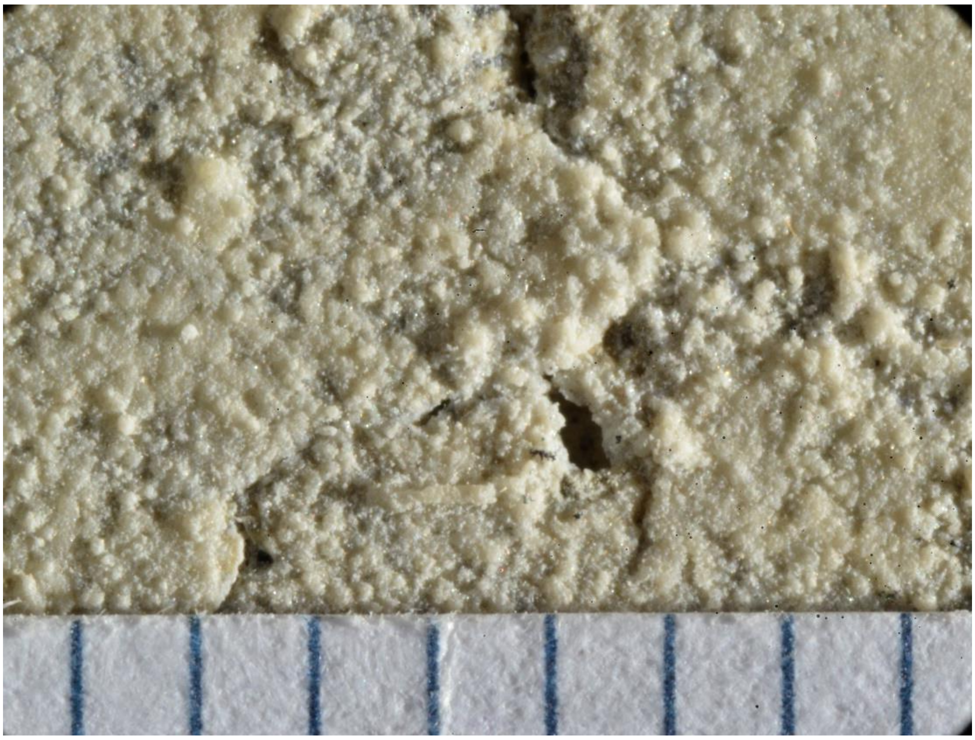

Figure 69: Evidence of crystals and crack in process to be sealed.

Specimen code: PfM28dfRcw-1

Figure 70: Specimen in pre-cracking state.

Figure 71: Specimen in post-cracking state.

Figure 72: Specimen in post-conditioning state.

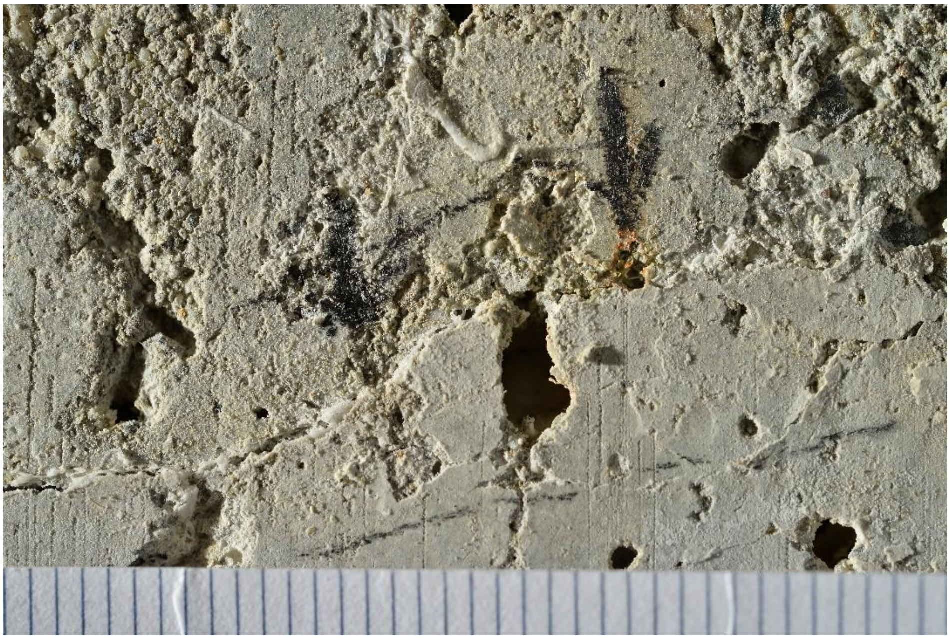

Figure 73: Evidence of crystals and crack in process to be sealed.

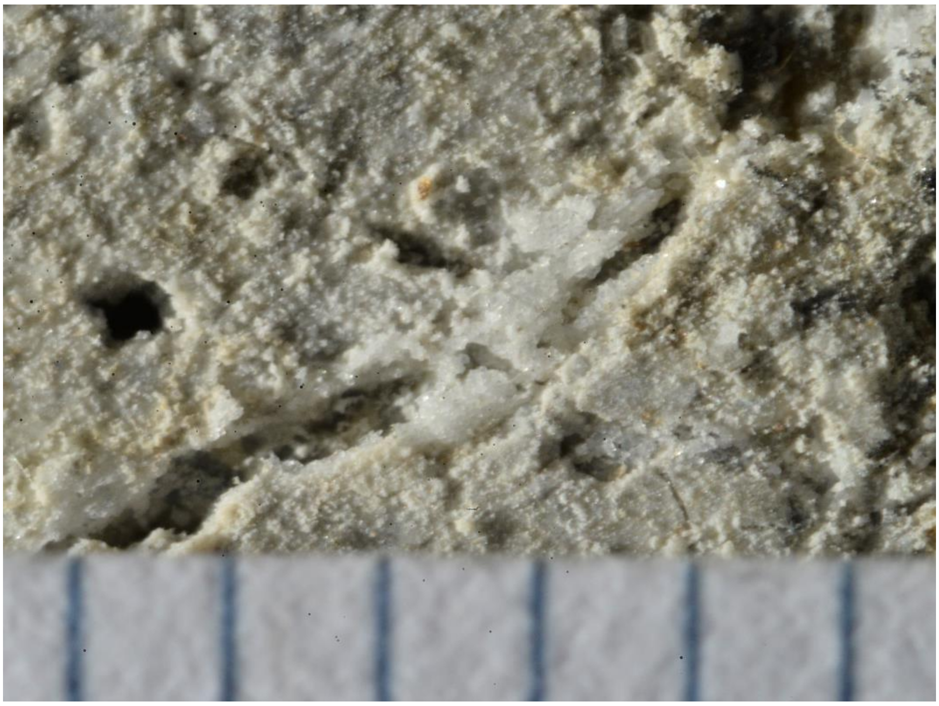

Figure 74: Evidence of crystals and crack in process to be sealed.

Chapter 5: Conclusions

This section summarizes the contributions generated from this research work, that are categorized according to the different sections explained in chapter 4, in which the results obtained during the experimental campaign were analyzed and discussed in detail.

In the present work, a methodology has been proposed to evaluate the promotion of self-healing by a crystallizing additive (Admixplus) and a crystallizing treatment (Multiseal). The influence of the exposure conditions, curing time as well as during the healing or conditioning stage has been evaluated.

Below is presented a list of the conclusions regarding each section analyzed.

Compressive Strength

- During the evaluation of the influence of the exposure condition in the curing phase, increases are presented when comparing the reference specimens, which do not contain any kind of additive, with the specimens containing admixplus of 10.1% and multiseal of 10.6% .

-The specimens cured in water for a period of 28 days. The reference specimens show higher values of compressive strength compared to multiseal, due to multiseal's ability to create an impermeable barrier, which prevents water from reaching the concrete matrix and does not allow continuous hydration of the cement during this time. While the specimens containing Admixplus showed values of compressive strength greater than those of the Multiseal specimens and comparable with the reference values.

-For the 6-month period of immersion in water, both types of specimens with Admixplus and Multiseal show increases in their compressive strength values of 21.7% and 7% respectively compared to the reference ones. Multiseal and Admixplus registered higher values of resistance to compression in the condition submerged in water for 6 months, compared to the control specimens.

Ultrasonic pulse velocity test

The results obtained from the healing index in the three exposure conditions show that:

-Exposure to air: the presence of self-healing is not obtained in any of the different configurations studied.

-In the case of sprayed water, higher values of self-healing are evidenced in the test cubes where Multiseal was added before damage and whose exposure during the curing phase was in air; samples with Admixplus whose initial exposure was in air presents the highest values of healing index for this configuration, while the initial exposure in water shows better healing values for a period of 28 days.

- In case of water curing in the healing phase, higher healing index values are shown in specimens with Multiseal and initial exposure in air.

-The specimens that obtained the best healing index values have been those treated with Multiseal when subjected to submerged in water, both in their pre-damage and post-damage curing. While in the sprayed water condition, Admixplus obtains the highest healing values.

-Exposure during the curing phase before the damage plays a fundamental role in the results obtained both for the Multiseal evaluation and for Admixplus, with exposure to air being the most beneficial.

-The exposure during the conditioning phase that presented the highest values of healing index has been that in which the samples have been submerged in water. Indeed, it is evidenced that water is essential to promote self-healing; the humidity present during the condition exposure to air, i.e. 50%, it is not enough to activate the self-healing mechanisms.

-The experimental evidence has shown that the best results are obtained for specimens with Admixplus or Multiseal which, before the damage, were not subjected to curing in water; the presence of water before damage, in fact, induces crystallization within the cement matrix even before the damage, resulting in a lower ability of the concrete to self-repair by crystallization following the damage.

-On the contrary, the best self-curing capacities are obtained in the case of specimens with Admixplus or Multiseal which have been characterized by a seasoning in the air prior to damage and, following the latter, by a wet seasoning, i.e. in the air with water nebulization or directly into the water. In this case, in fact, the crystallizing capacity is used in a higher percentage following the damage, resulting in a greater recovery of the properties of the material.

-An interesting result highlighted by Multiseal is linked to the fact that if this treatment is applied following the damage, in the case of simple water nebulization there is no significant recovery of the properties, therefore negligible self-healing, because water repellent of the treatment that does not allow water to penetrate inside and trigger the reactions that give rise to crystallization. This water-repellent effect is instead overcome if the sample with Multiseal applied after the damage is totally immersed in water; in the latter case the water, despite the water-repellent effect of the Multiseal, manages to penetrate through the cracks in the specimen so as to trigger the crystallization reactions. On the other hand, if the Multiseal is applied before damage, even the spray of water alone is effective in activating the crystallization.

-To classify the specimens, three different level of damage and three different level of self-healing have been introduced. The specimens that belonged to the levels of medium and severe damage, were part of the best groups of healing during the analysis phase of the recovery of the initial properties.

Chapter 6:

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