Evaluation of self-healing in concrete with limestone coarse aggregate impregnated with Na$_2$SiO$_3$ solution

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Abstract

This study investigated the self-healing process in concrete using limestone coarse aggregate impregnated with sodium silicate solution and encapsulated with polyvinyl alcohol (PVA). It discussed the self-healing mechanism by sodium silicate solution and evaluated the effect and the efficiency of this healing agent. To do this, limestone coarse aggregate was vacuum impregnated with a sodium silicate solution, encapsulated with PVA, and mixed into the concrete paste. The compressive strength was improved up to 50% in the concrete samples with sodium silicate. It also evaluated the porosity, density, and absorption ranges. It found a reduction of 4% in the range of absorption. Using x-ray diffraction (XRD), the chemical elements of the healing products were determined and the presence of the crystalline phases Etringite, Calcite, Dolomite and Minrecordite. This agreed with the chemical composition of dolomitic limestone’s (CaMg(CO$_3$)$_2$). The self-healing process was observed in the concrete samples cured at 28 days and was attributed to the formation of calcite crystals and silica gel C-S-H. Using the Scanning Electron Microscopy (SEM), the hydration products like calcite and C-S-H were visualized. Self-healing in the concrete could be observed due to the impregnation of Sodium Silicate in the aggregates.

1. Introduction

Concrete is the most widely used manufactured material in the world due to its mechanical properties, molding characteristics, mechanical properties of concrete via uniaxial compression test, and availability of the raw material for its elaboration. Many components are essential for the elaboration of concrete structures and their useful life depends on various types of damages which may include the generation of cracks at the micro and macro scale (Zhong and Yao 2008). Concrete is a brittle material, making it even more susceptible to cracking due to internal and external stresses that can be generated by mechanical loads such as tension and compression or environmental loads such as changes in temperature and humidity or a combination of both (Suleiman and Nehdi 2018, Zhong and Yao 2008). Microcracks, for their part, can act as flow networks for the penetration of polluting agents such as water and other chemical solutions and/or can spread and coalesce forming larger cracks (macro cracks) compromising the integrity of the structures in use (Sidiq, et al 2019, Van Tittelboom and De Belie 2013, Han and Zhang 2017). The mechanical resistance at compressive strength and durability are seriously affected by the generation of micro and macro cracks that deteriorate the structures, leading them to catastrophic failure. The repair or maintenance of concrete structures requires high costs and can become very complex due to various types of factors that can influence such as their location, the accessibility to damaged areas which are often not visible, in addition to the danger repair work such as bridges, underground tunnels,
and containers for hazardous liquids, among others (Ahn and Kishi 2010, Wang et al 2018, Restuccia et al 2017). It is possible to decrease or eliminate these problems through the use of technologies such as self-healing, which seals and heals cracks, recovering mechanical resistance at compressive strength, or as an indicator of durability based on calcium carbonate precipitation and continuous hydration. of anhydrous cementitious materials, when water and carbon dioxide are available (Van Tittelboom et al 2012, Solis and Alcocer 2019). Concrete possesses the inherent autogenous ability to seal cracks of limited width using the self-healing mechanism, however, recovery activity is relatively low considering some other factors, (Jiang et al 2015, Van Tittelboom and De Belie 2013). To improve self-healing behavior in concrete, various systems and techniques have been developed, such as the addition of autonomic healing agents to cementitious materials, as well as characterization techniques and quantification methods for their evaluation (Nguyen et al 2019, Savija 2018, Suleiman et al 2019, Xue et al 2019). Most of the healing agents are introduced and distributed in the concrete in encapsulation systems, which are later released when cracks break the walls of the system, producing new components that link the faces of the new surfaces sealing the cracks (Beglarigale et al 2018, Irico et al 2017, Tang et al 2015). Among the most studied healing agents are epoxy resins, methyl methacrylate (MMA), polyurethane, sodium alkali-silica silicate solutions (Na₂SiO₃), cyanoacrylates (CA) (K. Van Tittelboom et al 2011, Yang et al 2011, Kim et al 1999). Sodium silicate solutions have adequate potential as a healing agent for efficient crack recovery and could potentially restore the integrity of damaged concrete structures (Huang and Ye 2011, Kanellopoulos et al 2015, Li and Herbert 2012, Mostavi et al 2015, Pelletier et al 2011, Sidiq et al 2019). The SiO₂ from the healing agent reacts with the calcium hydroxide Ca (OH)₂ of the hydrated cement paste to form the CSH (tobermorite) gel which is the main product of the hydrated cement paste (Giannaros et al 2016, Huang and Ye 2011, Sidiq et al 2019). However, (Irico et al 2017) reported that sodium silicate not only reacts with the Ca (OH)₂ of the hydrated cement but also reacts with the hydrated phases of calcium aluminate (A_F, A_Fm, TAH) to form CSH/CASH pseudo-crystalline products, so sodium silicate solutions efficiently promote crack healing. Most healing agents are microencapsulated in containers or shells of different materials and shapes, which are released when the microcapsule is broken. A. (Beglarigale et al 2018) used the microencapsulated sodium silicate in polyurethane microcapsules as a healing agent and evaluated the fracture behavior of the optimized microcapsules in contact with the cracks. (Giannaros et al 2016), added microencapsulated sodium silicate in liquid and solid form in cement specimens and evaluated the rheological and mechanical properties. They reported that the addition of microcapsules inhibits the resistance to compression of cement; however, an improvement in sorptivity reduction was observed which is an indicator of durability. For their part, Luciana et al (New self-healing techniques for cement-based materials - ScienceDirect, s. f.), in their research used two different shells for the encapsulation of sodium silicate: spherical glass capsules and pharmaceutical capsules. They reported that the sodium silicate was efficiently released from the capsules when the fracture intercepted them. However, they reported that a quantity of sodium silicate could diffuse in the cementitious matrix since it presented a limited recovery in resistance.

On the other hand, the aggregates in the concrete are a fundamental part of the good performance in the use of the concrete structures, since three-quarters of the concrete mix corresponds to the aggregates (fine and thick). Limestone aggregates are considered high absorption and have a high percentage of fine particles that lead to a greater demand for water when used in concrete mixtures and therefore there is a greater demand for cement to maintain the established a/c ratios and achieve its design strength (Durabilidad del concreto con agregados de alta absorción, s. f.; Rómel Solís and Moreno 2006, Trejo-Arroyo et al 2019). These characteristics can be exploited since the high absorption aggregates facilitate the transport of fluids. They can serve as the receptor element where the healing agent is lodged, in this case, sodium silicate. (Alghamri et al 2016), in their research, evaluated the potential of sodium silicate impregnation in lightweight aggregates and its performance as self-healing in concretes made with these aggregates. They reported a recovery in flexural strength in concretes made with this impregnated aggregate and a reduction in water sorptivity, as an indicator of durability, and also confirmed an increase in CSH gel formation due to interaction with the healing agent. In the present study, the impregnation method of limestone aggregates with sodium silicate was used as a healing medium to evaluate the self-healing effect on mechanical strength and durability in concrete samples.

2. Experimental procedure and conditions

2.1. Materials

The materials used for the preparation of the concrete mixes were Portland Ordinary Cement (OPC) purchased by a national supplier; water and coarse and fine limestone aggregates from the limestone crushing process of a local quarry in the city of Chetumal, Mexico. The physical properties of the aggregates were obtained according to the ASTM standards and shown in table 1. The most outstanding aspects are the unfavorable conditions, typical of limestone materials, where the absorption values are high and the specific gravity is low. Only the
coarse aggregates were used for impregnation. Sodium silicate was used as the self-healing agent (J.T. Baker, USA) and polyvinyl alcohol was used as the sealant (Sigma Aldrich with 89, 000–96, 000, 99 % hydrolyzed).

The materials used in the preparation of concrete mixes are:

(a) Sodium silicate (J.T. Baker, USA) was used as the self-healing agent.

(b) Polyvinyl Alcohol (Sigma Aldrich with 89, 000–96, 000, 99 % hydrolyzed).

(c) Limestone coarse and fine aggregates supplied by a local distributor in Chetumal City, Mexico, were used in this study. Only the coarse aggregate was utilized for impregnation. The properties of both fine and coarse were characterized granulometrically in the laboratory.

(d) The cement used in this study was Ordinary Portland Cement, which was supplied by a national producer.

### 2.2. Methods and preparation techniques

#### 2.2.1. Impregnation procedure

The coarse aggregates were selected with a diameter of 4–19 mm and dried in an oven at the temperature of 110 °C for 24 h. First, a test was carried out to determine the absorption rate of the coarse aggregates under atmospheric conditions for a period of 72 h. The impregnation was carried out by immersing the limestone aggregates in a sodium silicate solution, the aggregates were immersed for three different periods (1, 2, and 3 days).

At the end of the three days, the excess sodium silicate solution was filtered and the aggregates were surface dried with a cloth obtaining saturated and superficially dry particles. Their weights were monitored at the end of each period using a digital scale with 1.0 g of accuracy. Subsequently, a series of steps were developed for the impregnation process in the laboratory which consisted of a vacuum chamber with two ports connected (ventilation and manometer) to a vacuum pump. The aggregates were placed inside the vacuum chamber together with the sodium silicate solution; this solution was initially raised 50 mm above the level of the aggregates to ensure their total immersion. The vacuum chamber was hermetically sealed and pressurized to −0.3 bar.

The percentage of absorption achieved in limestone aggregates and under environmental conditions was only 6%, for the period of 72 h (figure 1(A)). However, the retention of the liquid was not enough to allow working with the aggregates, for which the vacuum impregnation was subjected to a period of 72 h to achieve the migration of the water particles to the matrix of the aggregates (figure 1(B)). The expected retention and the adequate percentage of absorption were obtained reaching a percentage of absorption del 20% by remaining in the vacuum chamber for 60 min, therefore this treatment was applied for all the aggregates.

At the end of three days of vacuum impregnation, the excess sodium silicate solution was filtered and the surface of the aggregates was dried with tissues. This resulted in, saturated and surface dry particles.

#### 2.2.2. Encapsulation procedure

As a sealing agent for the saturated aggregates of the sodium silicate solution, polyvinyl alcohol (PVA) was used, using the immersion coating method. Encapsulation of coarse aggregates with the sealing agent is important to prevent any leakage of the healing agent and its premature interaction with the cementitious matrix. The PVA solution was prepared with deionized water and magnetic stirring. The aggregates were immersed in the dried coating solution simultaneously blowing a stream of hot air. Subsequently, the coarse aggregate limestone encapsulated and impregnated with sodium silicate was used to make the concrete mix for the experimental cylinders.

#### 2.2.3. Concrete samples and curing

Mixture design was performed according to the ACI 211.1 (Dixon et al 1997). 0.5 w/c. Effective absorption of 80% for the mixing water correction was considered. The concrete batches were 80 liters made in 8 min. Cylindrical specimens of 15 × 30 cm were cast for compressive strength tests and 10 × 20 cm for physical tests.

| Material       | Property       | Value       |
|----------------|----------------|-------------|
| Coarse aggregate | Maximum size   | 9.5 mm      |
|                | Specific gravity| 1.24        |
|                | Compact unit weight | 1623 kg m⁻³ |
|                | Absorption     | 4.56%       |
| Fine aggregate  | Specific gravity| 1.58        |
|                | Fineness modulus| 2.9         |
|                | Absorption     | 1.17%       |
(porosity, density, and absorption). All specimens (control and experimental) were subjected to a process of moist curing by immersion. Six mixes of concrete were prepared according to the American Society for Testing and Materials (ASTM standards).

The first mix was the control sample and the second mix the coarse aggregates were replaced by the same volume of impregnated limestone coarse aggregate particles and this mix. For both mixes, 4 cylindrical specimens with dimensions of 80 mm of diameter, 200 mm height, and 5 cylindrical specimens with dimensions of 160 mm diameter and 300 mm height were prepared. All specimens were unmolded after 1 day of dry curing and then were exposed to wet curing for 7, 14, and 28 days into a water tank.

Physical tests were performed in concrete fresh unit weight and slump (ASTM C 143-08, 2019) (ASTM C143/C143M−08 Standard Test Method for Slump of Hydraulic-Cement Concrete, s. f.) and trapped air (ASTM C 231) (ASTM C231/C231M-17a Método de Ensayo Normalizado de Contenido de Aire del Concreto Recién Mezclado Mediante el Método por Presión, s. f.). During the tests performed there was a slight increase in trapped air and tempering of the control concrete compared to the experimental concrete. Subsequently, compressive strength (ASTM C 39, 2019) (ASTM Standard Test Method C39, s. f.), porosity, density, and absorption tests were made in hardened concrete.

2.2.4. Self-healing process

The tests were carried out with the Micro-indenter Vickers Nanovea Hardness, Tester Micro Photonics Inc. The micro-hardness of one preparation was evaluated for 28 days of curing of experimental concrete and one of control concrete the same time of curing. In each sample, they were carried out on average four Vickers indentations in different parts of it until obtaining the desired trace for monitoring.

To monitor the self-repair process in the concrete, two samples were selected for each time of curing in the experimental concrete and one in the control concrete. The Vickers indentation was carried out and an indentation imprint was selected. Through the use of the Scanning Electron Microscopy (SEM) these indentation imprints and cracks were observed. The SEM utilized for this investigation was JEOL 6400 with the complement JEOL JSM 6400.

The average width of the crack in micrometers and nanometers respectively is measured. The samples were evaluated four times that correspond to the first day of the cracking and 90th day after the cracking. During the monitoring period, the samples were stored in a silica desiccator at normal humidity and temperature conditions.

X-Ray Diffraction studies were carried out in a sample for each curing time by an x-ray Diffractometer Bruker D8 Advanced Davinchi that uses a radiation source the Kα line of the copper (CuKα).

3. Results and discussions

In figure 2, the average values for compressive strength (Fc in MPa) are shown. If the outcomes are compared at 7 and 14 days of age between the control and experimental specimens, it is observed that they are very similar. However, at 28 days of age, when the optimum compressive strength has been reached, there is a 10%
improvement for experimental specimens whose aggregates were impregnated with the sodium silicate solution before casting.

The increase in the compressive strength could have been given by: (i) the formation of CH and CaCO3 crystals in the concrete matrix. These results agree with the previous investigation by Haoliang (Huang and Ye 2011) where reported about the improvements in mechanical properties of an ECC with the use of sodium silicate as an agent of autonomic repair with more than 20% strength recovery in comparison with the samples without sodium silicate. (ii) The PVA improved the physical properties and mechanical performance given that prevented the leakage of the sodium silicate and at the same time, it filled the pores to the outside of its structure, which concords with the results reported by (Kou and Poon 2010). They concluded that the addition of PVA reduced the fragility of the pores in the transition zone between the cement paste and the aggregates.

For the results in absolute density tests, it is observed that both the experimental concrete and the control concrete one passed the range $\geq 2.25$ of density which is an optimal density thus, the compressive strength is favored (figure 3(A)). It was shown that both sodium silicate and PVA did not affect the density of the concrete even significantly.

Figure 3(B) shows that the absorption percentage decreases from 7 to 14 days of age and then increases after 28 days. However, its increase is more evident in the control concrete sample. This may be because, in the experimental concrete, the action of sodium silicate and PVA has increased the number of hydration crystals that fill the micro-cracks and micro-pores that are part of the start of setting in the concrete by the plastic contraction.
For the average porosity results of the experimental and control concrete, a difference of up to 4% more porosity is observed for the control concrete, this result agrees with the results obtained by Jae-Ho Kim et al (Kim et al 1999) who reported that the porous transition zone between cement paste and aggregates was reduced in number and size of pores by PVA action, which reduced the percentage of porosity. The tendency of both concrete to decrease its porosity to 14 days and increase it to 28 days maybe because as soon as the concrete begins to harden, after 7 days the internal formation of pores and holes begins. At this point, the concrete has not yet reached its maximum strength and there is a large number of unreacted particles of cement. After 14 days the concrete has decreased its porosity by crystallizing the cement occupying air pores inside and outside. At 28 days the sodium silicate solution begins to be released, and since it is considered a hydrophilic compound, it begins to attract water particles, formatting channels through which they interconnect with the coarse aggregates and micro-pores of the exterior (figure (4)). The aforementioned statement supports the results of the mechanical tests. According to the cylinders with 28 days of curing, a greater difference was obtained between the experimental average result and the control. Assuming therefore that the sodium silicate potentiated the resistance of the aggregates and therefore of the concrete.

One of the main advantages of using the coarse aggregate as a means of transport is that its distribution is uniform throughout the concrete which ensures that the repair agent will be in the entire concrete mix. Therefore, it will be able to act independently of the area in that cracking occurs, which is not assured with the use of other self-healing techniques such as the addition of microcapsules or micro-tubes.

The image of figure 5(a) corresponds to the experimental sample of 28 days of curing. An area corresponding to the limestone aggregates impregnated with the sodium silicate solution; is observed in the insert of the micrograph obtained at higher magnifications (2500x), a kind of partial covering on the grains with a different texture that is not observed in concrete with normal aggregates. In the image of figure 5(b), a micrograph of the experimental sample is observed at lower magnifications. It shows clearly the region of the impregnated aggregates, the cementitious matrix, and the interfacial transition zone (ITZ) between the aggregates and the cementing paste. At the moment of generating a crack, this can originate from the aggregates or in the ITZ zone, since the aggregates are impregnated with the sodium silicate solution, this solution can be released and react with the calcium hydroxide coming from the cement paste in the presence of water, which can generate the C-S-H tobermorite gel, which is mostly present in samples cured at 28 days because it is a pseudo-amorphous phase and does not present peaks of crystallinity.

The image of figure 5(c) corresponds to the experimental sample of 7 days of curing. It is possible to observe a high percentage of the formation of AFT ettringite crystals which are common to be formed in the first stage of hydration. The presence of belite (dicalcium silicate C2S) is also observed, which represents that the cement paste is still in the hydration stage. The image of figure 5(d) also shows the presence of some crystals of portlandite Ca(OH)$_2$. As mentioned above, the sodium silicate when released from the impregnated aggregates can react with the portlandite and also with the ettringite or calcium aluminate phases for the formation of the tobermorite gel, thus consuming said phases as mentioned in the literature (Irico et al 2017), as suggested, decreases its presence in the samples after 28 of curing days.

Figure 6 Shows the SEM images and exposes the monitoring at 1 and 90 days, performed on the control concrete cured at 28 days monitored, at an increase of 1000×. The average width of the cracks generated was of
~3 μm (figure 6(A)) and observed and increase as a function of time approximately 50% at 90 days (figure 6(B)). A mayor cracking were observed (a)–(d) considering that the cracking were induced with the same load for all the samples.

In figure 7, four representative cracks were indicated in the periphery of a generated indentation. Except that indicated by the letter c, the self-healing of the cracks is evident, even in the outline of the same residual indentation.

This image that corresponds to the concrete cured for 28 days is obtained in an indented impression generated in the area near the coarse aggregate, which is not yet the interfacial transition zone (ITZ). So it is presumable that the release of the sodium silicate occurred between 14 and 28 days of curing and already began to react in the cementitious paste. 
If these cracking values are compared with the results of the mechanical test, significance can be seen as the hydration process of the cement progresses. Since as the resistance increases in function of hydration time, the size of the cracks generated in the experimental concrete is smaller, thus, this can be attributed to the sodium silicate added to the mixture (Han et al 2017).

In figure 8, the diffractograms of the experimental material are presented at 7 and 28 days which present crystals corresponding to the process of formation of the crystalline phases Etrinigte, Calcite, Dolomite, and Minrecordite. It is possible to support the process of loss of ettringite needles by observing the decrease in the characteristic peak; it is due to the reaction of sodium silicate with calcium aluminates, which is corroborated with the lower presence of crystals in the micrographs obtained by SEM. In agreement with Byoungsun P. and Edvardsen et al (Edvardsen 1999, Park and Choi 2018), the main mechanism for self-healing is the precipitation of calcium carbonate crystals ($\text{CaCO}_3$) and this crystallite phase is the main responsible for the increase in the compressive strength as the mechanical test revealed. The presence of dolomite in the diffraction pattern corresponds to the aggregates used, which were defined as dolomitic by their high magnesium oxide ($\text{MgO}$) contents (Trejo-Arroyo et al 2019).
4. Conclusion

According to the physical-chemical and mechanical tests carried out on the concrete samples, the following conclusions have been reached. The distribution of the aggregates is uniform throughout the concrete which ensures that the repair agent will be in the entire concrete mix.

The process of vacuum impregnation and encapsulation of the coarse aggregate is a technique that can be applied to improve the mechanical properties of the aggregate, mainly its strength.

The axial compressive strength improved compared to the theoretical design strength and compared to the resistance obtained in the control concrete, obtaining up to 56% more strength than expected. Similarly, comparing the control cylinders with the experimental cylinders, the resistance increased as a function of time, for the cylinders tested after 28 days of curing 10% greater resistance was obtained to the resistance of the control cylinders.

The porosity reached a difference of 4% lower in the experimental concrete.

The SEM also showed images of crystallinity and morphology of the coarse aggregate that has not been reported in the literature for the study of limestone aggregates and corresponds more to that presented by dolomitic stones than limestone’s, but in its composition have more than 77% magnesium, compared to limestone.

In the evaluation of chemical behavior through x-ray diffraction, the presence of Calcium and Magnesium is observed as the main chemical elements in the recovered samples, a fact that agrees with the chemical composition of dolomitic limestone’s (CaMg (CO3)2).

The self-healing process is observable in the concrete samples cured at 28 days. This process is attributed to the formation of calcite crystals and silica gel C–S–H.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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