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## New self-healing techniques for cement-based materials

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### Abstract

In recent years, researches concerning cement-based materials has been focused not only on the strength and the toughness but also on the durability. In fact, the interest on concrete's self-healing process is increasing, due to the rapidly deterioration of that material which tends to crack and thus quickly deteriorate.

In this paper, a new self-healing technology for cement-based materials is proposed. This technology is based on the encapsulation method of repairing agent inserted in randomly distributed *shell* inside the material during its preparation. Two different kind of *shells* were used: glass spheres and pharmaceutical capsules. The material the shells are made of has to be endowed with a series of fundamental characteristics. That material has to be inert with respect to the repair agent so that it doesn't react with it, resisting to the severe stress condition that the shells undergo during the mixing, and at the same time being capable of breaking down when the crack intercept them, having a good compatibility with the cement mixture.

The results demonstrate that it is possible to use this kind of shell to encapsulate the repairing agent: the crack breaks them and they release the healing agent, which allows patching up the crack.

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**Keywords:** innovative techniques; encapsulation; sodium silicate; self-healing; cement-based materials;

### 1. Introduction

Concrete is the most used construction material on Earth but it is susceptible to crack formation due to its limited tensile strength. Moreover, damage repair tends to be difficult when cracks are not visible or not easily accessible.

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Consequently, durability reduces and maintenance costs increase (Fregonara, E, 2016). Therefore, self-repair of fractures in concrete is of the highest interest: Turner, back in 1937, (Turner, L. 1937) observing damaged tanks and water pipelines, noticed that water was the key to the occurrence of self-repairing. After cracks formation, the delayed hydration of the mix along the interface of the cracks occurred: by reacting with water, the width of the crack was reduced, and, in some cases, the complete filling of the damaged zone was evidenced.

Crystals of calcium hydroxide and of calcium carbonate, produced by the reaction between the former and carbon dioxide, allowed cracks sealing. Hearn and Morley (Hearn, N., Morley, C.T. 1997) sixty years later, continued to support the thesis of Turner and confirmed that the presence of water was mandatory to activate the self-healing process in not fully hydrated cementitious materials. Neville (Neville, A.M. 2002) states that, in addition to water and carbon dioxide, the phenomenon is influenced by water temperature and relative humidity.

Nowadays there are other approaches than the autogenous healing of concrete previously described (Van Tittelboom, 2013): self-healing with mineral additives, self-healing by means of bacteria and self-healing based on encapsulated adhesives.

The self-healing process can be attributed to the reaction of the mineral additives dispersed in cementitious materials too (Ahn, T-H. 2010, Roig-Flores, M. 2016). These minerals are added to the concrete mixture during preparation. When a crack occurs, the additives are located on the surface of the break, when the water penetrates inside, these mineral additions react with water and the slit is filled with the reaction products.

In the 90s, Gollapudi (Gollapudi, U.K. 1995) suggested to use bacteria to induce the precipitation of calcium carbonate ( $\text{CaCO}_3$ ) to repair the cracks. The calcium carbonate precipitation can be caused by various phenomena, such as hydrolysis of urea and the oxidation of organic acids. Jonkers (Jonkers, H.M. 2010) claims that the bacteria spores that have a life of about fifty years, when inserted directly into the concrete mix, undergo a drastic decrease in life expectancy. Wiktor shows that the immobilization of bacteria in porous clay aggregates, before the conglomerate mixing, can greatly extend their life (Wiktor, V. 2011). In this way, the self-healing process is activated when the crack intersects one of these clay particles.

In many works, hollow glass tubes were used as encapsulation devices (Van Tittelboom, K. 2013) and the release of the healing agent is activated by the breakage of the brittle glass tubes during concrete damaging. The internal diameter of these tubes usually ranges from 0.8 mm to 4 mm. However, glass capsules may lead to the possible onset of alkali-silica reactions. To limit this drawback, ceramic capsules were therefore successfully experimented (Van Tittelboom, K. 2011), in addition to spherical or cylindrical polymeric capsules (Van Tittelboom, K. 2013). In the case of spherical capsules, the capsule diameters range from 5  $\mu\text{m}$  up to 5 mm, while for cylindrical capsules, the diameters range from 0.8 mm up to 5 mm (Van Tittelboom, K. 2013).

In general, the above described healing agents such as bacteria, mineral additives and adhesive agents, markedly improves the ability of self-healing of concrete, but they increase its cost too. Therefore, in this work, more than the investigation of new repairing agents, materials already present on the market for other purposes were assessed, with the aim of reducing as much as possible their incidence on final costs of self-healing concrete. After several hypothesis, small glass spheres (commonly used for jewelry) and pharmaceutical capsules were retained and used. Though the volume of healing agent they contain is limited, respect to glass or extruded tubes, these capsules can be randomly dispersed all throughout the cementitious matrix, and are not only ideally located in the sample center of prisms for three-point bending tests, as previously experimented (Formia, A. 2015; Formia, A. 2016).

## 2. Materials and methods

### 2.1. Sodium silicate as healing agent

After careful analysis, it was concluded to use the sodium silicate ( $\text{Na}_2\text{SiO}_3$ ). Commonly known as liquid glass, this compound is widely used in the building sector, for example as an additive for concrete waterproofing. It starred in several previous trials in the field of self-healing cementitious materials, allowing to get pretty good results (Brough, A. R. 2002; Chang, J. J. 2003; Yang, K. H. 2008; Huang, H. 2011; Gilford, 2013; Van Tittelboom, K. 2013; Formia, A. 2015; Formia, A. 2016; Alghamri, R. 2016). Sodium silicate has the ability to repair cracks because of its adhesive capacity and of its reaction with Portlandite  $\text{Ca}(\text{OH})_2$  and calcium silicate hydrates (CSH), two hydration products of Portland cement.

## 2.2. The preformed shell: glass spheres and pharmaceutical capsules

The choice of the sodium silicate container was oriented towards a new experimentation that is to say the use of pre-formed shells, which had to have a series of fundamental characteristics:

- to contain the remedial agent without reacting prematurely;
- to maintain their structure without breaking during the mixing step and to resist to considerable mechanical stress;
- to be capable of breaking down in the presence of cracks,
- to have a good compatibility with the cement mixture.

The size of the preformed shell was established trying to favor small sizes for optimal dispersion in the matrix.

Regarding the capsules, the use of pharmaceutical empty capsules was experimented (gastro, size 3 and volume of 0.30 mL each).

In a first approach, their resistance to water and sodium silicate was checked. Subsequently, the capsules were opened one by one, positioned on a working surface and held in a vertical position. With the help of a plastic pipette, it was possible to insert in each of them the sodium silicate solution (provided by Sigma Aldrich, Figure 1). Immediately after, the capsules were quickly shut to restrict the entry of air and of humidity inside them.

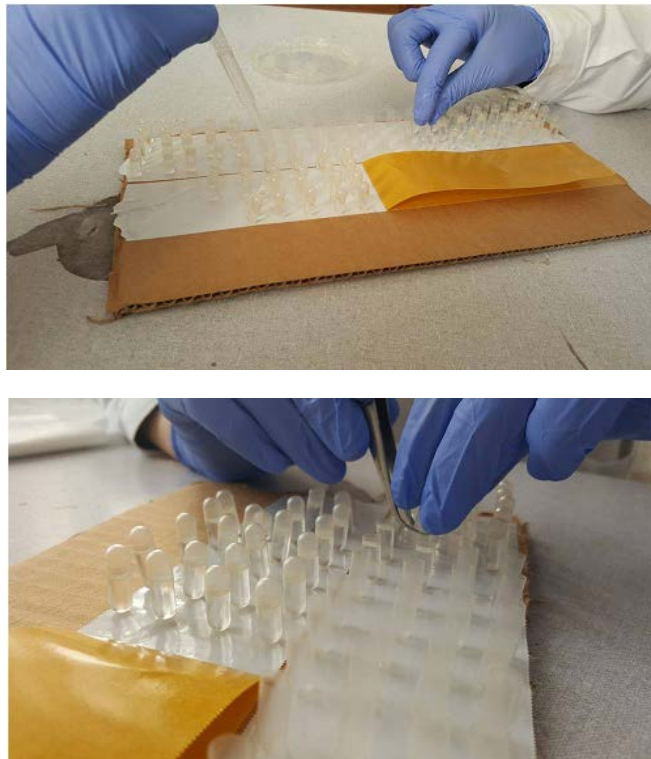


Fig.1. Sodium silicate encapsulation in pharmaceutical capsules.

To make the smooth surface of the capsules rougher and to make it more resistant in the mixing step, an epoxy resin and sand coating was then realized (Figure 2).



Fig.2. Epoxy resin and sand coating on pharmaceutical capsules.

About the glass spheres, the real innovation consists in the shape as glass tubes were already used in cementitious composites (Van Tittelboom, K. 2013; Gilabert, F. A. 2017).

For the experimentation, 100 hollow glass spheres with a maximum diameter of 8 mm, with a volume of about 0.26 mL and having a single hole were used. The glass capsules were filled with the sodium silicate solution as the pharmaceutical capsules, and were immediately sealed with a small amount of silicone (Figure 3).

Also in this case a final coating of epoxy resin and sand was done.



Fig.3. Glass spheres with sodium silicate as healing agent.

### 2.3. Other materials

CEN Standard sand, a natural siliceous sand consisting of rounded particles having a silica content of at least 98%, was used. It is distributed pre-packed in bags with a content of  $(1350 \pm 5)$ g, whose particle size distribution lies within specific limits according to UNI EN 196-1.

Ordinary Portland Cement Type-I (Buzzi Unicem 52.5R), light grey color, obtained by grinding of at least 95% of clinker and maximum 5% of minor constituents was used. It is characterized by the rapid development of the initial resistance, conforms to the harmonized European standard UNI EN 197/1 and possessed CE label according to European Regulation 305/2011 (CPR).

### 3. Samples preparation and test activity

According to Standard UNI EN 196-1, mortar specimens were manufactured with proportions by mass equal to one part of cement (450 g), three parts of standardized sand (1350 g) and one-half part of water (225 g), or with a water/cement ratio 0.5.

The dimension of each specimen are reported in Figure 4 below.

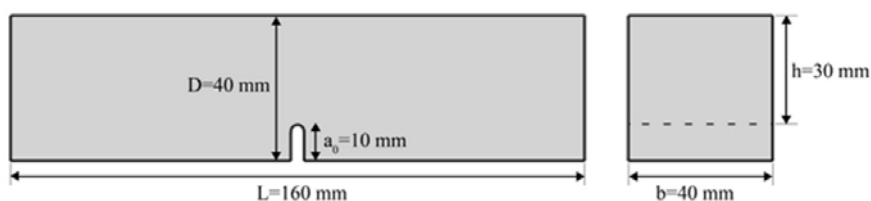


Fig.4. Dimensions of self-healing mortar.

Both types of preformed shell were included in the mixture with a percentage of 4 wt% relative to the cement. In particular:

- two samples containing about 30 pharmaceutical capsules each;
- two samples containing approximately 35 hollow glass spheres each;
- one "mixed" sample with 15 glass spheres and 15 pharmaceutical capsules inserted in the same mixture.

In Table 1 below the composition and nomenclature of each manufactured specimen:

Table 1. Composition and nomenclature of each self-healing mortar specimen.

Nomenclature	Shell typology	Weight (%)*	Healing agent
SH-GS-1	Glass spheres	4.00	Sodium Silicate
SH-GS-2	Glass spheres	4.00	Sodium Silicate
SH-PC-1	Pharmaceutical capsules	4.00	Sodium Silicate
SH-PC-2	Pharmaceutical capsules	4.00	Sodium Silicate
SH-MIXED	Glass spheres + pharmaceutical capsules	4.00	Sodium Silicate

\*with respect the weight of cement

The samples were initially mixed in a conventional mixer. Only at the end of the mixing procedure, the capsules and the glass spheres were added and mixed by hand (Figure 5).



Fig.5. Mixing procedure of self-healing mortar.

Immediately after the preparation of the mortar, the test specimens were molded and compacted in a mold fixed to a jolting apparatus. After 20/ 24 hours from the molding procedure, marked specimens were cured in water for 7 days.

After this time, samples were removed from the water and subjected to three-point bending (TPB) test in order to analyze the behavior to fracture and repair effectiveness. Before the mechanical tests, 10 mm deep U-shaped notches were made on the samples, in order to control the cracking's start of the specimen.

TPB test were carried out for each mortar notched specimen, by using a Zwick/Roell Z050 machine with a load cell capacity of 50 kN (Figure 6). The Crack Mouth Opening Displacement mode (CMOD mode) was used through a clip-on extensometer and a 0.01 mm/min test speed was adopted.

The samples were downloaded when the opening of the crack reached a value of 0.25 mm, regardless of the load residue, and were maintained in a humid environment for 28 days (at  $20 \pm 2^\circ \text{C}$  and 90% relative humidity), before the repetition of the test and the subsequent evaluation repair.

The 28-day period was chosen because in the literature it is known that sodium silicate as a repairing agent needs these times (Huang, H. 2011). After this, the samples were tested again in TPB for assessing their possible performance recovery.

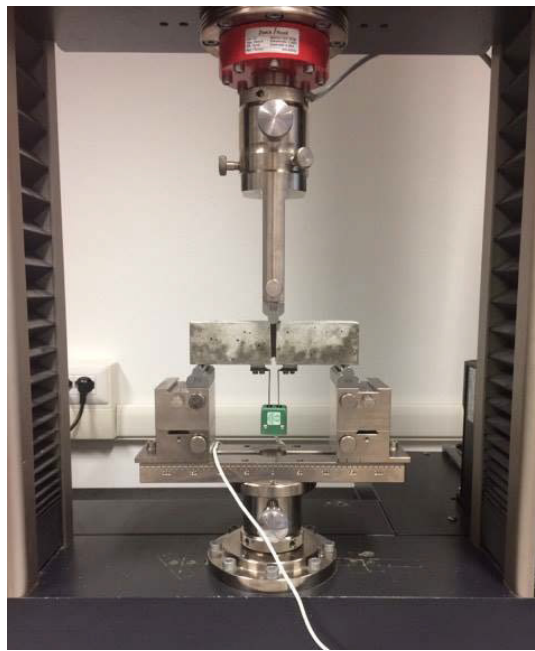


Fig.6. Three-point-bending tests in CMOD control mode.

#### 4. Results

The following results refer only to two specimens (SH-GS-1 and SH-PC-2), as they are the only ones for which it was possible to complete the second load stage, without breaking. This kind of problem could be related to natural variability in handmade samples and, in particular, the variable position of the preformed shell. Probably, during the second load cycle, the samples were broken because the crack did not encountered any preformed shell during the first load stage.

To evaluate the self-healing effect after the re-loading tests, the Load Recovery Index  $LRI_n$  has been used, as found in literature (Van Tittelboom, K. 2012; Formia, A. 2015). The  $LRI_n$  is defined as:

$$LRI_n(\%) = \frac{P_n - P_u}{P_p - P_u} * 100 \quad (1)$$



where:  $n$  is the re-loading cycle index (in our case,  $n = 1$ );  $P_n$  is the peak load of the re-loading test;  $P_p$  is the peak load reached during the first loading stage;  $P_u$  is the residual load of unloading preceding the re-loading stage.

Below, the Load vs. CMOD curves for both specimens (SH-GS-1 and SH-PC-2) resulting from first loading (Figure 7) and re-loading stages (Figure 8).

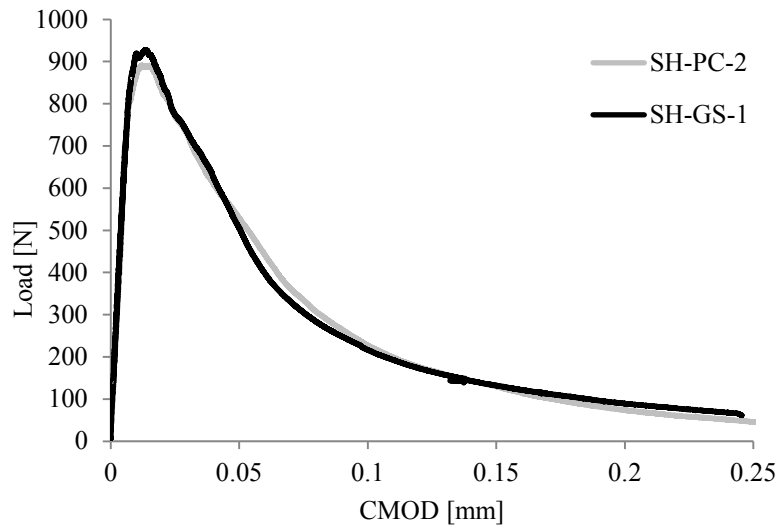


Fig.7. Load vs CMOD curve for SH-GS-1 and SH-PC-2, first load stage.

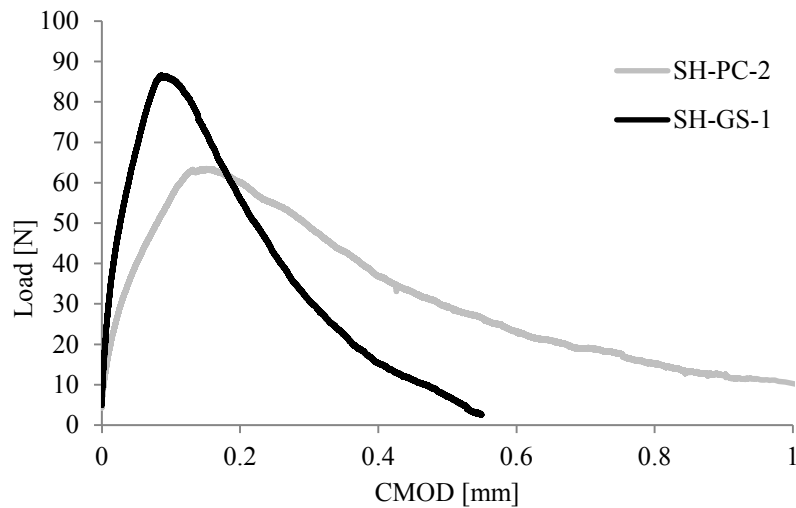


Fig.8. Load vs CMOD curve for SH-GS-1 and SH-PC-2, re-load stage.

The data obtained from the Load-CMOD curves hallowed to calculate the values of the Load Recovery Index LRI for each sample:



$$LRI_I(\text{SH-GS-1}) = 2.99\%, \quad LRI_I(\text{SH-PC-2}) = 2.12\%$$

## Conclusion

In this paper, a novel technique for the production of self-healing concrete was proposed: glass small spheres and pharmaceutical capsules were filled with sodium silicate as a healing agent. The preliminary results of three-point bending tests seem to indicate that sodium silicate was efficiently released by the capsules when the fracture intercepted them. However, a limited amount of solution was able to diffuse into the mortar cementitious matrix, and a limited strength recovery was evidenced. Based on these experimental results, it is possible to consider the encapsulation technique presented in this paper as a promising technique. Certainly, further research is needed to corroborate the results from a statistical point of view and also to better understand the behavior and the durability of the healing agent.

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