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## Innovative carboxylic acid waterproofing admixture for self-sealing watertight concretes

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### HIGHLIGHTS

- Performances of innovative self-sealing admixture were investigated.
- Fumaric acid-based waterproofing admixture improves concrete watertightness.
- Self-sealing ability was confirmed on 400 μm width cracks.

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### ABSTRACT

The present paper evaluates the performances of an innovative carboxylic acid-based admixture to improve concrete watertightness and self-sealing ability of the cement matrix. Results indicate that fumaric acid-based waterproofing admixture improves concrete watertightness. In particular, addition of 1% by cement mass of the carboxylic polymer causes a reduction in the water penetration under pressure of 7-day wet cured concrete by 50% compared to that of the corresponding reference concrete. The ability to seal cracks (400 μm width) due to plastic shrinkage was also confirmed by Karsten tubes tests, optical microscopy and SEM observations on cracked and sound concrete slabs.

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### 1. Introduction

For many decades, concrete has been considered an eternal material, unaffected by any forms of degradation. However, reinforced concrete structures have shown several vulnerabilities depending on the design, placing and environmental exposure conditions. As a consequence of this, many of the buildings built in the twentieth century, including infrastructures, suffer extensive damage.

The widespread distribution of reinforced concrete diseases is proven by the continued growth of expenditure in the area of maintenance and restoration of existing buildings that in recent years have significantly exceeded investments for new buildings [1].

Nevertheless, the maintenance and repair of concrete structures are often demanding. In fact, these operations are usually laborious

and expensive, or even difficult to implement, especially in the case of infrastructures or large-scale concrete structures, where factors such as location or service continuity can increase the complexity of the operations [2].

For these reasons, the development of products and techniques that lead to a reduction of maintenance operations over the entire lifespan of buildings are essential in the realization of any concrete structures, also because the protection of the environment and the reduction in the consumption of energy [3] and natural resources [4–7] are key issues. Long lasting concrete structures can be built by means of very efficient superplasticizers [8–10], corrosion inhibitor [11–13] and carbon nanotubes [14,15]. However, concrete is very prone to cracking. Consequently, innovative self-sealing products capable of filling dangerous cracks are necessary. Over the last few years, these products have won significant attention from the scientific community.

The self-healing of cementitious materials was evidenced for the first time in fractured hydraulic structures by the French Academy of Sciences in 1836 and it was studied in the late nineteenth century by Hyde and Smith [16]. Glanville conducted a more systematic analysis in 1926 [17] by studying the cracking of bridges.

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The concepts of self-healing and self-sealing were also clarified. The former indicates the ability of the material to restore the mechanical characteristics and the latter only refers to the ability to seal cracks. Jacobsen et al. [18] observed the self-healing phenomenon in concrete specimens exposed to freeze-thaw cycles. Clear [19], Hearn [20–22] and Edvardsen [23] evidenced the occurrence of such phenomena in large scale hydraulic structures. Wu et al. [24] highlighted that the self-repair of cracks in cementitious materials is due to a complex combination of chemical-physical processes [25] involving the formation of calcium carbonate or calcium hydroxide, the blocking of cracks by impurities in the water and loose concrete particles resulting from crack spalling, the further hydration of the unreacted cement or cementitious materials, and the expansion of the hydrated cementitious matrix in the crack flanks.

Between all the above-mentioned mechanisms, calcium carbonate crystallization due to the chemical reaction between calcium hydroxide and carbon dioxide plays a crucial role [26]. The process involving the hydration of unreacted cement is worthy of note, but it is predominant during the first years of life of structures and, therefore, cannot be considered a prevalent mechanism.

Besides the autogenous mechanisms, over the last two decades several techniques have been proposed (Fig. 1) in order to improve the self-healing or self-sealing capacity of cementitious materials [27]. The use of hollow brittle fibers [28–31] containing repairing agents – such as epoxy resin, methyl methacrylate, and ethyl cyanoacrylate – was proposed in order to simulate the action of arterial bleeding. In the human body, the fracture of capillaries releases curing agents – i.e., platelets – which heal the wound. The effectiveness of hollow glass fibers or porous polypropylene fibers has been demonstrated. Microencapsulation is a process in which tiny particles or droplets are surrounded by a coating to produce small capsules of micrometric dimensions. The shell protects the release agent, both during the mixing procedure and within the

concrete. The healing ability is ascribed to microcapsule rupture along with the concrete cracks. Microencapsulation has been considered by several authors [32,33]. Nishiwaki [34] showed several critical points in the use of such a technique, mainly related to the small size of the microcapsules and the interaction between them and the cement matrix.

Kishi et al. [35,36] investigated the effect of various additives including expansive agents, geo-materials, chemical admixtures, as well as their combination. It was concluded that the addition of carbonates such as  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{Li}_2\text{CO}_3$  to ordinary concrete mixtures promotes cement recrystallization and salt crystal precipitation inside cracks. In particular, the self-healing ability of cracks can be enhanced by the use of suitable dosages of carbonates and expansive agent [37,38].

Some researchers have proposed the use of bacteria [39,40] to promote the formation of sealing species inside concrete cracks. The ureolytic bacteria [41] promote the precipitation of calcium carbonate due to the combination of various factors including the concentration of dissolved organic carbon, the pH level, the concentration of calcium ions, and the availability of suitable nucleation sites.

Between the aforementioned method and techniques (Table 1), addition of chemical admixtures to ordinary concrete during mixing process seems to be the easiest way to favor cement recrystallization and salt crystal precipitation inside cracks and, hence, to promote the self-sealing ability of cement matrix. For these reasons, the present study was aimed to evaluate performances of self-sealing concretes manufactured with an innovative fumaric acid-based admixture (WP) added to concrete during the mixing process. The admixture WP, in addition to being safe (nontoxic), is easily used in ready mix plants due to its powder form and its dosages, generally close to  $3 \text{ kg/m}^3$ . Furthermore, fumaric acid-based admixture determines a precipitation of denser crystals compared to other commercial admixtures, guaranteeing a better self-sealing capacity (Fig. 2).

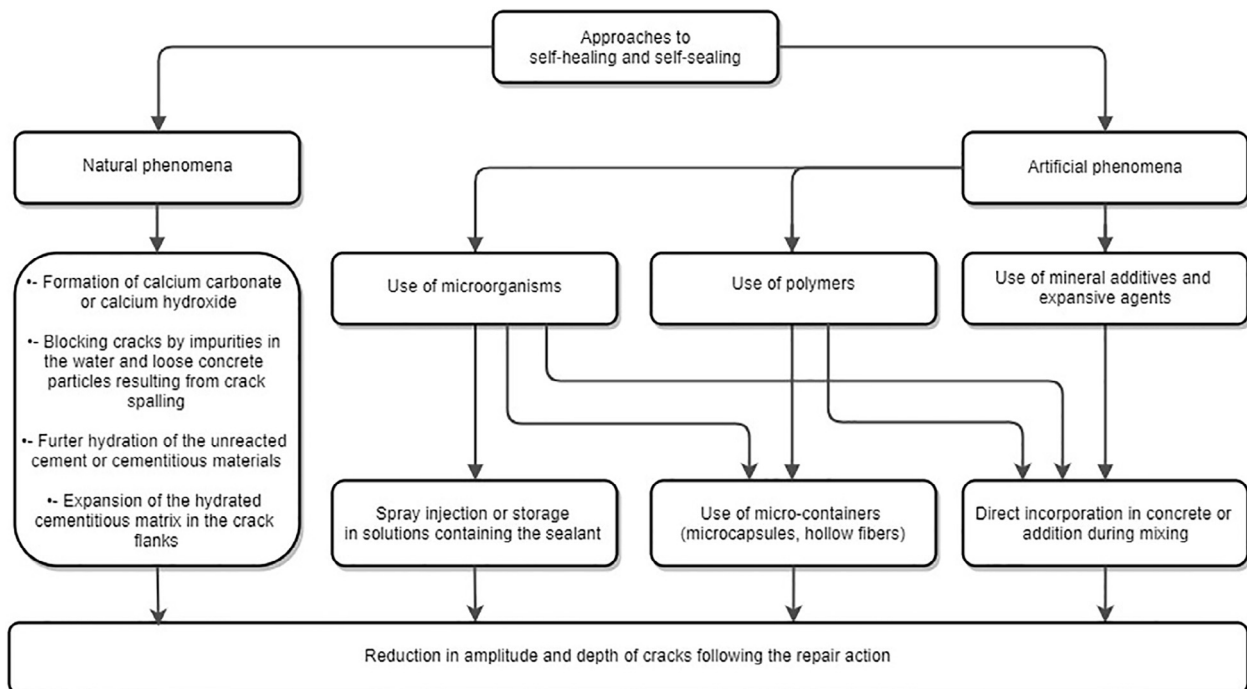


Fig. 1. Approaches to self-healing and self-sealing.

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