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Glass encapsulated minerals for self-healing in cement based composites

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HIGHLIGHTS

- Mineral compounds encapsulated for self-healing action in cement-based composites.
- Water is a very critical factor in the proliferation of healing materials.
- Durability recovery for most mineral healing compounds was remarkable.

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ABSTRACT

This study presents the encapsulation of mineral compounds as healing materials for cement-based composites. Three liquid (sodium silicate, colloidal silica and tetraethyl orthosilicate) and one powdered (magnesium oxide) minerals were encapsulated in thin walled soda glass capsules. Load regain was obtained for samples healed under three different curing regimes; ambient conditions, high humidity exposure or immersed in water. Water immersion resulted in crack area closure that ranged from 85% to 100% for all mineral treated samples. The measured reduction in both sorptivity and intrinsic gas permeability varied from 18% to 69% depending on the measured parameter and mineral type. Sodium silicate and colloidal silica presented with the best and more consistent response in all applied measurements, both in terms of load and durability recovery. These results demonstrate how self-healing can be achieved by utilising cost effective mineral compounds which are also compatible with the host cementitious matrix.

1. Introduction

The structural integrity of all civil infrastructure is achieved with the utilisation of individual elements which are designed to respond sufficiently when exposed to one or more mechanical or environmental actions. All the design codes and guidelines focus on how structures, comprised of individual elements, will be able to retain structural resilience when exposed to adverse effects. The material performance is not considered a priority and degradation is an inevitable process that requires maintenance regimes. In the UK alone this translates to a cost of ~£40 billion/year on repair and maintenance of existing, mainly concrete, structures [1]. In the United States the situation is worse; in 2006 a study reported that concrete structure owners nationwide pay ~$18 to $21 billion/year on repair, protection and strengthening whereas the associated costs for maintenance due to steel corrosion reach $125 billion/year [2]. In addition, the American Society of Civil Engineers in a recent report estimates that the maintenance of US civil infrastructure requires an investment of $3.6 trillion over a period of seven years in order to return to the 1988 quality standards [3]. It is therefore apparent that self-healing concrete can be a promising solution to this problem.

As reported by Ferrara and Krelani [4] autogenous healing was first documented by the French Academy of Sciences in 1836 and was described as the carbonation of the calcium hydroxide produced during cement hydration. In 1913, Abrams observed that cracks formed during pull-out tests, on reinforced concrete, closed when specimens were left to rest after testing. Abrams believed that the observed autogenous healing was "the effect of retarded or interrupted hydraulicity of cement" [5]. It was not until 1956 when the first comprehensive research on autogenous healing was published by Lauer and Slate [6]. They proved that the developed healing products were a combination of calcium hydroxide and calcium carbonate crystals. The formation of the latter was attributed to the reaction of calcium hydroxide with carbon dioxide, present in either water or air. Dhir et al. in 1973 [7] showed that mortars with high cement content and low water to cement ratio exhibited greater potential to develop autogenous healing after being loaded at their maximum stress. These observations

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were further verified in early 1980s when high binder content fibre reinforced cement based composites were found to exhibit autogenous healing when cured in water [8,9]. However, as extensively pointed out in the literature there are some limitations to autogenous healing [10–13]. Firstly the consequent hydration of unhydrated cement particles depends strongly on the age of the concrete. Secondly, all researchers agreed that water is necessary for triggering the hydration reactions. Thirdly, autogenous healing appeared very effective in closing small cracks, $\leqslant$150 μm, but it could not adequately heal larger cracks unless a compressive force was applied to bring the crack faces together.

The RILEM state-of-the-art report on self-healing materials [14] distinguishes the self-healing phenomena in cement based materials in two broad categories: (i) *autogenic* – referring to self-healing processes that use materials' components that could otherwise be present and not specifically designed for self-healing and (ii) *autonomic* – referring to self-healing actions that use materials' components that do not naturally exist in the cement based composites, in other words using engineered additions. In the same report the techniques for the assessment of healing are divided into experimental procedures for: (i) verifying crack closure and healing materials (microscopy, XRD, FTIR), (ii) verifying recovery against environmental actions (capillary water absorption, permeability) and (iii) verifying recovery against mechanical actions (three/four point bend tests).

Developing autonomic self-healing cement-based materials was originally proposed in 1994 by Dry [15]. Dry proposed the embedment of hollow glass tubes, 100 mm in length, in the tension zone of cementitious matrices which were filled with healing material (in the form of methyl methacrylate). Upon cracking of the matrix (and hence the glass tube) the healing material was released and filled the formed cracks. Polymerisation was induced with external application of heat [15]. Results showed a very good recovery on the flexural strengths for the healed samples. The principle suggested by Dry was later adopted and expanded by other researchers [16,17]. Joseph et al. [16] and De Belie and Van Tittelboom [17] also encapsulated one part adhesives (cyanoacrylates) in glass capillary tubes. Joseph et al. observed that upon crack formation only a small amount of the adhesive was leaking into the crack. The phenomenon was attributed to the large capillary forces that developed in the tubes and solved by using longer open-ended tubes. De Belie and Van Tittelboom reported early polymerisation of the cyanoacrylate while it was in the glass tube and prior to cracking of the cementitious matrix. De Belie and Van Tittelboom suggested the use of two part adhesives, encapsulated separately, as a solution to premature polymerisation of cyanoacrylates. Their results with two part adhesives showed good self-healing potential. In all the above mentioned studies self-healing was assessed in terms of load/strength regain of cracked and healed samples. In addition to this, De Belie and Van Tittelboom [17] also used water permeability tests to assess self-healing and showed that intrinsic permeability coefficient decreases by an order of magnitude for samples healed with epoxy. Resins can recover the mechanical properties of cracked cement based matrices relatively well. However, they have three major drawbacks: (i) their mechanical properties are not compatible with cement-based matrices which can impose problems on their mechanical interlock with the cementitious matrix, (ii) they bear health and safety concerns as many of them contain formaldehydes and isocyanides and (iii) they are expensive in bulk quantities. Nonetheless, for large cracks or for specific applications certain adhesives, such as expansive polyurethane, have a good potential as healing materials.

The use of mineral compounds that are compatible with cement matrices could resolve the issues related with the use of adhesives and resins. Some minerals can chemically interact with the host matrix producing hydration and carbonation products. These products have very similar structure and properties with the host cementitious matrix and hence such minerals can be classified as more "compatible". For example sodium silicate is used as a setting accelerator in normal concretes [18], as an alkali activator in alkali-activated cements [19] and in some cases to improve the durability of concretes [20]. Sodium silicate was used as an encapsulated healing compound in some recent studies [21–23]. However, these studies presented very limited data regarding the effectiveness of sodium silicate as a healing agent as well as the size of cracks that were healed. Another mineral compound, colloidal silica, has been used as a liquid additive in cement-based mixtures in order to introduce nano-SiO_2 particles into the mix for enhanced mechanical and durability performance. It was shown that colloidal silica could improve the mechanical and durability properties of cement based composites [24,25]. More recently, ethyl-silicates were used to improve the properties of cement based grouts and ceramics, due to their high purity SiO_2 content [26,27]. Neither colloidal silica nor ethyl-silicates have been used as self-healing agents in concrete. Magnesium oxide (MgO) is used as a shrinkage mitigating additive in concretes primarily due to its expansive properties. Magnesium oxide was recently reported as an expansive cement additive used to improve autogenous healing properties [28] but it has never been used in encapsulated form.

This study investigates the potential of minerals, encapsulated in thin-walled glass capsules, to act as healing compounds in cement-based composites. Silicon oxide minerals were selected for their ability to react with the portlandite present, in cement-based matrices, to form a surplus of calcium silicate hydrates, the main hydration products in cementitious matrices. In concrete technology literature the effect of addition of silicon oxides in cement-based materials is well documented. Silicon oxides react with the portlandite and produce surplus of calcium silicate hydrate resulting in a denser and more durable material. On the other hand, when in contact with water MgO hydrates to produce brucite, an expansive crystalline phase. Then brucite further reacts with water and in the presence of carbon dioxide, which exists in the air and in the water, precipitates magnesium carbonate. The associated chemical reactions for the minerals used are shown in Eqs. (1)–(6):

Sodium silicate

$$Na_2SiO_3 + Ca(OH)_2 \xrightarrow{+H_2O} x(CaO \cdot SiO_2)H_2O + Na_2O \quad (1)$$

Colloidal silica

$$SiO_2 + Ca(OH)_2 \xrightarrow{+H_2O} x(CaO \cdot SiO_2) \cdot H_2O \quad (2)$$

Ethyl silicates

$$Si(OC_2H_5)_4 + 4H_2O \xrightarrow{OH^-} Si(OH)_4 + 4C_2H_5OH \quad (3)$$

$$Si(OH)_4 + Ca(OH)_2 \xrightarrow{+H_2O} x(CaO \cdot SiO_2) \cdot H_2O \quad (4)$$

Magnesium oxide

$$MgO + H_2O \rightarrow Mg(OH)_2 \quad (5)$$

$$Mg(OH)_2 + CO_2 + 2H_2O \rightarrow MgCO_3 \cdot 3H_2O \quad (6)$$

The healing potential of three liquid (sodium silicate, colloidal silica and ethyl silicate) and one powder (MgO) minerals was investigated under three different exposure conditions, namely: ambient, high humidity (relative humidity 90%) and immersed in water. The glass capsules were embedded in mortar prisms and tested for recovery against mechanical and environmental actions. The healing effectiveness was assessed using optical and scanning electron microscopy, X-ray diffraction and (XRD) and Fourier transform infrared spectroscopy (FTIR).