Glass encapsulated minerals for self-healing in cement based composites

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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.

Keywords: Self-healing, encapsulation, minerals, durability recovery, strength recovery.

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 \textsterling40 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 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, ≤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, 100mm 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 [17,18]. Joseph et al. [17] and De Belie and Van Tittelboom [18] 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 [18] 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 [19], as an alkali activator in alkali-activated cements [20] and in some cases to improve the durability of concretes [21]. Sodium silicate was used as an encapsulated healing compound in some recent studies [22–24]. 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 [25,26]. More recently, ethyl-silicates were used to improve the properties of cement based grouts and ceramics, due to their high purity SiO$_2$ content [27,28]. 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 [29] 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 equations 1 to 6:

**Sodium Silicate**

\[
Na_2SiO_3 + Ca(OH)_2 + H_2O \rightarrow x(CaO \cdot SiO_2) \cdot H_2O + Na_2O
\]  

(1)

**Colloidal Silica**

\[
SiO_2 + Ca(OH)_2 + H_2O \rightarrow x(CaO \cdot SiO_2) \cdot H_2O
\]  

(2)

**Ethyl Silicates**

\[
Si(OH)(CH_2)_{4} + 4H_2O \rightarrow Si(\cdot OH) + 4CH_2OH
\]  

(3)

\[
Si(\cdot OH)_{4} + Ca(OH)_2 + H_2O \rightarrow x(CaO \cdot SiO_2) \cdot H_2O
\]  

(4)

**Magnesium Oxide**

\[
MgO + H_2O \rightarrow Mg(OH)_2
\]  

(5)

\[
Mg(OH)_2 + CO_2 + 2H_2O \rightarrow MgCO_3 \cdot 3H_2O
\]  

(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).

2. Materials and preparation

2.1 The self-healing minerals
Table 1 summarises the properties, costs and reaction times for the three liquid mineral precursors
used. Cyanoacrylates were also included for comparative purposes. Before encapsulation, all the
liquid minerals were mixed with the fluorescent dye sodium fluorescein, which was used to monitor
the flow of the liquid into the crack plane. The grade magnesium oxide used was 92/200 with a
relatively high reactivity of 150 seconds in accelerated acidic test [30,31].

Table 1 – The chemical and physical characteristics of the liquid mineral precursors used

<table>
<thead>
<tr>
<th></th>
<th>Linear Formula</th>
<th>Mw (gmol⁻¹)</th>
<th>Density (g/mL)</th>
<th>Viscosity (cps)*</th>
<th>pH</th>
<th>Cost (£/L)</th>
<th>Reaction time</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEOS</td>
<td>Si(OC₂H₅)₄</td>
<td>208.3</td>
<td>0.933</td>
<td>5</td>
<td>7</td>
<td>47.6</td>
<td>~ 24 hr</td>
</tr>
<tr>
<td>Sodium Silicate (40% wt in H₂O)</td>
<td>Na₂O(SiO₂)ₓ xH₂O</td>
<td>122.06</td>
<td>1.39</td>
<td>60</td>
<td>12.5</td>
<td>21.3</td>
<td>~ 24 hr</td>
</tr>
<tr>
<td>Colloidal Silica (40% wt in H₂O)</td>
<td>SiO₂</td>
<td>60.08</td>
<td>1.3</td>
<td>35</td>
<td>9</td>
<td>24.8</td>
<td>~ 24 hr</td>
</tr>
<tr>
<td>Cyanoacrylates</td>
<td>C₆H₇NO₂</td>
<td>125.1</td>
<td>1.04</td>
<td>30 - 1500</td>
<td>-</td>
<td>300 - 500</td>
<td>20 – 120 seconds</td>
</tr>
</tbody>
</table>

*Note: Viscosity values at 20°C. Water viscosity at 20°C is 1cp

2.2 Encapsulation system and survivability tests
Soda glass capsules were used as carriers for the mineral healing compounds. The thin wall (0.45mm)
glass capsules were 50mm long with 6.15mm inner diameter and were able to carry ~1.5ml of liquid
cargo. The capsules were open at one end, and then filled with the healing material and sealed using
layers of thin PVC film coated with a layer of low viscosity lacquer, as shown in Figure 1.
Fig. 1: (a) Filling the glass capsules with the cargo mineral and (b) applying a thin layer of lacquer on the PVC film.

The survivability of the encapsulated materials and the efficacy of the capsules sealing were investigated by storing them for seven days in the laboratory under two different conditions: i) exposed to the air and ii) immersed in a high pH solution (pH=12) similar to that of a cement. All four mineral compound capsules performed well with no leakage (no fluorescent dye leakage traceable) and no change in weight, texture or colour. However, the capsules containing the cyanoacrylate glue started to harden after only 4 days and completely hardened after a week.

2.3 Sample preparation and curing

The glass capsules were embedded in 50x50x220mm mortar prisms. The mortar mixtures were prepared with a sand to cement ratio of 1.5:1 and consisted of CEM-I 52.5 cement, fine sand (2mm maximum grain size) and water to cement ratio of 0.4. A mild steel wire of 1.6mm in diameter, used to prevent catastrophic damage of samples during and after loading, was placed at the top half of the specimens with a cover of 10mm. Two glass capsules were placed next to each other and were both positioned at the middle of each specimen with a cover of 6.5mm to the bottom face. The capsules were locked in position by using small hardened cement paste spacers. Representative images of the sample preparation procedure are shown in Figure 2.
For the MgO encapsulated samples, only one of the two capsules contained the reactive powder whereas the second capsule contained water which, after rupture, was expected to disperse the MgO powder into the crack. The control samples were prepared with capsules containing water. The prism samples were used to assess load regain and water uptake by means of sorptivity measurements. To investigate the effect of the minerals on gas permeability, discs 10mm thick and 50mm in diameter were cast. The mortar mixtures were prepared on a rotating pan mixer and the moulds were filled in three layers. Pouring of each layer was followed by subsequent vibration using an electric motor vibration table. Samples were taken out of the moulds after 24 hours and then stored in water for seven days. On the seventh day the prisms were cracked and left to cure in the predefined curing conditions. The aim of this study was to investigate the potential of various minerals as healing compounds under different exposure conditions. In all three curing regimes the temperature was kept constant at 21°C ± 1°C and specimens were left to heal for 28 days.

3. Experimental methods

3.1 Cracking of samples

3.1.1 Mechanical loading and healing efficiency

The mechanical loading of the prisms was performed on the 30kN static testing frame. Prior to cracking, all specimens were notched with a rotating diamond blade. The notch depth and width were
1.5 and 2.0mm respectively. Prior to the testing, a clip gauge was attached close to the notch edges to
monitor crack mouth opening. The experimental set-up is shown in Figure 3.

![Experimental set-up for cracking the notched mortar prisms.](image)

The prisms were loaded over a length of 150mm and at a rate of 0.125mm/min and the loading was
stopped when the crack opening reached 0.40mm. Upon load removal all specimens had a remaining
crack width in the range of 0.20-0.25mm. The selection of this crack opening was based on the fact
that both the European and American standards define the value of 0.40mm and as the absolute
threshold for the maximum acceptable crack width in serviceability limit state [32]. Cracks of this size
may not pose immediate threat from the structural point of view but fall in the range of the maximum
allowed crack sizes for most environmental exposure conditions and hence they can be rather
detrimental in terms of durability. Following cracking the samples were then placed in the three
different curing conditions for 28 days to enable healing process. A second round of loading was
applied using the same test parameters. However, this time the specimens were brought to failure. In
order to compare the healing efficiency of each mineral, the load recovery rate coefficient (LR%) was
calculated in each case as follows:

\[
LR(\%) = \left( \frac{P_{\text{max},h} - P_{\text{un}}}{P_{\text{max},i} - P_{\text{un}}} \right) \times 100
\]
where $P_{\text{max,i}}$ is the load at which initial cracking occurred and $P_{\text{max,h}}$ is the maximum load attained by the healed sample during the second test. $P_{\text{un}}$ is the point of the residual load after failure at which the predefined crack width was reached and the load was removed.

3.1.2 Cracking of discs

The discs used for gas permeability measurements were cracked in a 50kN compression frame. Adhesive tape was attached on the periphery of the discs to avoid splitting of the specimens after cracking. The experimental set-up is shown in Figure 4.

![Figure 4: Experimental set-up for cracking mortar discs for gas permeability tests.](image)

Due to their small dimensions it was impossible to embed glass capsules in the discs. Therefore, immediately after cracking the different healing compounds were delivered into the crack plane using a syringe and a hypodermic needle. All cracks were injected with 1ml of healing material. MgO powder was not tested in this case.

3.2 Healing characterisation

3.2.1 Crack area measurements

The bottom crack faces in all the specimens were monitored over time using a stereoscope. Digital images were captured at three different positions of the crack face, which were the same for all
specimens, as shown in Figure 5. More specifically images were captured from the middle of the crack face and from two points ~15mm at either sides of it. Image analysis software (Image-J) was then used to analyse the acquired captions and the total crack area was calculated for each case. The crack area value obtained concerns only the two dimensional part of the crack that is observable by the stereoscope.

Fig. 5: Bottom face of a cracked sample showing the locations at which images were taken.

3.2.2 FTIR, XRD and SEM analysis

Fourier transform infrared spectroscopy (FTIR), X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM) tests were conducted to characterise the developed healing materials. Following the second cycle of testing and the loading of the specimens to failure, material was extracted carefully from the crack planes using a file and a scaler tool. For use in XRD and FTIR the extracted material was finely dry-grounded with a pestle and mortar. The XRD analysis was carried out using a diffractometer with a Cu-Kα radiation source with scans between 5° and 60° and the FTIR tests were conducted with a mid-infrared spectrometer, both on the powdered samples. For SEM analysis small chipped pieces were selected, gold coated and examined with a 5kV accelerating voltage high resolution SEM.

3.3 Healing efficiency: durability indicators

3.3.1 Liquid capillary absorption coefficient
The sorptivity (liquid capillary absorption coefficient) was obtained from a simple short-term one-dimensional experiment as described in the technical guidelines by RILEM [33]. Liquid uptake was measured only for the crack so that the efficiency of the healing process was directly evaluated. Hence, the bottom side of the specimens was coated with sealing adhesive aluminium tape, leaving only the crack face exposed for capillary suction as shown schematically in Figure 6.

Fig. 6: Schematic illustration of the liquid capillary absorption test.

The durability prisms were left to cure for 28 days after initial cracking and then placed in the oven at 40°C for 72 hours to remove moisture. Weight changes of the specimens due to capillary suction were monitored for 4 hours in all specimens. The water suction quantity per unit area $M_w$ is proportional to the square root of absorption time $t$ according to [34]:

$$M_w = S\sqrt{t}$$

where $S$ is the sorptivity coefficient of concrete, regressed as the slope of the curve between $M_w$ and the square root of time.

3.3.2 Coefficient of gas permeability

The coefficient of gas permeability was evaluated using liquid methanol as the gas source [35]. Once cracked and injected with the healing compound, the disks were left to cure for 28 days and then dried under vacuum for 48 hours to remove moisture. The discs were then fixed with epoxy sealant at the top of the glass pressure cells containing methanol, as shown schematically in Figure 7, which in turn were immersed in a 40°C water bath.
Fig. 7: Schematic illustration of the gas permeability test.

The mass variation with time due to vaporisation of methanol were recorded at predefined time intervals until a steady-state mass loss was reached. The coefficient of gas permeability was obtained using the following equations [35,36]:

\[ k = \frac{\alpha L}{A} m^* \]
\[ \alpha = 2\eta TR_u \frac{P_2}{(P_1^2 - P_2^2)} \]

where \( k \) is the intrinsic coefficient of gas permeability \( (m^2) \), \( L \) is the length of the specimen, \( A \) is the cross-sectional area of the specimen, \( m^* \) is the rate of mass loss \( (g/h) \), \( \eta \) is the dynamic viscosity \( (N \cdot s/m^2) \), \( T \) is the temperature of the vapour \( (^\circ C) \), \( R_u \) is the gas constant \( (8.31 \text{ J/mol K}) \), \( P_1 \) and \( P_2 \) are the inlet and the outlet pressures \( (N/m^2) \) respectively. For mechanical and durability testing a total of three samples per healing compound per different curing regime were used.

4. Results and discussion

4.1 Crack closure and load recovery

During the first round of testing the peak load was followed by a distinctive breaking sound, an indication that the glass capsules had ruptured. Following the fracture, liquid was observed at the bottom and side faces of the control prisms, the prisms containing TEOS capsules and the prisms with the MgO powder and water capsules, as shown in Figure 8.
Fig. 8: Representative image of specimen where liquid was observed immediately after crack: (a) side face and (b) bottom face.

This was, however, not the case for prisms with SS and CS containing capsules. In the case of CS capsule prisms, some liquid was observed only after about 30 minutes. Figure 9 shows the results of the percentage reduction of the total crack area as obtained by image analysis (Figure 10).

Fig. 9. Percentage reduction of the total crack area following 28 days of healing in the three different environments listed.
Fig. 10. Representative image from a prism with SS containing capsules: (a) crack area on the day of cracking and (b) crack filled after 28 days of healing (Note: the hashed band corresponds to 500 μm).

The importance of water in the proliferation of healing products in the crack is clearly evident when comparing the percentage reduction in the crack area between the different storage conditions. For all mineral compounds cured in water, the total crack area reduction was ≥ 90% with both SS and CS systems reaching 100%, i.e. the cracks completely sealed at the end of the healing process. Conversely, for samples stored at high humidity and ambient conditions, the observed crack sealing is less prominent. Nonetheless, in the presence of high humidity crack area closure improved compared to ambient conditions. It is clear that when the specimens were immersed in water, the water penetrated into the cracks and improved the diffusion of the mineral compounds, thus accelerating the reactions that yielded healing products in the crack.

As shown in Figure 11, the load regain values do not reflect the high values of the total crack area closure seen in Figure 9. Having said that, it is evident that all mineral healing compounds did improve the load carrying capacity of the prisms compared to the control for all the exposure environments. While the control samples reached a maximum of only 2.9% load regain the sodium silicate samples gave the best results in all three cases, reaching a maximum of 20% load regain for
samples that healed immersed in water. Once again water is a critical factor in the development of all the healing processes observed. This is translated to an increase of at least three times in the recorded load regain values between samples cured at high humidity and samples immersed in water.

**Fig. 11.** Load regain percentage for all mineral healing compounds following 28 days of healing in the three different environments listed.

In the second round of loading, the samples were brought to complete fracture and it is important to note that as the crack opening increased in values above 0.5mm-0.6mm, additional liquid leaked from the embedded capsules. This indicates that after the initial release of the healing compounds, some quantity remained intact in the capsules. This content of healing compounds could potentially be used in a second round of healing at larger crack sizes. Since in this study the differences between samples cured under water and samples cured at ambient and high humidity conditions were large, the analysis of the healing products as well as the study of the durability indicators were focused on samples that healed when immersed in water.

4.2 Characterisation of the formed healing products

The XRD patterns of the healing products collected from the crack planes of the samples cured under water are shown in Figure 12 in which most of the peaks are common to all samples.
Fig. 12. XRD diffractograms for all healing products (1: Ca(OH)$_2$; 2: Mg(OH)$_2$; 3: SiO$_2$; 4: Ettringite; 5: C$_3$S/C$_2$S; 6: CaCO$_3$/MgCO$_3$; 7: MgO).

Comparison of the XRD patterns of the mineral treated samples with the control samples shows the development of different crystalline phases. In all the samples, typical Portland cement hydration products are observed including portlandite, ettringite, poorly crystallised calcium silicate hydrates and unhydrated calcium silicates and MgO. The existence of calcite is attributed to partial carbonation of calcium hydroxide during its water curing. In the case of MgO samples, brucite, rather than portlandite, is seen as the dominant phase due to the hydration of MgO. Silicon oxide was detected in all cases but for SS and CS in particular, the intensity of this peak is very strong, suggesting that a significant amount of SiO$_2$ deposited on the crack plane. The ettringite peak observed in control samples is reduced significantly in the mineral treated samples. Calcium silicate hydrates (CSH) did not show any distinct peaks due to their poor crystalline nature. Moreover, there is an overlap of the peaks of the unhydrated silicates with the hydrate silicate phases. Nonetheless, based on similar observations reported in the literature the existence of amorphous CSH is evident by the diffuse peaks expressed from ~28° up to ~35° and the somewhat sharper one at 50° [37]. These peaks are stronger for all the liquid healing compounds compared with the control samples as well as with the samples containing powder MgO.
Figure 13 illustrates the FTIR spectra of the healing products extracted from the crack planes of the samples. Regardless of the type of healing compound used, specific infrared bands can be observed in all samples. These bands are summarised in Table 2.

Table 2

<table>
<thead>
<tr>
<th>Mineral Phases</th>
<th>Infrared band range (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ettringite</td>
<td>1000 - 1150</td>
</tr>
<tr>
<td>Calcium Silicate Hydrate</td>
<td>900 - 1000</td>
</tr>
<tr>
<td>Carbonate phases (Calcium and Magnesium)</td>
<td>1400 – 1500 / 870 - 890</td>
</tr>
<tr>
<td>Unhydrated Calcium Silicates</td>
<td>500 - 600</td>
</tr>
<tr>
<td>Magnesium Oxide</td>
<td>550 - 600</td>
</tr>
</tbody>
</table>

Fig. 13. FTIR spectra of the healing products developed in specimens stored under water (Note: Stars indicate locations attributed to the existence of CSH).

All samples demonstrated characteristic bands in the range between 1400-1500 cm⁻¹ due to stretching C-O bonds, which correspond to carbonate phases. The carbonate phases also give some less strong peaks in the range between 870 and 890 cm⁻¹. The MgO treated sample gave very strong peaks at both carbonate phase regions which is an indication that most of the MgO powder released into the crack
carbonated during the healing period with MgO reacting with the available CO$_2$ in water producing MgCO$_3$. The rest of the samples gave peaks with lower intensity at the same regions which is also reflected in their XRD patterns where their carbonate peaks are considerably lower than that for MgO. This observation can also explain the discrepancy between the crack area closure % and load regain % for MgO (Figures 9 and 11). Although the carbonate phases can block/seal the crack they are known for their weak strength. In contrast to the powder MgO the liquid healing compounds were dispersed on the crack faces more effectively. Due to their relatively low viscosities it is believed that they dispersed better on the crack walls and hence interacting chemically more effectively with the host matrix. The better chemical interaction to some extent was verified by tracing the calcium silicate hydrates for different samples. The existence of calcium silicate hydrates (CSH) was confirmed by Si-O stretching vibrations that gave peaks between ~970 and 1000 cm$^{-1}$. In the mineral treated samples the CSH peak results in larger bands when compared with the control samples (Control: 961 cm$^{-1}$; MgO: 966 cm$^{-1}$; TEOS: 964 cm$^{-1}$; CS: 978 cm$^{-1}$; SS: 998 cm$^{-1}$). This phenomenon can be attributed to increased polymerisation of silicate chains and the production of more CSH. This also explains the better defined and stronger expressed peaks around 550 cm$^{-1}$ especially for CS and SS samples. Since the polymerisation of silicate chains is stronger in these cases, this creates significant changes in the unhydrated calcium silicate phases (C$_3$S and C$_2$S) expressed between 500 and 600 cm$^{-1}$. As a result the deformation of silicate tetrahedra becomes better defined and this is reflected in the measured transmittance intensity. Ettringite is identified in the band range between 1000 and 1150 cm$^{-1}$. The present observations are in agreement with published data on infrared spectroscopy of cement based composites [38,39]. It appears that the use of minerals as healing materials results in more intense production of CSH which is evident by mechanical testing and verified by FTIR readings.

Figure 14 shows SEM images from crack walls after re-cracking of the control sample as well as of samples containing encapsulated liquid minerals. The cracked control sample (Fig. 14a) has the largest content of ettringite and a high porosity which corresponds to the dark spots observed in the image. The content of ettringite is reduced in all other samples (Fig. 14b to 14d). This observation verifies the XRD measurements where control sample showed stronger peaks corresponding to the
existence of ettringite. Calcite and portlandite phases are present in all samples as a result of the ongoing cement hydration. In the case of the sample healed with CS a residue of SiO₂ was observed in the crack face (Fig. 14c). This residue has the form of small pellet-like agglomerates that appear to react with calcium hydroxide crystals (equation 2) to produce more CSH as indicated in the area highlighted in Fig. 14c. The sample with encapsulated SS has significantly less porosity than the other samples (Fig. 14d). A deposition of silica film was observed in the SS sample (Fig. 14d). It is very likely that the SiO₂ residue observed in the CS sample as well as the deposited silica film can be the reason for having very strong silicon oxide peaks in the XRD pattern of both the CS and SS samples. This observation shows that unreacted silicon oxide is present on the crack walls. If further healing time was allowed or if a load was applied laterally to bring the crack faces together then possibly more healing products could have formed.

(a)                                                                                          (b)

Ettringite
Calcite / Portlandite

Deposited mineral
Calcite / Portlandite

(a)                                                                                          (b)
Fig. 14. SEM images from crack walls after re-cracking: (a) cracked control sample; (b) sample containing capsules with TEOS; (c) CS sample and (d) SS sample.

The powder MgO (Fig. 15a) revealed the presence of Mg-rich expanded compounds such as hydromagnesite (flower-like) and dypingite. Flower like hydromagnesite crystals deposited on the healing surface, forming the dominant phase of the produced healing materials (Fig. 15b). Hydromagnesite structures with similar appearance have been previously reported in the literature [40].
Fig. 15. SEM images from crack walls after re-cracking: (a) powder MgO sample and (b) hydromagnesite/dypingite phases in MgO treated sample.

The above SEM observations as well as the analysis of the microstructure suggest that the encapsulated minerals are released into the crack successfully and with the aid of water and CO$_2$ form healing materials in the form of hydration and carbonation products. It was also shown that the liquid minerals deposited a residue on the crack walls. Different levels of silicate polymerisation confirmed by FTIR suggest that the liquid minerals interact chemically with the cementitious material of the crack walls producing hydration products. A network of crystals forms within the crack and bridges the gap between crack walls. Figure 16 shows a conceptual schematic of the processes taking place in the crack. After the formation of the crack and the consequent rupture of the glass capsules the SiO$_2$ or MgO rich healing compounds are released into the crack (Fig. 16a). Water and carbon dioxide penetrate into the crack triggering a series of chemical reactions between them, the healing compounds and the Ca(OH)$_2$ that exists in the host cement based matrix. With the process of time, the cracks gradually seal as a consequence of the ongoing chemical reactions which result in the formation of hydration products in the close vicinity of the crack walls as well as in the precipitation of carbonation products (Fig. 16b).
Fig. 16. Conceptual illustration of the glass capsules system: (a) Crack formation results in the release of the healing compounds within the crack and (b) Consequent interaction of the healing compounds
with water, CO2 and Ca(OH)2 result in the formation of hydration products and the precipitation of

carbonation products that seal the crack.

4.3 Recovery of durability indicators

Figure 17 presents the results from the capillary absorption test. The results were benchmarked with
uncracked samples cured for 35 days. The results of this study suggest that in all cases of mineral
healing compounds, the capillary absorption performance of the cracked sections was significantly
improved. The largest reduction was observed in the samples healed with sodium silicate which
showed a 50% reduction in the sorptivity coefficient compared with the control cracked samples and a
very similar response to the control uncracked samples. The samples treated with TEOS and CS
showed sorptivity coefficient reduction of 18% and 43% respectively compared with the cracked
control specimens. Samples containing capsules with TEOS are far from the benchmarked value with
almost 69% difference, whereas specimens with CS capsules are similar with the uncracked control
samples with a difference that reaches 18%. Specimens containing capsules with powder MgO
resulted in a 46% reduction in sorptivity coefficient compared to the cracked control samples, and
their behaviour is close to the benchmarked value with a difference of 12%. These results suggest that
the materials formed at the crack are not limited in close proximity to the crack opening but extend
deeper in the crack forming a barrier that significantly decreases the capillary absorption. If the
formed healing materials were located only near the crack mouth it would have been easier for the
water to penetrate such a thin and localised layer and yield larger sorptivity values than the ones
recorded.
Fig. 17. Sorptivity coefficient for all types of samples healed immersed in water.

The results presented here suggest that the mineral compounds tested can be used to improve the sorption properties of cracked cement-based sections. In addition the results indicate that the compounds formed in the cracks of all samples play an important role in the overall reduction of the sorptivity coefficient. Moreover, it is plausible that the mineral deposition observed on the crack walls has acted as an additional barrier on the water diffusion in the material. As mentioned previously although the crack sizes used in this study are within the serviceability limits, they can potentially result in long term durability associated problems. This becomes clearer if one takes into consideration the sorption rate of the cracked control samples which is almost double the sorption rate of samples healed with CS and SS. Therefore in samples healed with CS and SS it is plausible that reinforcement corrosion can be significantly reduced.

Figure 18 presents the gas permeability results for all the samples healed with liquid minerals. As in the case of sorptivity the results have been benchmarked with uncracked samples cured for 35 days.
Fig. 18. Gas permeability coefficient for all types of discs healed immersed in water.

Similarly to the sorptivity results, treatment with injected minerals reduced the gas permeability coefficients in all samples when compared with a cracked control specimen. This reduction varied from 7% for TEOS treated discs to as high as 43% and 36% for discs healed with CS and SS respectively. Once more both CS and SS values were similar to the benchmark values of the uncracked samples. In fact CS samples resulted in a slightly better gas permeability coefficient compared with the uncracked discs. However, this difference was very small (~1.5%) and could be attributed to the larger standard deviation observed in the CS discs. Control cracked and TEOS treated samples showed an increase of 72% and 59% respectively when compared with the uncracked discs.

Summarising the results from both liquid capillary absorption and gas permeability tests, it was concluded that CS and SS show very good potential as healing compounds. Once they are released in the cracks and in the presence of water, they form crystalline and semi-crystalline structures which over time block the crack opening and prevent deleterious substances from penetrating the material.

Figure 19 summarises the % differences ($\Delta$ %) between the control samples and all specimens for all tests described in this work.
Fig. 19. % enhancement between the cracked control values and all other samples (Δ% in this plot concerns only samples cured immersed in water).

It is evident that both CS and SS have the best and more consistent response in all applied measurements, with differences being consistently above 10%. The third of the liquid minerals used in this study, TEOS, produced encouraging results. However, the TEOS potential as a healing agent is compromised by its low viscosity; once the capsules rupture and TEOS is released in the crack its high flowability makes it prone to leak from the crack. Moreover, it is very possible that some TEOS may have diffused in the bulk volume of the sample due to capillary suction from the crack walls.

Figure 20 illustrates the correlation between the measured properties for all control samples and samples healed with liquid minerals and immersed in water. As expected there is a good correlation between percentage of area closure and sorptivity. It can be observed also that gas permeability coefficient and sorptivity are linearly proportional to each other.
Fig. 20. Correlation between different properties measured for all control samples and samples healed with liquid minerals and immersed in water (LR%: % of load regain; CA%: % of crack area closure; k: gas permeability coefficient and S: sorptivity).

5. Conclusions

In this study the efficiency of encapsulated mineral compounds as potential healing materials was investigated. In the light of the observed results and discussion the following conclusions can be drawn:

- All mineral compounds showed potential as prospective self-healing materials in a cement based system. Specifically, colloidal silica and sodium silicate were more efficient and consistent as healing agents and can thus be used readily. TEOS and MgO can also be utilised as healing agents following some modifications that would allow full advantage of their potential to be taken. In the case of TEOS a viscosity modification is recommended since in the current experimental design its low viscosity results in leakage and diffusion of the compound, with not enough material retained in the crack for further reaction. For the powder MgO an alternative encapsulation configuration may be more efficient. The double capsule system discussed in this paper did not secure good dispersion of the MgO particles within the crack and resulted in an inconsistent performance.
The results showed that the presence of water is very crucial for the evolution of the self-healing phenomenon. Even high humidity alone is not enough to promote self-healing. Water is needed to penetrate into the cracks and accelerate the development of the healing products.

The minerals used in this study offer a relatively small load regain percentage, but are very potent in regaining properties associated with the durability of concrete structures.

This study demonstrates how mineral compounds are very effective in improving durability related parameters in cracked sections. Compromise of the structural integrity usually comes as a consequence of sudden catastrophic events and its restoration is most of the times impossible. However, smaller cracks which are usually overlooked can cause progressive damage due to long lasting durability associated phenomena. The results of this study indicate that relatively low-cost mineral compounds, fully compatible with the host matrix, have the potential to be used as encapsulated materials that upon damage will autonomously heal the formed cracks.

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Additional data related to this publication is available at the University of Cambridge’s institutional data repository: https://www.repository.cam.ac.uk/handle/1810/249213

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