Sealing of cracks in cement using microencapsulated sodium silicate

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Sealing of cracks in cement using microencapsulated sodium silicate

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Abstract
Cement-based materials possess an inherent autogenous self-healing capability allowing them to seal, and potentially heal, microcracks. This can be improved through the addition of microencapsulated healing agents for autonomic self-healing. The fundamental principle of this self-healing mechanism is that when cracks propagate in the cementitious matrix, they rupture the dispersed capsules and their content (cargo material) is released into the crack volume. Various healing agents have been explored in the literature for their efficacy to recover mechanical and durability properties in cementitious materials. In these materials, the healing agents are most commonly encapsulated in macrocontainers (e.g. glass tubes or capsules) and placed into the material. In this work, microencapsulated sodium silicate in both liquid and solid form was added to cement specimens. Sodium silicate reacts with the calcium hydroxide in hydrated cement paste to form calcium-silicate-hydrate gel that fills cracks. The effect of microcapsule addition on rheological and mechanical properties of cement is reported. It is observed that the microcapsule addition inhibits compressive strength development in cement and this is observed through a plateau in strength between 28 and 56 days. The improvement in crack-sealing for microcapsule-containing specimens is quantified through sorptivity measurements over a 28 day healing period. After just seven days, the addition of 4% microcapsules resulted in a reduction in sorptivity of up to 45% when compared to specimens without any microcapsule addition. A qualitative description of the reaction between the cargo material and the cementitious matrix is also provided using x-ray diffraction analysis.

Keywords: self-healing, microencapsulation, sodium silicate, autonomic

Introduction
Measured by tonnage, concrete is the most consumed material on the planet. Carbon-dioxide emissions associated with cement production alone constitute around 5% of global CO2 emissions [1]. Concrete is relatively cheap, very versatile and has high compressive strength. On the other hand, the tensile strength and ductility of concrete is limited and, for this reason, steel rebars are used. Cracking of reinforced concrete is inevitable due to mechanical actions, environmental actions or their combination. Although certain sizes (those less than 0.40 mm) of microcracks do not necessarily effect the structural integrity of the concrete, they propagate and coalesce forming larger through cracks that can affect structural integrity. But, even if microcracks do not coalesce, they still pose a threat to the structure as they can become the channels that will allow corrosive substances to enter concrete.

Steel corrosion can be induced chemically from sulfates, sea water or acids. Steel corrosion results in the formation of expansive products, which result in further cracking of the concrete. In extreme cases this eventually causes spalling, and thus further infiltration as a result of an increase in permeability. Complete disintegration of steel rebars or pre-stressed tendons can then lead to catastrophic structural failure. For
this reason, it would be beneficial if cracks could be sealed when they surface. Currently, acceptable levels of performance of concrete structures are maintained though costly routine inspection and repair. It is estimated that around 40%–60% of the European construction budget is devoted to repair and maintenance of existing structures—a large proportion of these being concrete structures [1]. In the UK, the size of the UK repair industry is in excess of £1 billion [2]. In the United States alone, the annual cost for repair, protection and strengthening of concrete structures is estimated to be between US $18 billion and US $21 billion [3].

Various techniques have been explored to protect the steel from these aggressive substances and the potential for corrosion. They include surface waterproofing, epoxy coated reinforcement, stainless steel reinforcement, fibre-reinforced plastic reinforcement and cathodic protection. However, none of these techniques have solved this ongoing problem and all have significant, either technical or economical, limitations [4, 5].

Modern concrete design codes limit acceptable crack widths. Eurocodes limit crack width to 0.40 mm for reinforced concrete in serviceability limit state [6]. In other structure classes, such as those for water retaining structures or high density concrete for nuclear applications, concrete must be considered impermeable and for this reason crack width is limited to 0.05–0.20 mm depending on the exposure conditions and tightness class [7].

Concrete does possess some inherent self-healing capability and is able to seal limited-width micron-sized cracks. The distinction between sealing and healing is that the latter provides a recovery in mechanical properties whilst the former is manifested from visual crack-closure or from recovery in a durability indicator. Various chemical, physical and mechanical processes all contribute to autogenous (synonymous with autogenic) self-healing [8]. Hearn and Morley [9] classified the different autogenous healing mechanisms along with their degree of influence. At early age, on-going hydration of cement is mainly responsible for closing cracks. In particular, if insufficient mixing of the cementitious material takes place, unhydrated cement nuclei remain dispersed within the cementitious matrix. The volume of cement gel produced from hydration is approximately 2.3 times the original cement volume for ordinary Portland cement (OPC) [10] and thus can provide effective crack closure. At later age, the precipitation of calcium carbonate is the main mechanism contributing to self-healing of cement. Carbonation of calcium hydroxide occurs in the presence of carbon-dioxide. The maximum width of crack that can be healed by autogenous means is dependent on many factors including the type and quantity of cement, the usage and type of supplementary cementitious materials (SCMs), the age of concrete, the width/length of crack and the healing environment [8].

An enhancement in autogenous healing can be created through the use of SCMs such as blast furnace slag (BFS) and fly ash (FA) [11, 12]. BFS and FA improve autogenous healing by enhancing further hydration. The reason for this is that BFS and FA hydrate slower than cement and thus more unreacted binder materials remain in the matrix. Expansive agents [13, 14] as well as crystalline additives [15] have also been used to heal cracks up to 0.4 mm. Specimens with crystalline additives were found to have a higher pH value which would favour calcium carbonate precipitation and provide increased corrosion protection. The addition of SCMs for improved autogenous healing is not considered autonomic healing as they are conventionally added into cementitious materials.

Fibre additions have been used to create engineered cementitious composites (ECCs). Here, the embedment of fibres causes a distribution of multiple microcracks with a specific width when loaded; as opposed to few very large cracks that would be observed in conventional concrete. This limitation of crack width allows the cementitious material to heal autogenously. Several researchers have explored autogenous healing in ECCs in the laboratory [16], in a natural environment [17] as well as in alkaline and chloride environments [18, 19].

Autonomic self-healing differs from autogenous self-healing in that it uses material components that would otherwise not be found in the material [1]. These materials can either be added directly into the cementitious mixture or stored using a carrier material. By utilising these engineered additions, the healing potential and performance are improved. Dry was first to explore autonomic healing of concrete by encapsulating sealants, adhesives and waterproofing chemicals into glass tubes [20–22]. The tubes were placed into the tensile section of concrete specimens. When cracking occurred, the tubes released their contents and filled the crack volume. Various healing agents have since been investigated for their efficacy in sealing or healing cracks in cementitious materials [23]. Their performance is quantified through a measure in mechanical recovery or a durability indicator. More recently, encapsulated minerals have been selected for their improved compatibility with the hardened cementitious matrix as well as low cost [24]. Silica-based healing agents, such as sodium silicate, are considered excellent mineral candidates for self-healing of cementitious materials. Sodium silicate reacts with calcium hydroxide (CH) in the presence of water to form a calcium silicate hydrate (C–S–H) gel-the main product of cement hydration. The reaction between sodium silicate and calcium hydroxide in the presence of water is given as:

$$\text{Na}_2\text{SiO}_3 + \text{Ca(OH)}_2 + \text{H}_2\text{O} \rightarrow (\text{CaO} \cdot \text{SiO}_2)\text{H}_2\text{O} + \text{Na}_2\text{O}.$$ 

The conversion of calcium hydroxide (CH) to C–S–H is favourable as the presence of CH is detrimental to both the cement’s chemical and mechanical durability. CH is water soluble and susceptible to acid attack. Also, the interfaces around CH are typically highly porous, thereby increasing permeability and decreasing strength [25]. Sodium silicate has already found multiple uses in cementitious materials. For example, it is used as an alkali-activator in alkali-activated cements [26]. In concrete, it is used as a setting accelerator and also applied in the form of silicate mineral paint to enhance waterproofing and improve durability [25, 27].
Huang and Ye [28] added sodium silicate stored in sponge that was sealed with wax (5 mm capsule diameter) into ECCs. The use of a large volume fraction of capsules was more than that able to react with the CH in the cementitious matrix. For this reason, the residual sodium silicate was observed to crystallise. The self-healing efficiency was observed to be highly dependent on the concentration of sodium silicate. Formia et al [29] encapsulated sodium silicate in cylindrical cementitious hollow tubes of various diameters that were produced by extrusion. It was found that the sodium silicate solution was not released from small (2 mm internal diameter) tubes. The use of larger extruded tubes (7.5 mm internal diameter) however, resulted in significant load and stiffness recovery even after a second stage of reloading. Kanellopoulos et al [24] explored the efficacy of silica-based healing agents using glass vials placed in the tensile section of mortar specimens under different healing environments. Cracks induced by three point bending (3PB) led to release of the encapsulated material and its subsequent reaction with the cementitious matrix. Results showed the ability of sodium silicate to recover sorptivity and gas permeability properties to values comparable with uncracked specimens.

Autonomic self-healing using embedded microcapsules (capsules less than 1000 μm in diameter) was first developed by White et al [30] for polymeric materials. Since then, the proposed technology has seen application in other materials such as metals, ceramics and concrete [31]. The fundamental principle of this self-healing mechanism is that when cracks propagate in the cementitious matrix, they rupture the dispersed capsules and their content (cargo material) is released into the crack volume. In autonomic self-healing concrete via microencapsulation, the autogenous capability of cement is enhanced through the addition of microcapsules. Dependent on the self-healing mechanism, this cargo material may react with the cementitious matrix (hydration and carbonation products) or the environment (air, CO₂, moisture) to form products that seal, or heal, the crack. A couple of researchers have added microencapsulated sodium silicate into cementitious materials. Pelletier et al [32] added microcapsules to mortar specimens at 2% volumetric fraction. Random microscale cracks were induced and the ability of microcapsule-containing specimens to recover toughness and flexural strength after healing was compared with control samples. However, there is a lack of microcapsule characterization as well details of the size of cracks healed in specimens. Gilford et al [33] focused mainly on how microcapsule preparation parameters (temperature, agitation rate, pH) effect the shell thickness and size of microcapsules. Microcapsules were added to cylindrical concrete specimens that were damaged and left to heal for a 48 h period. The addition of microcapsules was found to increase the stiffness post-healing to a level higher than that before damage. Both reports by Pelletier et al and Gilford et al lack confirmation of microcapsule survivability during mixing as well as proof of release upon cracking. Also, a quantitative description of the reaction between the microencapsulated material and the cementitious matrix is required to determine the volumetric fraction of microcapsules required to achieve a certain level of healing.

As researchers are most interested in the self-healing performance brought about from the addition of microcapsules, there has been limited report on the effect of microcapsule addition on mechanical properties. There is also a lack in report of the effect of microcapsule addition on rheological properties of cement paste. In assessing whether an autonomic self-healing system incorporating microcapsules is feasible, it is most important to describe the effect that microcapsule addition has on the initial properties of the cementitious material. If properties are reduced significantly, and this value falls below that required for the application, a lower proportion of microcapsules should be used or the selected microcapsules may be discarded as unsuitable.

Microcapsule admixtures are used extensively in the construction industry. Common uses include those for air-entrainment, temperature control using phase change materials and increased fire-resistance [34]. There are many physical, mechanical, environmental, processing and practical requirements for microcapsules used specifically for self-healing of cementitious materials [35]. A vital physical requirement is that microcapsules they must survive the aggressive mixing process of concrete. This includes the stresses exerted from the aggregates as well as the mixing equipment. However, they must be brittle enough so that they rupture when cracks propagate through them. This main requirement has been addressed by using microcapsules that exhibit rubbery and elastic properties when hydrated (i.e. during the mixing process) but change to brittle glassy behaviour when unhydrated (i.e. when the material is cured) [36].

It is hypothesised that the effect of the addition of sodium-silicate-containing microcapsules on cement hydration is two-fold. Firstly, the addition of microcapsules creates spherical voids which impede the binding of cement hydration products. This reduces hydration and thus lowers the amount of heat released. Secondly, if any capsules are broken during mixing, the released sodium silicate will accelerate cement hydration.

The effect of microcapsule addition on the mechanical properties of a cementitious material is dependent on multiple variables such as the size of microcapsules, mechanical properties of microcapsules as well as the bond strength between the microcapsules and cementitious matrix. If microcapsules are relatively small compared with the OPC particle mean size (5–30 μm), it is possible that they enhance durability and mechanical properties by filling pre-existing voids within the cementitious matrix. Larger microcapsules are able to carry larger quantities of healing agent and it has been shown that, at a fixed volume fraction, larger microcapsules provide increased healing efficiency [37]. If the shell material has high strength and stiffness as well as good bonding properties to the cementitious matrix, then microcapsule addition may improve properties. Dispersed spherical particles have been added extensively in particulate-reinforced composites to improve both mechanical and physical properties [38].

This aim of this work is to describe the effect of sodium silicate-containing microcapsule addition on the rheological
and mechanical properties of cement. The efficacy of micro-encapsulated sodium silicate to close cracks and reduce sorptivity is quantified. Two different microcapsules encapsulating both liquid and solid sodium silicate are used. A qualitative description of the reaction between the cargo materials and the cement matrix is also provided.

Materials and experimental methods

Microcapsule characterisation

Two different microcapsules used for autonomic self-healing of cementitious materials, \textit{L500} and \textit{T130}, were provided by \textit{Lambson Ltd} and \textit{Thies Technology, Inc.} respectively. The \textit{L500} microcapsules contain a liquid sodium silicate solution dispersed in mineral oil and emulsifier. The quantity of sodium silicate is approximately 42\% that of the total encapsulated material. The \textit{T130} microcapsules are manufactured using an \textit{in situ} polymerisation technique using poly-urea as shell material. A summary of microcapsule properties are given in table 1. Optical microscope images of the microcapsules can be seen in figure 1. Microcapsules were observed to swell in water (the \textit{L500} microcapsules more so than the \textit{T130} microcapsules) and return to their original size after drying. They maintained their structural integrity throughout this period thus retaining the encapsulated cargo material. Long-term survivability in high pH (>13) as well as in a calcium chloride solution was confirmed.

<table>
<thead>
<tr>
<th>Name</th>
<th>Shell material</th>
<th>Cargo material</th>
<th>Mean size ~ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{L500}</td>
<td>Gelatin-gum Arabic</td>
<td>Na$_2$SiO$_3$ (in a liquid solution)</td>
<td>500</td>
</tr>
<tr>
<td>\textit{T130}</td>
<td>Poly-urea</td>
<td>Na$_2$SiO$_3$ (solid)</td>
<td>130</td>
</tr>
</tbody>
</table>

Microcapsule addition to cement paste

Both the \textit{L500} and \textit{T130} microcapsules were mixed into cement paste. Microcapsules were added to CEM I 52.5N cement manufactured to comply with the requirements of BS EN 197-1. As the \textit{L500} microcapsules are dispersed in a liquid solution, they are extracted using filter paper and a vacuum pump. When extracted, they are in a hydrated state and for this reason are unlikely to absorb much water when added into the cementitious mixture. The \textit{T130} microcapsules are in powdered form and thus added directly to the cementitious mixture.

Isothermal calorimetry for cement hydration

A Calmetrix I-Cal 2000 high precision isothermal calorimeter compliant with ASTM C1679 was used to measure the heat of hydration of OPC incorporating microcapsule additions. Microcapsules were added at volumetric fractions ($V_f$) of 4\% to cement paste with a 0.4 water-to-cement ($w/c$) ratio. Thus, three different mixes were investigated; (1) OPC only, (2) OPC with 4\% \textit{L500} microcapsule addition, and (3) OPC with 4\% \textit{T130} microcapsule addition. The thermostat was set to 23 °C and left to stabilise for 24 h. Pre-conditioning of the cement powder and water took place for 2 h before being mixed for one minute using a plastic spoon. The quantities of cement and water used were 30 g and 12 g respectively and the mass of microcapsules was 0.4 g. Logging of the heat of hydration was then carried out for 48 h. This time was sufficient to obtain the initial setting peak. The peak power is calculated as the maximum power (first peak) minus the power during the induction period (first trough). The initial setting time was then calculated as the time at one-third of the peak power.
Testing of viscosity using rheometry

A Brookfield DV3T Rheometer was used to measure the viscosity of mixes. Once again, three different mixes were investigated; (1) OPC only, (2) OPC with 4% L500 microcapsules, and (3) OPC with 4% T130 microcapsules. Samples were prepared by mixing cement paste for three minutes before placing 10 ml into the rheometer sample cup. A SC4-27 spindle was inserted before leaving the sample to settle for five minutes. After this time, preshearing from 0 to 30 s$^{-1}$ was carried out for one minute to erase shear history due to mixing. The sample was then left for 30 s to stabilise. After this, a shear stress versus shear rate relationship was obtained by subjecting the sample to shear rates varying from 8.5 s$^{-1}$ to 60 s$^{-1}$ (ramp up) and back down to 8.5 s$^{-1}$ (ramp down) [39]. The gradient of the linear regression of the ramp down portion of the shear stress versus shear rate relationship was then used to obtain the (plastic) viscosity.

Casting and testing procedure

**Cube specimens.** Cube specimens (40 × 40 × 40 mm) were cast to quantify the effect of microcapsule addition on the ultimate compressive strength (UCS) of cement paste. Microcapsules were added at volumetric fractions ranging from 0% to 4% in unit intervals to OPC at 0.4 w/c ratio. Sample mixing was carried out using a Kenwood 1500 W food blender. Specimens were compacted using a vibrating table and then covered with a plastic film to prevent evaporation of water. After 24 h, samples were demoulded and submerged in water in a constant temperature environment of 21 °C ± 1. Four cubes were tested at each of 7, 14, 28 and 56 days after the day of casting using a 250 kN servohydraulic testing frame.

**Prismatic specimens.** Three different cement mixes were tested all with a water-to-cement ratio of 0.4. The first was a control mixture of cement and water only. The remaining two mixtures contained the addition of each of the T130 and L500 microcapsules at 4% volume (approximately 1.3% by mass of cement). Mixes were prepared in an identical manner to that outlined above and six prisms (40 × 40 × 160 mm) were cast for each of the three mixes. Specimens were cast with a 1.6 mm mild steel wire addition (figure 2) into the prisms compressive section with a cover of 10 mm from the top to prevent complete sample separation. After 7 days following the date of casting, sample were removed from the water immersed environment and a central 3 mm notch was then induced using a diamond table saw. This was done to ensure cracks initiated in the centre of the specimen during testing. Samples were mechanically cracked under three-point bending using an Instron 5567 30 kN static testing frame at a rate of 0.125 mm s$^{-1}$ (figure 3). Crack width was controlled using a clip gauge (figure 4) and testing was terminated automatically once the measured width reached 0.3 mm. Optical microscopy images were taken of samples to measure...
the crack width after unloading and also to monitor areal crack healing.

Durability testing. Sorptivity tests were carried out using a short-term one-dimensional experiment. Sorptivity is a measure of a material's ability to absorb or desorb liquid by capillarity. Testing procedure was adapted from the RILEM TC 116-PCD guidelines [40] in order to create a more suitable testing procedure for cracked specimens. Cracks were isolated using aluminum tape on the bottom face of specimens to ensure that absorption only occurs through the crack area (shown schematically in Figure 5). Changes in sample weight (to 0.1 g precision) due to water suction were recorded over 4 h and 16 min. The cumulative water absorbed per unit area of inflow surface is then related to the sorptivity by [41]:

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

where $S$ is the sorptivity coefficient with units g/(√min)$^{-1}$ and $t$ is the time in minutes. The sorptivity coefficient ($S$) was therefore obtained through linear regression of $M_w$ and $\sqrt{t}$. Specimens were tested every seven days over a 28 day healing period. Each week, samples were removed from water and left to dry for four days before testing. Cracks were also observed weekly using a digital microscope to monitor visual crack closure.

Microstructural analysis samples. A qualitative description of the reaction between the cementitious matrix and the encapsulated material is desired. For this reason, hardened Portland cement (HPC) paste was ground after seven days of water-curing and additions of sodium silicate and microcapsules were added. Four samples were investigated. (1) HPC only, (2) HPC with sodium silicate and water addition, (3) HPC with L500 microcapsules and water addition, (4) HPC with T130 microcapsules and water addition. The sodium silicate and microcapsules (2 g) were added to 10 g of HPC with 5 g of water. Microcapsules were crushed to guarantee release of the encapsulated material when mixed with the HPC. Mixes were left for seven-days in a petri-dish before being extracted. Samples were ground using a pestle and mortar and tested using x-ray diffraction (XRD) analysis scanning at angles ranging between 10° and 60° using CuKα radiation. A flow chart of the experimental process is given in Figure 6.

Results and discussion

Microcapsule distribution and release

Sliced cross-sections were taken of the L500-containing specimens using a diamond blade table saw to confirm excellent survivability and distribution of microcapsules across the sample cross section. The microcapsules are large...
Rupture of embedded microcapsules is observed in greater detail using scanning electron microscopy (SEM) as observed in figure 8 for the both microcapsules.

Rheological properties

Viscosity measurements for the three mixes are summarised in table 2. Values are in agreement with reported values for cement paste at 0.4 water–cement ratio [42]. It is clear that viscosity increases with the addition of microcapsules. The volumetric addition of 4% L500 microcapsules resulted in an increase in viscosity by 52% whilst addition of T130 microcapsules resulted in a 47% increase. The ability of microcapsules to absorb water is likely to contribute to this reduction in workability. As a result, this will reduce the compressive strength of the hardened cement paste. However, the effect of microcapsule addition in mortar and concrete is likely to be less detrimental than that measured in cement paste.

Profiles of cement hydration obtained using calorimetry and can be seen in figure 9. Setting time and peak power for the three mixes is summarised in table 2. The addition of L500 microcapsules shows a slight reduction in peak power but almost no change in setting time. The addition of 4% T130 microcapsules accelerates the initial setting time and reduces the peak power by 28%. This is not necessarily caused by the breakage of microcapsules during mixing but rather the shell and cargo material debris within the powder-the latter of which accelerates hydration.

Effect on mechanical properties

Once again, the L500 microcapsules were large enough to be observed with the naked eye. Their survivability and

<table>
<thead>
<tr>
<th>Mix</th>
<th>Viscosity, $\mu$ (Pa s)</th>
<th>Initial setting time (hh:mm)</th>
<th>Peak power (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>0.2973</td>
<td>04:08</td>
<td>3.67</td>
</tr>
<tr>
<td>OPC + 4% L500</td>
<td>0.4544</td>
<td>04:04</td>
<td>3.48</td>
</tr>
<tr>
<td>OPC + 4% T130</td>
<td>0.4370</td>
<td>03:04</td>
<td>2.64</td>
</tr>
</tbody>
</table>

Figure 9. Initial setting peaks of cement hydration curves for OPC (black line), OPC with 4% L500 microcapsule addition (blue line) and OPC with 4% T130 microcapsule addition (red line).
subsequent rupture upon cracking is observed on the fracture planes of cube specimens tested for their UCS (figure 10). Increasing quantities of microcapsules are observed as the addition increases from 1% to 4%.

Rheological results presented above suggest a reduction in compressive strength will be observed for microcapsule-containing cement paste samples. Compressive strength results for varying volume fraction of microcapsules is given in figure 11 for the L500 and T130 microcapsule additions. A decrease in compressive strength becomes increasingly evident at later ages. In particular, it can be seen that the compressive strength of capsule-containing specimens plateaus after 28 days. This is noticed when using both the L500 and T130 microcapsules. Although the L500 microcapsules are larger, their detrimental effect on compressive strength is less than that of the T130 microcapsules. The flexural strength of capsule containing specimens was seen to increase for the T130 containing specimens whilst it reduced slightly for the L500-containing samples. After seven-days water curing, 4% addition of microcapsules resulted in a 20% increase for T130-containing specimens and a 17% reduction for L500-containing specimens. Measurements taken on the bottom face and mid-sample showed average crack widths of 0.09 mm for the control mix, 0.12 mm for the T130-loaded specimens and 0.22 mm for the L500-loaded specimens.

Figure 10. Crushed cement cubes containing 1%–4% volumetric additions of L500 microcapsules and tested after 56 days.

Figure 11. Compressive (cube) strength of cement containing 1%–4% addition of (a) T130 and (b) L500 microcapsules tested at 7, 14, 28 and 56 days.

Recovery of durability

Sorptivity results are summarised in figure 12 for the three different mixes. The capsule-containing specimens reduce the sorptivity significantly after short healing periods. The addition of 4% T130 microcapsules reduces the sorptivity drastically by 45% after a seven-day healing period and this continues to 34% after 28 days of healing. Observation of OPC and capsule-containing samples during testing at 7 days can be seen in figure 13. The samples containing L500 microcapsules also show improved sealing of cracks. After a seven-day healing period, the addition of 4% volumetric fraction of microcapsules reduces the sorptivity by 15% when compared with the control sample. After a 28 day healing period, the L500 samples absorb slightly more water than the control samples. This can be explained by the fact that the dried residual microcapsule shell material within the sample hydrates and absorbs water. This is favourable for two
reasons. Firstly, swelling of the microcapsules will contribute to blocking of cracks and avoid fluids from penetrating deeper into the matrix. This is vital to protect the steel reinforcement within concrete. Secondly, as water is required for the reaction between calcium hydroxide and sodium silicate to produce C–S–H, the retention of water in the vicinity of the ruptured capsule facilitates this reaction. Microscopic images also verify the improved sealing of cracks in capsule-containing specimens as observed in figure 14. The images suggest that visual crack sealing observations along are not sufficient to quantify sealing. Instead, a durability indicator (e.g. permeability, sorptivity) is necessary.

The T130 microcapsules do show superior crack sealing—indicated by a greater reduction in measured sorptivity values. However, the T130 microcapsules do contain more encapsulated sodium silicate. It makes sense therefore, to hypothesise that the T130 microcapsules will provide better healing than the L500 microcapsules due to a larger available quantity of sodium silicate that has the potential to react with the calcium hydroxide in the cementitious matrix to form C–S–H. Further investigation is required to determine whether powdered sodium silicate is preferred to liquid (or dispersed) sodium silicate for use as a healing agent. On the one hand, the use of liquid sodium silicate allows for better transport into the crack plane. However, on the other hand, as the samples are cured in water, there is the possibility that some of the encapsulated liquid diffuses into the water. The powdered cargo material is more likely to remain in the residual shell material (and thus within the crack volume) after the microcapsule shell has been mechanically ruptured. With reference to measured crack widths upon loading, the recovery in sorptivity for L500-containing specimens is more impressive considering the cracks in L500 samples are much
larger than those in T130 samples and significantly larger than the control samples.

**Microstructural analysis**

Samples with added sodium silicate or crushed microcapsules (samples 2–4) showed clear binding properties during their extraction after seven days of reaction (figure 15). XRD spectra of the four different samples can be seen in figure 16. Typical Portland cement hydration products can be observed including portlandite (calcium hydroxide), ettringite and semi-crystalised calcium silicate hydrates. C–S–H itself does not show distinct peaks due to its poor crystalline nature. Calcium hydroxide (CH) peaks ($2\theta = 18.007, 28.671, 34.101$ and 47.12) are very distinct in 7 day hardened cement paste (HPC) XRD (black line, figure 16) as expected. These peaks are still visible after the microcapsule or sodium silicate additions. However, their intensity has been significantly reduced indicating a consumption of portlandite. XRD analysis of HPC mixed with crushed L500 (blue line, figure 16) or T130 (red line, figure 16) capsules and water shows similar characteristics to the HPC mixture with sodium silicate (pink

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**Figure 14.** Cracks observed in (a) cement specimens, (b) cement specimens with 4% volumetric addition of L500 microcapsules and (c) cement specimens with 4% volumetric addition of T130 microcapsules. Images on the left-hand side show samples after seven days of healing whilst those on the right-hand side are after a 28 day healing period.
Figure 15. Samples extracted after a seven day reaction period. (1) HPC only, (2) HPC with sodium silicate and water addition, (3) HPC with L500 microcapsules and water addition, (4) HPC with T130 microcapsules and water addition. Samples 2–4 show clear binding properties.

Figure 16. X-ray diffractogram of hardened cement paste (HPC, black line), HPC with sodium silicate addition (pink line), HPC with 4% L500 microcapsule addition (blue line) and HPC with 4% T130 microcapsule addition.

The portlandite peaks in the HPC + L500 mix are the largest of the three mixtures although they are still significantly smaller than those in the HPC mixture alone. As the L500 microcapsules contain a sodium silicate dispersion in oil, the amount of sodium silicate released will be less than that released from the T130 microcapsules. It is no surprise therefore, that the amount of consumed portlandite is less. The HPC + sodium silicate XRD and HPC + crushed T130 microcapsules are observed to be almost identical. This affirms the release of the cargo material and its reaction with the ground cement paste. XRD of HPC mixed with sodium silicate in the absence of water (not shown here) is identical to XRD of HPC alone. This demonstrates the need for water for sodium silicate to react with hydrated cement.

Unhydrated calcium silicate (mainly tricalcium silicate and dicalcium silicate) peaks are observed between the portlandite peaks at 28.671 and 34.101. The peaks observed within this region are larger for the HPC sample compared to the samples with microcapsule or sodium silicate additions. In this same region, amorphous C–S–H peaks overlap along with calcite at 29.405. Calcium carbonate formation is due to the carbonation of calcium hydroxide during water curing. This peak is observed to be larger in the HPC + sodium silicate mix and HPC + L500 mix. It is clear that the addition of sodium silicate (or crushed sodium-silicate containing microcapsules) leads to a consumption of CH and production of C–S–H.

Once again, it is worth noting that the L500 microcapsules contain less sodium silicate than the T130 microcapsules and this is evident when comparing the XRD spectra.

Conclusion

Two different sodium silicate-containing microcapsules (T130 and L500) were added to cement paste to quantify the effect of their addition on rheological and mechanical properties. The addition of 4% (with respect to cement volume) microencapsulated sodium silicate was shown to reduce sorptivity of cracked specimens over a 28 day healing period. Thus, the efficacy of microencapsulated sodium silicate to close cracks and provide sealing was quantified. A qualitative description of the reaction between the cargo material and cement matrix was also provided. X-ray diffractograms confirm the consumption of calcium hydroxide and the production of calcium-silicate-hydrate from the reaction of the cargo material with the cementitious matrix. Future work is focused on optimising the volumetric fraction of microcapsules and to determine the quantity required for a certain level of healing. Quantification and characterisation of the healing products will then be compared with those obtained from microstructural observations in this work.

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