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Microencapsulated sodium silicate for self-healing cement-based in-ground barriers

Silicate de sodium microencapsulé pour barrières enterrées à base de ciment auto-cicatrisant

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ABSTRACT: In-ground vertical barriers are one of the most commonly-used contaminated land remediation technologies to prevent the migration of contaminants. Despite the popularity of in-ground barriers, problems related to their durability and mechanical properties impact serviceability, leading to the need for urgent repair. In-ground barrier materials, therefore, need to be more resilient, so that their whole life carbon emissions and whole life costs can be significantly reduced. Self-healing methodologies, including microencapsulated minerals, have been developed over recent years, with the focus on concrete. The mechanism of self-healing microencapsulation system is that when cracks propagate in the matrix, they rupture the capsules, leading to the release of healing agents into the crack volume. In this study, microencapsulated sodium silicate was incorporated in in-ground barrier materials and the mineral reacts with the calcium hydroxide in the cementitious matrix to form the calcium-silicate-hydrate gel. The characterisation of two different microcapsules and their effects on the properties of in-ground barrier materials were presented. Self-healing efficacy of in-ground barrier materials was examined in terms of crack sealing and the recovery of mechanical properties.

RÉSUMÉ: Les barrières verticales enterrées constituent l'une des technologies d'assainissement des sols contaminés les plus couramment utilisées pour empêcher la migration de contaminants. Malgré la popularité des barrières enfouies dans le sol, des problèmes liés à leur durabilité et à leurs propriétés mécaniques affectent leur facilité d'entretien, ce qui nécessite des réparations urgentes. Les matériaux de barrières enterrées doivent donc être plus résilients, de sorte que leurs émissions de carbone et leur coût tout au long de leur durée de vie puissent être considérablement réduits. Des méthodologies d'auto-guérison, notamment des minéraux microencapsulés, ont été développées ces dernières années, se concentrant sur le béton. Le mécanisme du système de microencapsulation auto-cicatrisant prévoit que, lorsque les fissures se propagent dans la matrice, elles cassent les capsules, entraînant la libération d'agents cicatrisants dans l'espace de la fissure. Dans cette étude, du silicate de sodium micro-encapsulé a été incorporé dans des matériaux de barrières enterrées; le minéral réagit ainsi avec l'hydroxyde de calcium dans la matrice cimentaire pour former le gel de silicate de calcium-hydrate. Cette étude examine les caractéristiques de deux types de microcapsules et leurs effets sur les propriétés des matériaux de barrières enterrées. L'efficacité de l'auto-guérison des matériaux de barrière dans le sol est analysée en termes de colmatage des fissures et de récupération des propriétés mécaniques.

Keywords: in-ground barrier; self-healing; microcapsule; sodium silicate

1 INTRODUCTION

The contamination of soils due to industrial activities has become a serious global issue with the impact of human activity being seen in food security and safety. In-ground barriers are widely used to prevent the contaminants from spreading with the groundwater beyond the boundary of the contained area. Soil mixing is a ground treatment technique in which soil is mixed in-situ, usually with cementitious binders such as cement, lime or bentonite. It was first used as a ground improvement technique and has recently been utilised in the remediation of contaminated sites (Al-Tabbaa and Stegemann, 2005; Al-Tabbaa et al., 2012; Al-Tabbaa et al., 2014).

The cracking of in-ground barriers in contaminated sites can occur due to mechanical factors and environmental factors (O'Connor, 2015). The formation of damage is not problematic as long as counteracted by self-healing processes. For cementitious materials, the mechanisms for achieving self-healing are classified into two categories: autogenous and autonomic self-healing. The self-healing process is termed autogenous when the recovery process uses components that could otherwise be present when not specifically designed for self-healing. The engineered addition of materials or components capable of promoting self-healing in cementitious material characterises autonomic self-healing, since the recovery process uses components that wouldn't otherwise be found in the material (De Rooij et al., 2013). The microcapsule-based self-healing system sequesters the healing agent in discrete capsules until damage triggers rupture and release of the capsule contents. The overall autonomic self-healing process is illustrated in Figure 1, where the capsules act as a reservoir of the healing agent inside of the matrix. When the shell is damaged, the healing agent is available to heal the crack.

Sodium silicate (SS) is considered as an excellent healing agent for self-healing of cementitious materials. SS reacts with calcium hydroxide in the presence of water to form a calcium silicate hydrate (CSH) gel - the main product of cement hydration.

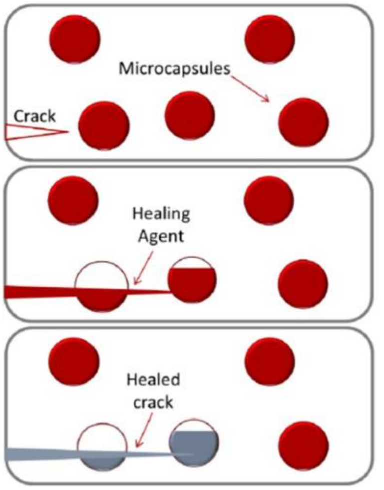


Figure 1. The concept of autonomic microcapsule-based self-healing (Souza, 2017)

Giannaros (2017) investigated the self-sealing of cracks in concrete using microencapsulated SS. The improvement in crack-sealing for microcapsule-containing specimens is quantified through sorptivity measurements. The addition of microcapsules resulted in a reduction in sorptivity of up to 45%. Kanellopoulos et al. (2016) also measured healing levels of cracks in mortars incorporating microencapsulated SS, and it is shown in all cases that the inclusion of microcapsules improved the crack closure and reduced the water absorption significantly. The above work has all focussed on structural applications of concrete, with no attention paid on geotechnical or geo-environmental applications. Many geotechnical applications including in-ground barriers are inaccessible as they are buried underground and therefore very difficult to repair. This makes the concept of developing self-healing materials for geotechnical and geo-environmental engineering rather attractive (Al-Tabbaa & Harbottle, 2015).

In this study, two batches of microencapsulated SS were investigated as a candidate for self-healing in in-ground barrier materials. The performance of the microcapsules in aggressive environments and survivability in the mixing process were used as indicators for the feasibility of the approach. Moreover, SEM of the ruptured microcapsules on the fracture plane demonstrated the physical triggering of the shell. Self-healing efficacy was examined regarding crack sealing and the recovery of properties. The results are discussed with regard to the potential use of microencapsulated sodium silicate to promote self-healing of in-ground barrier materials.

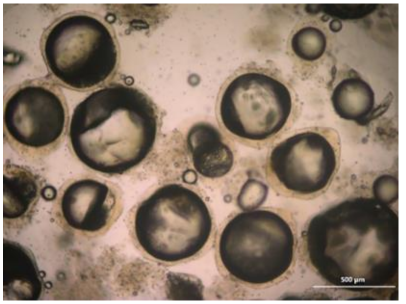
2 MATERIALS AND SAMPLE PREPARATION

2.1 In-ground barrier materials

The in-ground barrier materials include cement and kaolin clay. The cement was CEM I 52.5 N supplied by Hanson UK. Polywhite E China Clay was used, which is a medium particle size kaolin produced from deposits in the southwest of England.

2.2 Microcapsules

To investigate the performance of sodium silicate as a healing agent, two different polymeric microcapsules manufactured by the commercial partners were used. The LAM microcapsules were manufactured by Lambson Ltd. using complex coacervation, as described by Kanellopoulos et al. (2017). The gelatin-gum Arabic shell is observed in Figure 2a, encapsulating the core comprised of an emulsion of SS in mineral oil. The average diameter of the microcapsules is 282µm and the size distribution is shown in Figure 3a. The second type of microcapsule (THI) was manufactured by *Thies Technology Inc* using interfacial polymerisation, resulting in a polyurea shell, as shown in Figure 2b. The buckling of the capsule due to the loss of liquid core and the residual debris resulting from the microencapsulation process were also observed. The size distribution and average diameter of 210µm of the THI microcapsules are shown in Figure 3b.



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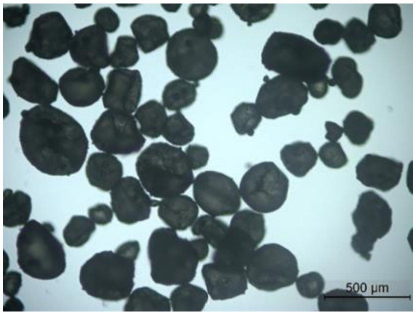
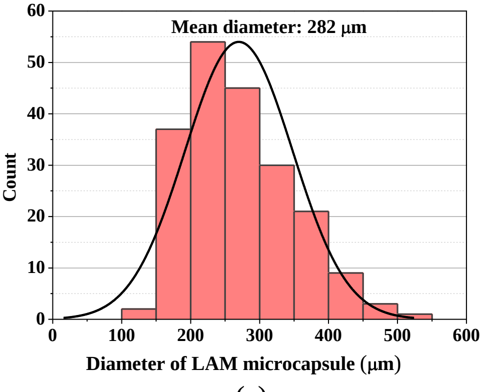


(b)

Figure 2 Optical microscope images of (a) LAM and (b) THI microcapsules



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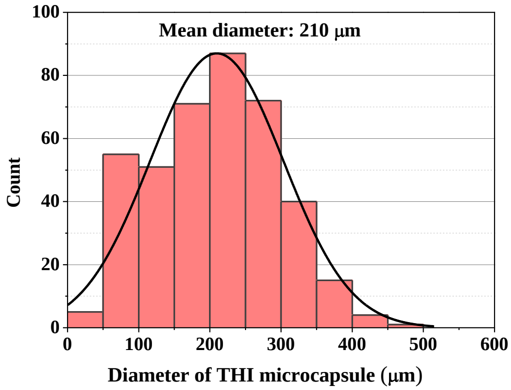


(b)

Figure 3 Size distribution of (a) LAM and (b) THI microcapsules

2.3 In-ground barrier material sample preparation

LAM and THI microcapsules were added in kaolin-cement (KC) mixes for the investigation of self-healing performance of different capsules. As the Lambson microcapsules were stored in a preservative solution to avoid aggregation, they were washed and filtered shortly before mixing. The THI microcapsules are in powder form and thus added directly to the cement. Control samples without microcapsules were also cast and denominated KC-CTRL. Mixes containing microcapsules are identified by the type of microcapsules used followed by the proportion of added microcapsules with respect to the grout weight; e.g. KC-LAM-4% refers to a kaolin-cement mix containing 4% LAM microcapsules with respect to the grout weight.

The grout used in this study was a cement grout with a water/cement ratio of 1:1. The in-ground barrier materials were prepared by mixing the grout with kaolin clay, and a soil:grout ratio of 1:1 was selected for this study. The kaolin clay with a moisture content of 50% was used to produce a medium stiff clay.

The grouts and kaolin were first prepared separately and then mixed together for ten minutes. The mix was then placed into plastic moulds 50mm in diameter and 100mm in height. Once the samples developed a sufficient amount of strength, which was usually after one week of curing, the specimens were removed from the moulds. On the 28th day the relevant tests were conducted and then the samples were returned in curing tanks for the 28-day self-healing process.

2.4 Experimental methods

2.4.1 Unconfined compressive strength

The vertical load was applied axially at a constant rate of strain of 1.14 mm/min until failure from which the strength was then calculated. Also, a linear variable differential transformer (LVDT) was used to measure the vertical displacement of the specimen in order to calculate the axial strain.

2.4.2 Crack width observation

Cracks generated in disc specimens (50mm in diameter and 10mm in height) using UCS tests were observed over time using a stereoscope. Digital images were captured at different positions on the surface. The cracks were photographed on the day of the cracking and at the end of the healing period at the exact same locations.

2.4.3 SEM analysis

The scanning electron microscope (SEM) instrument used was a Phenom ProX. Small chipped pieces were extracted from the crack faces of the specimens. Samples were coated with platinum and examined under a 10kV accelerating voltage.

2.4.4 TGA analysis

Thermogravimetric analysis (TGA) was performed to characterise the thermal properties of the microcapsules. To investigate the microcapsules, ~5 mg of material was used. The TGA was performed under air atmosphere, between 50 and 300°C at a rate of 10°/min, using PerkinElmer STA6000 and an alumina crucible.

3 RESULTS AND DISCUSSION

3.1 Microcapsule survivability

To examine the impact of contaminants on the stability of the microcapsules, the LAM and THI microcapsules were immersed in different chemicals that mimicked the contaminated soil environment, as shown in Figure 4. As well as the mechanical force experienced during the soil mixing process, the microcapsules must also remain stable when exposed to different aggressive chemicals in contaminated land. To mimic the contamination of the acidic environment and the presence of organic pollutants, the microcapsules were placed in toluene and 1% sulphuric acid. After 21 days, LAM and THI microcapsules showed excellent survivability and retained their shell integrity (Figure 4). TGA of these microcapsules showed that chemicals have little effect on LAM microcapsules, and that sulphuric acid can alter the TGA curve of THI microcapsules after 150 ºC (Figure 5). This is because the residual debris (mainly sodium silicate) resulting from the microencapsulation process of THI can react with sulphuric acid, generating orthosilicic acid, which can precipitate on the shell of the microcapsules and decompose into silicon dioxide at 150 ºC. This hints the stability of the microcapsules in an aggressive environment. Likewise, long-term survivability of LAM and THI microcapsules in high pH (>13) was confirmed by Giannaros (2017).

LAM and THI microcapsules also survived well the aggressive soil mixing process. Following mixing, a sample of fresh kaolin-cement mix was extracted and observed under the microscope. Distinct microcapsules could be clearly observed on the surface (Figure 6). The above results suggest that both microcapsules will remain stable during the mixing process and when exposed to aggressive contaminants.

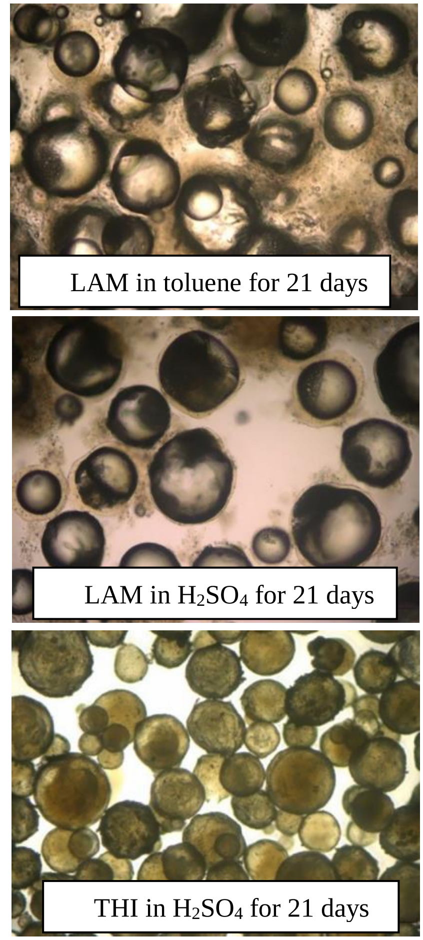
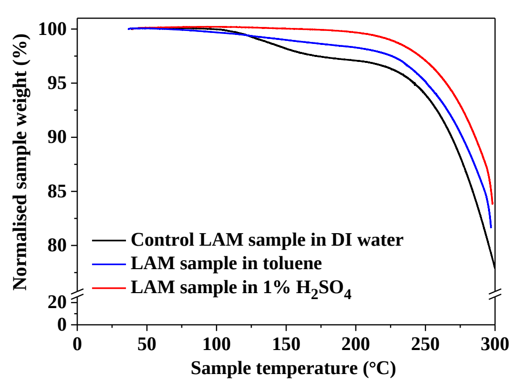


Figure 4 Optical microscope images of micro-capsules in different chemical environments



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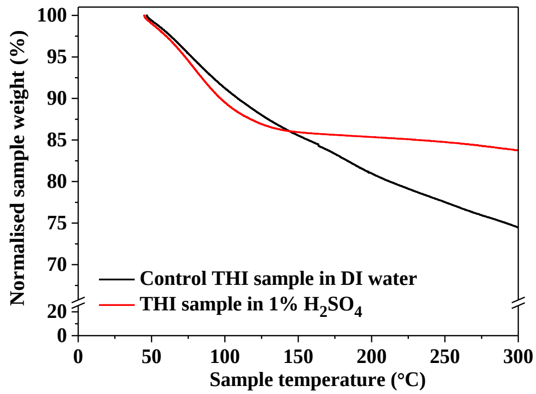


(b)

Figure 5 TGA results of (a) LAM and (b)THI micro-capsules in different chemical environments

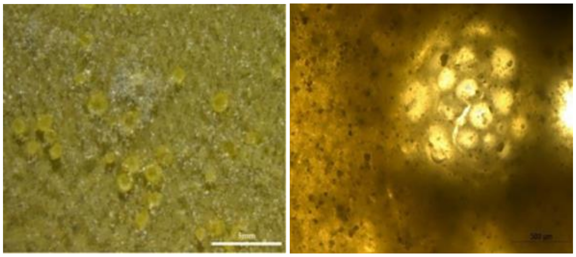
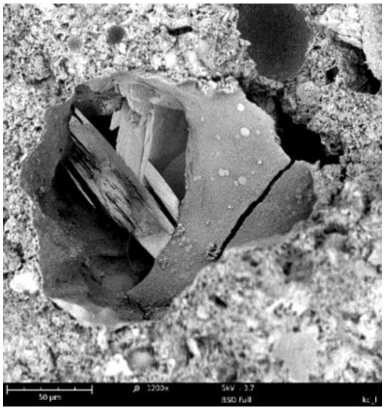


Figure 6 Optical microscope images of LAM (left) and THI (right) microcapsules in fresh soil mix wall materials

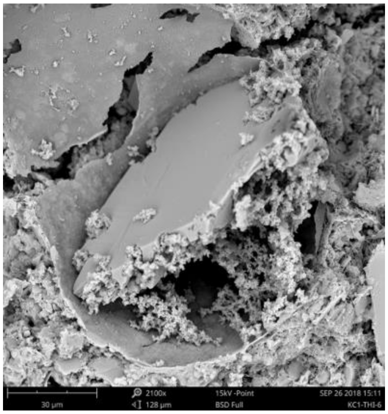
3.2 Physical triggering of microcapsules

Once the intact microcapsules were added to the matrix, the rupture of the shell upon cracking was assessed. The capsule bond with the matrix, its fracture toughness and elastic moduli may affect the likelihood of rupture. Figure 7 shows the SEM of the fractured surface of the kaolin-cement samples.

Consistent with the optical microscope observations, microcapsules were well dispersed throughout the surface with mainly ruptured microcapsules observed. Debris of ruptured shell material adhered to the cementitious matrix was observed, indicating good bond strength between the microcapsules and the cementitious matrix. Once the shell was ruptured, the encapsulated sodium silicate was released upon the crack surface and reacted with the surrounding hydration products. This was confirmed by the presence of dense hydration products around the microcapsule (Figure 7), including calcium silicate hydrates.



(a)



(b)

Figure 7 SEM images of ruptured (a) LAM and (b) THI microcapsules embedded in a kaolin-cement matrix

3.3 Crack sealing

Crack closure quantification was used for the evaluation and assessment of self-healing in the kaolin-cement samples. After pre-cracking and waiting 28 days for healing, stereoscope images of the surface crack mouth opening of disc specimens were taken, as shown in Figure 8. For

LAM-containing specimens, complete sealing of crack occurred only when the crack width is less than 120µm. For cracks wider than 120µm, the average crack mouth healing reached up to 70%. In contrast, all the surface cracks were completely healed after 28 days in the THI-containing specimen. For the THI sample, the largest healable crack was up to 210 µm. In the presence of water, the released healing agent (sodium silicate) reacts with the matrix producing secondary hydration products. The healing products that formed at the crack mouth mainly consist of CSH gel and calcite (Kanellopoulos et al., 2016). Calcite can also be observed as a healing product because the calcium cations at the crack mouth are exposed to carbon dioxide in the air.

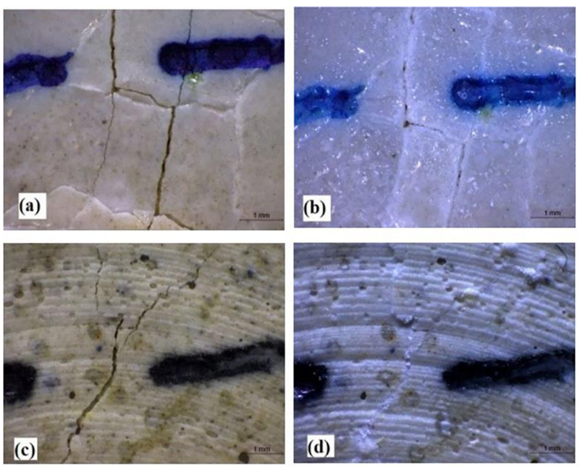


Figure 8 Typical stereoscope images of crack mouth taken on the day of cracking (left) and after 28 days of self-healing (right) for (a,b) LAM-containing sample and (c,d) THI-containing sample

3.4 Effect on mechanical properties and strength recovery

As the microcapsules are generally weaker than the surrounding matrix, they create weak preferential crack paths that lead to reduced strength (Giannaros, 2017). UCS recovery in Figure 9 is the ratio of the secondary strength of damaged samples to the initial strength. Results show that the addition 4% of LAM and THI microcapsules decreased the UCS by 23% and 11%, respectively. The greater detrimental effect of LAM microcapsules on UCS might be attributed to the larger size and presence of a liquid core.

UCS recovery results are also presented of the control and LAM- and THI-containing samples. The capsule-containing specimens improve the UCS recovery significantly after 28-day self-healing periods. The addition of microcapsules improves the strength recovery to 106% with 4% LAM microcapsule added, and a more significant improvement was shown that the sample with 4% THI regained over 120% of its original strength after 28-day of autonomic self-healing.

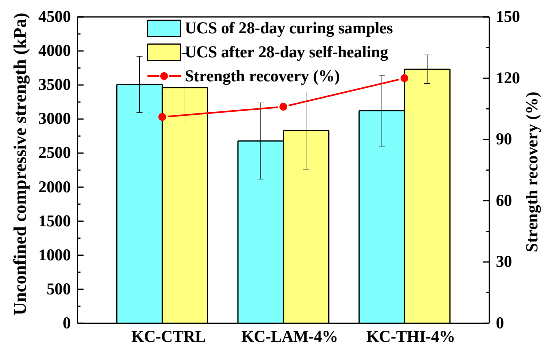


Figure 9 Unconfined compressive strength recovery after 28 days of self-healing

4 CONCLUSIONS

Microcapsules containing sodium silicate were investigated to be used for self-healing of geo-environmental applications. Two sets of microcapsules were investigated: (i) LAM with gelatin-gum arabica shell and SS emulsified in mineral oil as a core and (ii) THI with polyurea shell and solid SS as a core material. Both sets of microcapsules remain stable when exposed to aggressive chemicals mimicking contamination and survived the soil mixing process. Once crack triggered the rupture of the shell and release of the SS, crack sealing of the samples took place due to the reaction between sodium silicate and the matrix. Recovery of strength has been observed in microcapsule-containing soil mix specimens.

The capability of the microcapsules to retain the core prior to triggering and the effectiveness of sodium silicate as the healing agent make the approach feasible for autonomic self-healing of in-ground barrier materials. This can positively impact the design and implementation of in-ground barriers to achieve more serviceability and resilience.

5 ACKNOWLEDGEMENTS

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