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# A Review of Self-healing Concrete for Damage Management of Structures

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| **Corresponding Author:** | Henk Jonkers<br>Technische Universiteit Delft<br>Delft, NETHERLANDS |
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| Please submit a plain text version of your cover letter here.<br>**If you are submitting a revision of your manuscript, please do not overwrite your original cover letter. There is an opportunity for you to provide your responses to the reviewers later; please do not add them here.** | Dear editor,<br>herewith we would like to submit our review paper titled 'A Review on Self-healing Concrete for Damage Management of Structures' for publication in the upcoming special issue on self-healing materials.<br>Kind regards,<br>Henk Jonkers<br>Delft University of Technology<br>Sevinweg 1<br>NL-2628 CN Delft<br>E-mail: h.m.jonkers@tudelft.nl |
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| **Corresponding Author Secondary Information:** | |
| **Corresponding Author's Institution:** | Technische Universiteit Delft |
| **Corresponding Author's Secondary Institution:** | |
| **First Author:** | Nele De Belie |
| **First Author Secondary Information:** | |
| **Order of Authors:** | Nele De Belie |
| | Elke Gruyaert Gruyaert |
| | Henk Jonkers |
| **Order of Authors Secondary Information:** | |
| **Abstract:** | The increasing concern for safety and sustainability of structures is calling for the development of smart self-healing materials and preventive repair methods. The appearance of small cracks (< 300 μm in width) in concrete is almost unavoidable, not necessarily causing a risk of collapse for the structure, but surely impairing its functionality and accelerating its degradation, and diminishing its service life and sustainability. This review provides a state-of-the-art of recent developments of self-healing concrete, covering autogenous or intrinsic healing of traditional concrete followed by stimulated autogenous healing via use of mineral additions, crystalline admixtures or (superabsorbent) polymers, and subsequently autonomous self-healing mechanisms, i.e. via application of micro-, macro- or vascular encapsulated polymers, minerals or bacteria. The (stimulated) autogenous mechanisms are generally limited to |

healing crack widths of about 100-150 µm. In contrast, most autonomous self-healing mechanisms can heal cracks of 300 µm, even sometimes up to more than 1 mm, and usually act faster. After explaining the basic concept for each self-healing technique, the most recent advances are collected, explaining the progress and current limitations, to provide insights towards the future developments. This review addresses the research needs required to remove hindrances which limit market penetration of self-healing concrete technologies.

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# A Review of Self-healing Concrete for Damage Management of Structures

*Nele De Belie*, Elke Gruyaert*, Abir Al-Tabbaa, Paola Antonaci, Cornelia Baera, Diana Bajare, Aveline Darquennes, Robert Davies, Liberato Ferrara, Tony Jefferson, Chrysoula Litina, Bojan Miljevic, Anna Otlewska, Jonjaua Ranogajec, Marta Roig-Flores, Kevin Paine, Pawel Lukowski, Pedro Serna, Jean-Marc Tulliani, Snezana Vucetic, Jianyun Wang, Henk M. Jonkers**

This review paper is the result of joint collaboration of scientists working in the field of development of self-healing concrete within the framework of the European Cooperation in Science and Technology (COST) Action 'Self-healing as preventive repair of concrete structures' SARCOS CA15202. The main objective of this Action is to favour international interest in developing a shared understanding on healing-based preventive repair technologies for concrete structures.

Prof. N. De Belie, Dr. J. Wang
Ghent University, Magnel Laboratory for Concrete Research, Technologiepark-Zwijnaarde 904, Gent, 9052, Belgium
E-mail: nele.debelie@ugent.be
Prof. E. Gruyaert
KU Leuven, Department of Civil Engineering, Technology Cluster Construction, Structural Mechanics and Building Materials, Gebroeders De Smetstraat 1, Gent, 9000, Belgium
E-mail: elke.gruyaert@kuleuven.be
Prof. A. Al-Tabbaa, Dr. C. Litina
University of Cambridge, Department of Engineering, Trumpington Street, Cambridge, CB2 1PZ, United Kingdom
Prof. J.-M. Tulliani, Dr. P. Antonaci
Politecnico di Torino, Corso Duca degli Abruzzi 24, Torino, 10129, Italy
Dr. C. Baera
Research Institute for Construction Development, Calea Floresti 117, Cluj-Napaoca, 400524, Romania
Dr. D. Bajare
Riga Technical University, Kalku Street 1, Azenes 16/20, Riga, 1658, Latvia
Prof. A. Darquennes
Institut National des Sciences appliquées de Rennes, Avenue des buttes de Coesmes 20, Rennes 35 708, France
Prof. T. Jefferson, Dr. R. Davies
Cardiff University, Queen's Buildings, The Parade, Cardiff, CF24 3 AA, United Kingdom
Prof. L. Ferrara
Politecnico di Milano, piazza Leonardo da Vinci 32, Milano, 20133, Italy
Prof. J. Ranogajec, Dr. B. Miljevic, Dr. S. Vucetic
University of Novi Sad, Bul. Cara Lazara 1, Novi Sad, 21000, Serbia
Prof. A. Otlewska
Lodz University of Technology, Lodz University of Technology, Institute of Fermentation Technology and Microbiology, Wolczanska 171/173, 90-924 Lodz, Polan
Dr. M. Roig-Flores

Instituto Eduardo Torroja de Ciencia de la Construccion, Consejo Superior de Investigaciones Científicas, Serrano Galvache 4, Madrid, 28033, Spain
Dr. K. Paine
University of Bath, Claverton Down, Bath, BA2 7AY, United Kingdom
Prof. P. Lukowski
Warsaw University of Technology, al. Armii Ludowej 16, Warsaw, 00-637, Poland
Prof. P. Serna
Universitat Politecnica de Valencia, Edificio 4G, Camino de Vera S/N, Valencia, 46021, Spain
Prof. H. M. Jonkers
Delft University of Technology, Stevinweg 1, Delft, 2628 CD, The Netherlands
E-mail: h.m.jonkers@tudelft.nl

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The increasing concern for safety and sustainability of structures is calling for the development of smart self-healing materials and preventive repair methods. The appearance of small cracks (< 300 µm in width) in concrete is almost unavoidable, not necessarily causing a risk of collapse for the structure, but surely impairing its functionality and accelerating its degradation, and diminishing its service life and sustainability. This review provides a state-of-the-art of recent developments of self-healing concrete, covering autogenous or intrinsic healing of traditional concrete followed by stimulated autogenous healing via use of mineral additions, crystalline admixtures or (superabsorbent) polymers, and subsequently autonomous self-healing mechanisms, i.e. via application of micro-, macro- or vascular encapsulated polymers, minerals or bacteria. The (stimulated) autogenous mechanisms are generally limited to healing crack widths of about 100-150 µm. In contrast, most autonomous self-healing mechanisms can heal cracks of 300 µm, even sometimes up to more than 1 mm, and usually act faster. After explaining the basic concept for each self-healing technique, the most recent advances are collected, explaining the progress and current limitations, to provide insights towards the future developments. This review addresses the research needs required to remove hindrances which limit market penetration of self-healing concrete technologies.

## 1. Autogenous and non-encapsulated autonomous self-healing

Aging and degradation of concrete are connected to its porous structure and are fostered by the unavoidable proneness of concrete to cracking. The tremendous developments of concrete technology which have enabled the design of concrete with extremely low porosity, have not altered likewise the inherent cracking hazard, with high performance concretes being even more brittle and sensitive to early age cracking than normal strength ones. This has resulted into the development of crack-treating methodologies, which can be categorized into passive treatments which are applied manually after inspection and only heal the surface cracks, and active methods which are incorporated at the construction stage, may fill both interior and exterior cracks and are regarded as self-healing techniques.

Autogenous crack healing capacity in cement based materials relies upon the “conventional” constituents of the cementitious matrix, and can also be stimulated through tailored additions.[1, 2]

### 1.1. Autogenous healing

Autogenous healing of cementitious materials is the basic phenomenon determining partial or total self-closure of cracks and implicitly, partial recovery of initial durability and physical - mechanical performances of the composites. Considered one of the main reasons for substantial life extending of ancient structures and buildings, [3] the autogenous self-healing phenomenon in cement based composites received the attention of the academic media, namely the French Academy of Science for the first time in 1836, [4] when autogenous healing of cracks was noticed in pipes, water retaining structures, etc. [5] Significant research activity developed along the last century, including both theoretical approaches and experimental procedures, established that autogenous self-healing phenomena are mainly related to the complex interferences of physical, mechanical and chemical mechanisms within the cementitious matrix. [6-9] **Figure 1** gives a schematic overview of the mechanisms that may contribute to autogenous healing when a crack is formed and exposed to water. The two most important mechanisms are the chemical processes: 1) Continuing hydration of unhydrated cement grains, and 2) precipitation of calcium carbonate crystals ($CaCO_3$) on the crack faces, as direct result of the chemical reactions between the calcium ions $Ca^{2+}$ (present in the concrete matrix) and the carbonate ions $CO_3^{2-}$ available in the water or carbon dioxide $CO_2$ available in the air entering the crack.

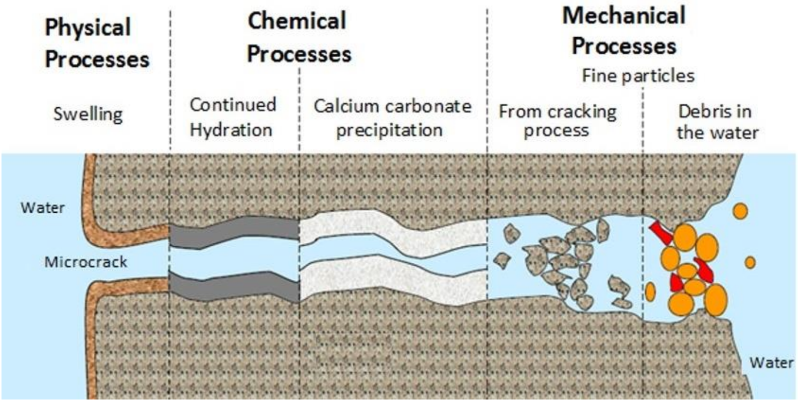

**Figure 1**. Main mechanisms producing autogenous self-healing of cementitious materials. Reproduced with permission.[6] 2013, Springer.

Autogenous healing produced by continuing hydration is valuable for regaining the mechanical properties of the composite, [8, 10] since these new hydration products have a strength similar to that of the primary calcium silicate hydrate gels (CSH) and clearly superior to that of calcium carbonate precipitation products. However, the nucleation and growth processes of hydration products formed at the crack faces are different from these in bulk cement paste. More water is available for the reaction (higher water/binder ratio) when external water has access to the crack and the free space is much larger in a crack than in a hydrating cement paste. Investigations regarding the self-healing produced solely by continuing hydration require avoidance of interactions with other processes, such as carbonation and are therefore few. Huang et al. however recently characterized and quantified the self-healing products formed in the cracks of young OPC cement paste (w/c = 0.3) due to continuing hydration reactions in sealed containers to avoid carbonation. [10] Interestingly, they found that the percentage of $Ca(OH)_2$ (CH) in the healing products is much higher (78% in the example given) than the percentage of CSH (17% in the example given), based on thermogravimetric analyses (**Figure 2**). This is in strong contrast with the distribution of hydration products in bulk cement paste.

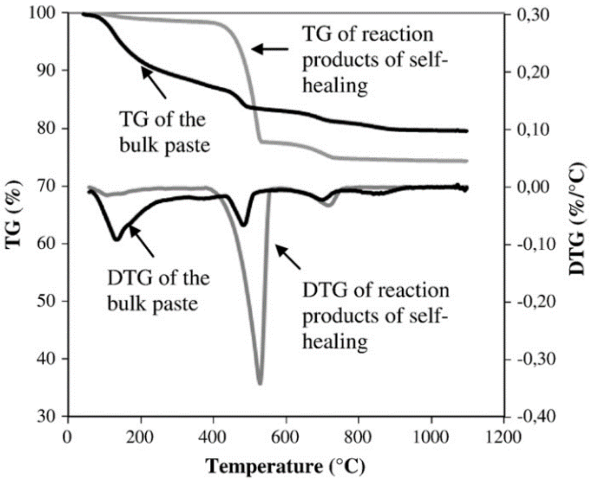

**Figure 2.** TG and DTG profiles for the hydration products formed in bulk cement paste and the hydration products formed due to continuing hydration at a crack wall.
Reproduced with permission.[10] 2013, Elsevier.

At the other hand, carbonation was proven to be the most efficient in terms of crack sealing and self-healing performance. [5-7, 9] Edvardsen provided a detailed analysis of the process: calcium carbonate precipitation is possible as long as calcium ions ($Ca^{2+}$) are available in the vicinity of the crack. [11] Even when water of neutral or slightly acidic pH enters the crack, its pH will locally rise due to contact with the highly alkaline concrete matrix which will release NaOH, KOH and $Ca(OH)_2$ into solution. Hence, the conditions will be appropriate for precipitation of calcium carbonate. Initially, when cracking is induced, calcium ions are available directly from the crack faces and the crystal growth is increased, during the so called ‘surface-controlled crystal growth’. After an initial layer of calcite is formed on the crack walls and the concrete matrix nearby is less rich as source of calcium ions, the transition to the so called ‘diffusion-controlled crystal growth’ happens, which implies that the $Ca^{2+}$ ions have to travel by means of diffusion through the concrete and the $CaCO_3$ layer in order to reach the interface with the crack surface and ensure the precipitation of the healing products. The second phase is evidently much slower than the initial one. In case of composite cements containing pozzolanic additions, a part of the calcium hydroxide, identified as major source for $Ca^{2+}$ ions is used in the specific pozzolanic reaction for CSH development. This will lead to a slower and weaker capacity of calcium carbonate precipitation. [6, 12]

The other mechanisms mentioned in Figure 1 are of minor importance and include the swelling of hydrated cement paste along the crack walls, due to water absorption by calcium silicate hydrates (CSH); and mechanical crack blocking by means of debris and fine concrete particles, direct results of the cracking process or due to impurities in the water entering the crack.

A significant number of experiments was conducted in order to investigate and evaluate the autogenous healing efficiency and also the factors and parameters influencing this intrinsic material property. [5-9,13,14] They offer reviews concerning the experimental approaches and obtained results of crack sealing and recovery of mechanical and durability related properties. It can be summarized that autogenous healing mechanisms are efficient only for small cracks, but a wide range of upper sizes for healable cracks are given: 10 to 100 µm, sometimes up to 200 µm but less than 300 µm, only in the presence of water. They are difficult to control and predict due to the scattered results generally achieved and they depend on several factors and parameters. The major influence factors are: (1) age and composition of the concrete itself; (2) presence of water; (3) width and shape of the concrete crack.

*(1)* The intrinsic healing potential of concrete is mainly governed by its *composition*: (i) cement type is considered to be less important, [11, 15] but the clinker content determines the $Ca^{2+}$ ions supply and subsequently the ability of the matrix to develop calcium carbonate precipitation products; (ii) silicate additions in concrete produce an effect as a function of their type and quantity in the mix, related to development of their characteristic pozzolanic reactions and consumption of the calcium hydroxide, affecting also the duration of healing mechanisms; (iii) aggregate type may determine the cracking pattern and as consequence indirectly affect the healing process; (iv) concrete class: the high strength concretes, characterised by low W/C ratio and increased binding constituents, contain important resources of unhydrated cement grains that can easily develop significant quantities of new CSH products as result of ongoing hydration; [8] (v) concrete age proves to be essential with respect to the healing mechanism: early age concrete contains more unhydrated binder particles and develops new CSH gels, continued later on by a combination of the two processes (further hydration and calcium carbonate precipitation), leading at later ages to mainly $CaCO_3$ deposits for crack closing [8]. Generally it is proven that early age concrete healing is the most prolific. [4, 11, 16-20] In recent research based on SEM/EDX observations and modelling, gradual strength regains of cracked concrete immersed in water were attributed to the development of portlandite and CSH, while the preceding stiffness regains were ascribed to the quick formation of ettringite and CA(S)H phases as well as small quantities of portlandite and CSH which could locally bridge the crack. [21]

*(2) Water*, proven to be the essential factor for autogenous healing, is necessary for the chemical reactions and as transport medium for the fine particles, and can influence the efficiency of the process also through its temperature, pressure and pressure gradient. In

general, water immersion has been reported as the best exposure for self-healing, while autogenous healing is very limited in air exposure. Few authors found better healing in cycling wet/dry conditions compared to complete water immersion conditions. Those authors assume that this is due to easier $CaCO_3$ formation because of abundant availability of $CO_2$ in the air during the dry cycle. Water alkalinity (increased pH) favours the process of $CaCO_3$ formation. Other factors like water hardness proved to be neutral. [11, 13, 22, 23]

*(3) Cracks* can geometrically determine the degree of their autogenous healing, namely through crack width (essential), length and depth, and cracking pattern (branched crack, accumulated crack). The narrower the cracks, the more efficient the autogenous healing. As consequence, by limiting and controlling the crack width, the autogenous, intrinsic healing potential of cement-based composites can be substantially improved. Fibre addition to the cementitious matrix resulted into the development of Fibre Reinforced Concrete (FRC) and High Performance Fibre Reinforced Cementitious Composites (HPFRCCs). [1, 12, 13, 24-28] Natural vegetable fibres, also employed in the formulation of advanced fibre reinforced cementitious composites, can provide a twofold action. While, on the one hand, contributing to an effective control of the crack propagation phenomena, they can also act as reservoirs and vehicles of water throughout the cementitious matrix, absorbing water during the wet stages of wet/and dry cycles and releasing it during the dry periods, thus activating the continuing hydration and carbonation reactions responsible of crack healing (**Figure 3**, **Figure 4**). [29, 30] They have been also shown effective in triggering, after healing, the formation of new cracks instead of the reopening of new ones.

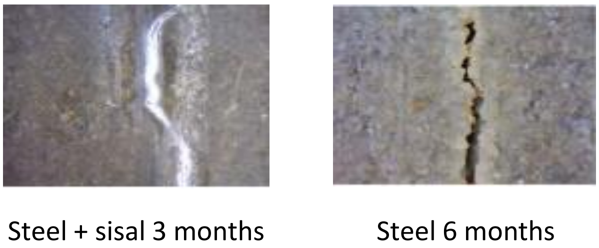

**Figure 3.** Comparison between crack healing in HPFRCC with steel+sisal fibers and steel only fibres subjected to wet and dry cycles. Specimens were pre-cracked at 2 months (0.5 mm crack opening). The bottom images show crack healing after 3 months curing in daily wet/dry cycles for the samples with steel and sisal fibres, and after 6 months curing for steel fibres only.
Reproduced with permission. [29] 2015, ACI.

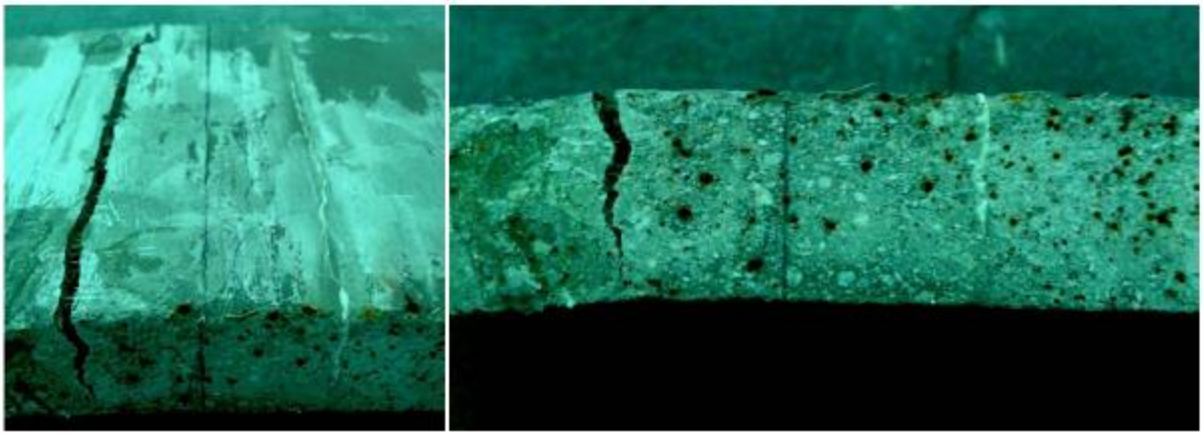

**Figure 4.** Healed crack and new crack formed in post-healing tests in sisal + steel HPFRCC. Specimens were pre-cracked at 2 months age up to 0.5 mm crack width and tested again after 3 months water immersion (from Ferrara et al., 2015, ACI SP 305. In the comments)
Reproduced with permission. [29] 2015, ACI.

Apart from crack geometry, the age of first cracking is another important factor related to autogenous healing efficiency, see also factor (1) above. [21, 17, 31, 32]

### 1.2. Stimulated autogenous healing (non-encapsulated)

From the previous section, it is obvious that autogenous healing is more effective when crack widths are restricted. The presence of water is another important factor. The stimulation of ongoing hydration or crystallization, also promotes autogenous healing. Therefore, methods to limit crack width, provide water, or enhance hydration or crystallisation, will be defined as stimulated or improved autogenous healing.

### *1.2.1. Use of mineral additions*

Nowadays, cementitious materials containing mineral additions are common while the number of possible mineral addition types increases with the worldwide development of local products. The use of mineral additions affects the hydration kinetics, the material properties as well as the autogenous self-healing potential. The majority of studies focusing on this subject are related to High Performance Fibre Reinforced Cementitious Composites (HPFRCCs) or Engineered Cementitious Composites (ECCs). Indeed, significant amount of supplementary cementitious materials are generally used to reduce the cement content in the mix design of cementitious composites. [33] This limits the material costs and the environmental burden since their production needs less energy and produces less carbon dioxide emission than that of cement. [34]

It has been pointed out by De Belie that modern concrete-makers could learn from the ancient Romans' knowledge to give concrete 'self-healing' properties, since fly ash is similar to the volcanic ash that Romans used in their mix. [35] The majority of studies on the mineral addition effects on self-healing (kinetics, final efficiency) mainly concern blast-furnace slag and fly ash (of which the reactive part is usually amorphous and therefore different from the crystalline admixtures discussed later on). As important amounts of these additions remain unhydrated even at later age, autogenous healing due to ongoing hydration is promoted. The pozzolanic reaction, specific to siliceous or siliceous and aluminous additions (fly ash, silica fume, blast furnace slag, calcined clay, etc.,) included in composite cements can reinforce the continuous hydration of cement grains regarding the long term CSH development and consequently a certain level of autogenous self-healing. According to several authors, [10, 36, 37] autogenous healing is improved when cement is partly replaced by blast-furnace slag (BFS) and fly ash (FA) (**Figure 5**). A minimum calcium hydroxide content is necessary for further reaction of blast-furnace slag and fly ash during the healing process. [38] Although specimens with fly ash have more unreacted binder materials and therefore expectedly a higher capacity for self-healing, more evident self-healing products have been observed in mixtures incorporating blast-furnace slag. [34] This can be explained considering that slag has a mixed cementitious and pozzolanic activity and can undergo delayed hydration reactions also in the presence of low calcium hydroxide (as because of cement replacement), unlike pozzolans. For these two types of mineral additions, anyway, the main autogenous healing mechanism under permanent immersion is ongoing hydration and the reaction products formed in cracks are composed of CSH, ettringite, hydrogarnet and hydrotalcite, [10, 39] while carbonation is the main mechanism during wet-dry cycles. Only a few studies are related to more local products such as metakaolin [40] and palm oil fuel ash [41].

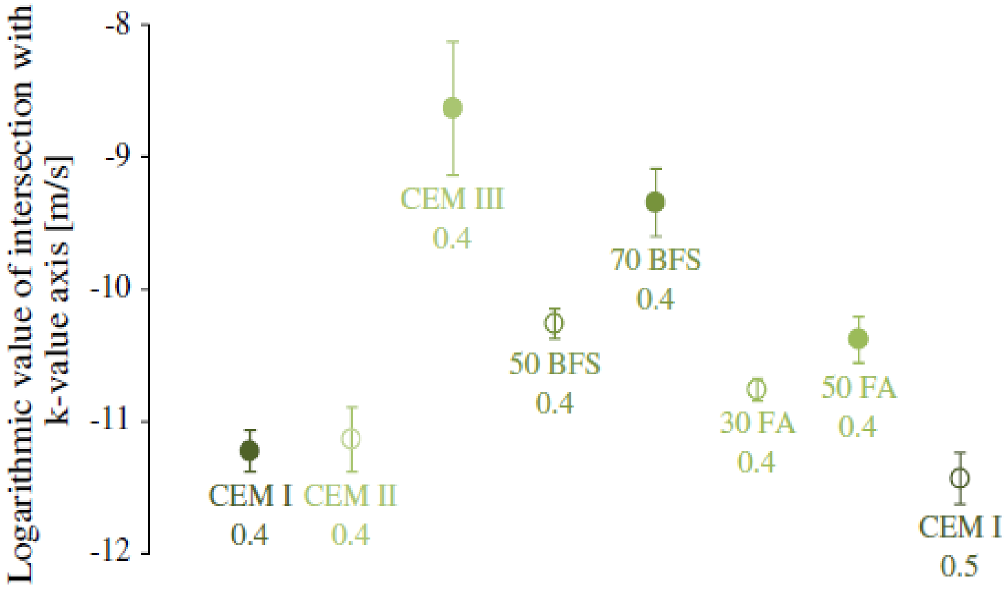

**Figure 5.** Reduction in water permeability for cracked mortars with different cement types, varying replacement percentages (30, 50 or 70%) of Portland cement by BFS or FA, and w/c

ratio of 0.4 or 0.5. Cracks up to 200 μm were created at 55 days of age and healed under water.
Reproduced with permission. [36] 2012, Elsevier.

The hydration kinetics of cementitious materials with mineral additions can be low during the first weeks. Therefore, over the last years, methods have been proposed to stimulate and accelerate the self-healing process: application of alkaline solutions, higher curing temperature, and blending of different mineral additions. For mixtures with a high content of fly ash, the self-healing process can take several months, [42] and different methods can be used to accelerate the chemical reactions like the increase of the under-water curing temperature, [43] and of the calcium content using calcareous fly ash, [44] limestone powder, [45] or hydrated lime [46]**.** For mixtures with fly ash/blast-furnace slag, several ionic solutions are used to activate the hydration reactions [33, 10, 47] or to simulate real environmental conditions like in seawater [48]. Based on the principle of alkali-activated cementitious materials, alkaline activators (NaOH, KOH, $Ca(OH)_2$, $Na_2CO_3$, sodium silicate) have been used alone or combined to accelerate the dissolution of unhydrated particles and to form a new aluminosilicate network. Some results show that materials with blast-furnace slag have probably a higher potential to be reactivated by alkalis than materials with fly ash. [47]

For the case of the materials with blast-furnace slag, Gruyaert et al. concluded that, out of the different tested options, a solution of $Ca(OH)_2$+$Na_2CO_3$ seems to be the most suitable activator to stimulate crack closure. [47] However, strength regain is limited with this process and it is not certain whether cracks with a width higher than 125 μm can be healed. [47] Several authors studied also healing by alkaline activation with NaOH. Results are similar to those of autogenous healing [47] or inferior under wet/dry conditioning regime [33].

Due to the presence of magnesium and sulphate ions in the sea-water, brucite may precipitate in specimens submerged in sea-water causing additional sealing of the cracks. In contact with artificially replicated sea-water, mixtures with Portland cement heal faster than mixtures with blast-furnace slag cement, [48] but still crack widths up to 100 µm can be healed. This difference in behavior is probably related to the lower calcium hydroxide content in the blast-furnace slag material and the lower concentration of ions available in the crack. [48]

### *1.2.2. Use of crystalline admixtures*

The term ‘crystalline admixtures’ is a label not necessarily reflecting functionality or molecular structure as the term stems from commercially available products whose constituents are generally not disclosed. One practical way to distinguish commercial crystalline admixtures from supplementary cementitious materials (SCMs) is in typical admixture dosage, which is typically 1% by cement weight for crystalline admixtures and >5% for SCMs. As reported by Ferrara et al., [49-50] crystalline admixtures (CA) have received special attention as chemical admixtures to promote self-healing due to their availability and use in the construction industry. Crystalline admixtures are classified as a special type of permeability reducing admixtures (PRA). [51-52] ACI-212 differentiates between PRAs that reduce permeability under non-hydrostatic conditions (PRAN) and those that are also capable to function under hydrostatic pressures (PRAH). CA are included in the latter, while typical water-repellent or hydrophobic products fall in the former category.

A wide range of materials is included in the group of permeability reducing admixtures, and that could also occur with the generic name of ‘crystalline admixtures’. Moreover, most commercial products contain proprietary constituents and their formulations are kept confidential. The fact that some publications report the presence of different oxide compounds in CA, such as sulfur trioxide [53] or sodium oxide [54], corroborates this point and may indicate different behaviors under the global name of ‘crystalline admixtures’.

That said, in general, CA are products formed by ‘active chemicals’, usually mixed with cement and sand, with highly hydrophilic behavior. They react in the presence of water, forming water insoluble pore/crack blocking precipitates that increase the density of CSH and resistance to water penetration. [51] It has been shown that CA improve the mechanical properties of concrete when using contents of 3, 5 and 7% of the cement content, subjected to moisture, though the aforementioned percentages may be quite high for an addition. Silva et al. report a successful case study of an anti-flotation slab of reinforced concrete where CA were used to ensure water-tightness. [55] CA are efficient in more than blocking pores as they also possess the capability of withstanding hydrostatic conditions and the ability of sealing hairline cracks when activated by moisture. [51] A recent LCA study has shown that the use of crystalline admixtures, in proportions limited to a few % of the cement weight (1%) are definitely competitive with respect to conventional waterproofing technologies in e.g. slab foundation structures. [56]

As a product of their reaction, CA form modified CSH, depending on the crystalline promoter, and a precipitate formed from calcium and water molecules. According to the cited ACI report, the matrix component that reacts is the tricalcium silicate (see Equation 1), but other studies indicate that CA react with portlandite instead. [50, 53]

$$3CaO–SiO_2 + M_xR_x + H_2O \rightarrow Ca_xSi_xO_xR–(H_2O)_x + M_xCaR_x–(H_2O)_x \qquad (1)$$

*Tricalcium silicate + crystalline promoter + water → modified CSH + pore-blocking precipitate*

Several researchers have published recent work analyzing the self-healing capability of CA admixtures.

Sisomphon et al. analyzed the recovery of mechanical properties of strain-hardening cementitious composites containing CA (1.5% by weight of cementitious materials), and reported hardly any benefit produced by the admixtures when compared with control specimens. [53] However, their results showed good efficiency when added in combination with a calcium sulphoaluminate expansive agent. Ferrara et al. also studied the effect of CA on strength recovery in normal strength concrete specimens, containing CA at a dosage of 1% by the weight of cement, achieving an improvement of 14% in the self-healing properties of concrete by the addition of CA. [49] In both cases, specimens were healed under water.

Later, Ferrara et al. published that the improvement can be significantly better in HPFRC, also through possible synergy between the crack-restraining action provided by the fibers and the inside growth of the healing products, which may have resulted into some kind of physical fiber prestressing. [50] De Nardi et al. had similar responses when using CA in lime mortars, in terms of the recovery of compressive strength. [57]

Improved performance under exposure to artificially replicated sea-water (both submersion and wet-dry cycles) was also reported by Borg et al. [58] as well as by Cuenca et al. [59] who also hypothesized a contribution of crystalline admixtures to chloride binding.

Recently, Cuenca et al. have investigated the self-healing capacity of concrete with and without crystalline admixtures under repeated cracking and healing cycles up to one year. [60] An innovative testing methodology, named Double Edge Wedge Splitting Test was used to pre-crack the specimens. [61] Immersion in water resulted in a persistence of the aforementioned action, with a moderately increasing trend depending on the duration of the first cycle, crystalline admixtures guaranteeing a 20% higher and always less scattered performance (**Figure 6**).

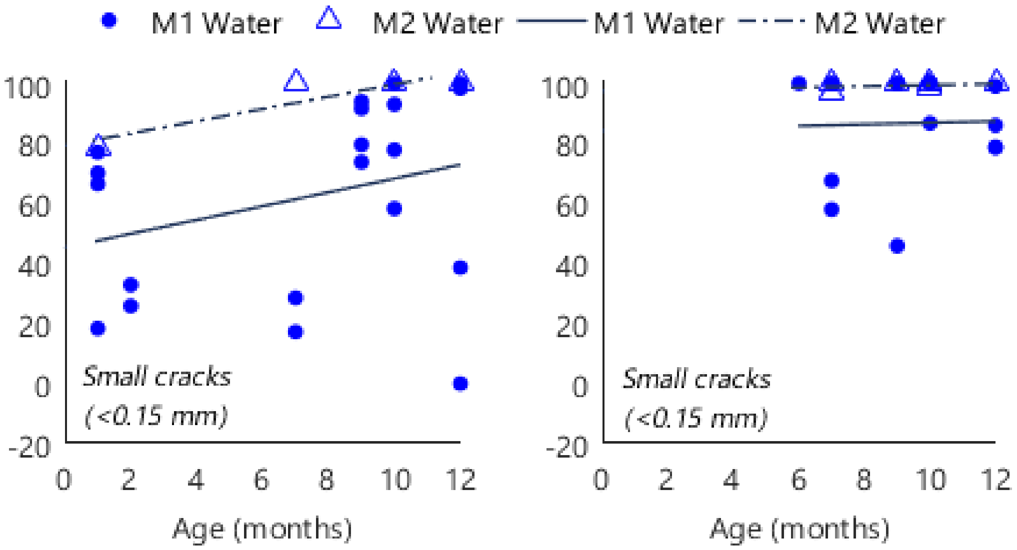

**Figure 6**. Crack sealing index along the one-year investigation time-frame as a function of exposure condition and crack width. M1-reference concrete, M2-concrete with crystalline admixture. Left: specimens undergoing 1 month first healing cycle; Right: specimens undergoing 6 months first healing cycle.
Reproduced with permission. [59] 2018, DSCS.

Roig-Flores et al. analyzed the healing effectiveness of CA in terms of water permeability at high pressure (2 bars) and visually inspected crack closure, in early age (2-3 days) cracked concrete samples. [62-63] CA was added in substitution of the fine material (limestone) to isolate the effect of the admixture from the filler effect. Their results showed that CA were not able to heal cracks when stored in 95-100% of relative humidity. However, when the specimens are healed under water, CA yield a more stable behavior than pure autogenous healing. However, the results were not drastically different from the control group, and there was no improvement of visual closing.

The interest of the industry in promoting the use of crystalline admixtures as stimulators of the autogenous healing capacity of concrete may represent an interesting market penetration driver and opportunity for self-healing concrete technologies. It has anyway to be remarked that the wide variety of product compositions and recommended dosages is in this respect a hindrance. Deeper investigation is needed mainly in view of finding the consensus on the one hand of what should be named crystalline admixture, based on the composition and on the action, and, on the other hand, on the test methods for the measurement and comparative evaluation of the healing capacity.

### *1.2.3. Use of superabsorbent polymers*

Superabsorbent polymers are natural or synthetic three-dimensionally cross-linked homopolymers or copolymers with a high capacity to absorb fluids. The swelling capacity depends on the nature of the monomers and the cross-linking density, [64] and can be as high as 1000 g/g [65]. The maximum swelling follows from the balance between the osmotic pressure, associated with the presence of electrically charged groups, and the elastic retractive forces of the polymer matrix. [66] Moreover, since osmotic pressure is proportional to the concentration of ions present in the aqueous solution, the absorption behavior is strongly conditioned by the ionic strength of the swollen medium. [26, 66, 67]

Besides the manifold application domains (e.g. sanitary and biomedical sector, agricultural sector) in which SAPs are already adopted, more and more research focuses nowadays on the use of SAPs in mortar/concrete. SAPs were introduced as internal curing agent in cementitious systems with a low water-to-binder ratio to reduce self-desiccation shrinkage during hardening. Water release and kinetics are very important in that respect and were fundamentally studied by Snoeck et al. using NMR, which showed the evolution in time of the free and entrained water by the SAPs clearly in the $T_2$ relaxation spectra. [68] The obtained results were linked to the Powers and Brownyard model and a good fit was obtained (**Figure 7**). Moreover, the importance of a gradual release of the entrained water (as obtained by one of the two investigated SAPs) to mitigate autogenous shrinkage was demonstrated.

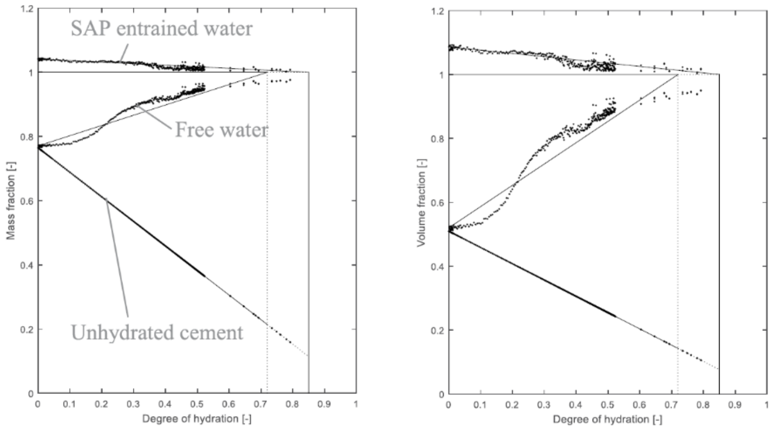

**Figure 7.** Mass (left) and volume (right) fraction of free and entrained water in function of the degree of hydration in a cement paste with an effective w/c ratio of 0.3 and an entrained w/c ratio of 0.054 obtained by addition of 0.22 m% SAP (vs. binder weight). The found signal intensity results were plotted on the theoretical lines described in the model of Powers and Brownyard.
Reproduced with permission. [68] 2017, Springer Nature.

Besides mitigation of autogenous shrinkage, SAPs can be added to cementitious materials to increase the freeze-thaw resistance, [69] and induce self-sealing and self-healing effects [70]. With regard to the latter aspect, the incorporation of SAPs is multifunctional.

First of all, SAPs, which take up mixing water during concrete mixing and shrink upon subsequent hardening of the matrix, leave behind macro-pores. [71] These macro-pores act as weak points in the matrix, attracting, [72] and stimulating multiple cracking [26, 70]. Both effects facilitate crack closure as SAP macropores will be crossed by the cracks and more narrow cracks are formed. [12] However, these macro-pores can be responsible for strength loss, although not necessarily as SAPs can also act as internal curing agent, [73] and stimulate further hydration, [74,75] as explained above. It all depends on the used type of SAP, particle size and shape, amount of SAPs, the w/c ratio of the mix, the addition of water to counteract the loss in workability and the mixing procedure amongst others. [76] In Snoeck et al., it has been shown that the uptake of mixing water by SAPs results in a lower apparent w/c-factor, and thus a lower porosity and lower permeability of the matrix when no extra water is added to compensate for the water absorption by the SAPs. [77] Attention should thus be paid when comparing water penetration in specimens with and without SAPs as the microstructure of these samples is different. Moreover, it has to be mentioned that the swelling of SAPs in cementitious materials, as determined mainly by the tea-bag method (proved to be more practical in terms of time-dependent study) or the filtration method (less variation in absorption after 24 hours, but not detecting polymer-inherent desorption), is always lower than in plain water. [78] This is due to the interaction of SAP-ionic groups with the large variety of ionic species that can be found in the cement matrix (as $K^+$, $Na^+$, $SO_4^{2-}$ and $OH^-$) and which are dependent on the type of cement, age of the specimen, use of alternative binders and additives. Recently, Lee et al. conducted a detailed research on the effect of the alkalinity and calcium concentration of pore solution on the swelling and ionic exchange of SAPs in concrete and showed that swelling is not a simple function of ionic strength. [79] $Ca^{2+}$ complexation depresses swelling, while alkalinity increases swelling because it inhibits ion exchange and therefore $Ca^{2+}$ complexation. In addition to osmotic pressure, these are significant factors controlling the swelling of SAP in cement paste. The higher the degree of ionic exchange, the lower the swelling ratio of the SAP.

Despite the considerations given above, for mixes with high w/c ratio and high SAP content (up to 1 mass % relative to the cement content in mortar, as needed to obtain self-healing properties), macro-pore formation may affect the mechanical properties. [76] In Pelto et al. [80] and Gruyaert et al. [81], it has been shown how the disadvantage of swelling at the moment of mixing can be overcome and how the sealing efficiency can be increased respectively by (i) coating of the SAPs by the Wurster process and (ii) development of synthetic superabsorbent polymers with improved swelling and pH sensitiveness. The coating should prevent swelling of the SAPs in fresh concrete and hence minimize the macropore formation. The best barrier properties were obtained with a multilayer coating of polyvinylbutyral as a primer, cycloolefin copolymer as a barrier layer, and sol–gel derived zirconium–silicon oxide as an adhesion promoting topcoat. [80] Although full absorption of the coated SAPs in cement filtrate solution was delayed by 20 min only, strength reduction of the mortar could be partly compensated. The benefit of pH sensitive SAPs was confirmed by Mignon et al. and the principle is explained in **Figure 8**. [82, 83] While the swelling of the SAP at the pH of 13 encountered in fresh concrete should be kept low, as it determines the size of the macropores and hence the strength reduction, the swelling at the more neutral pH of water inside the crack should be high, since it will determine the crack sealing efficiency.

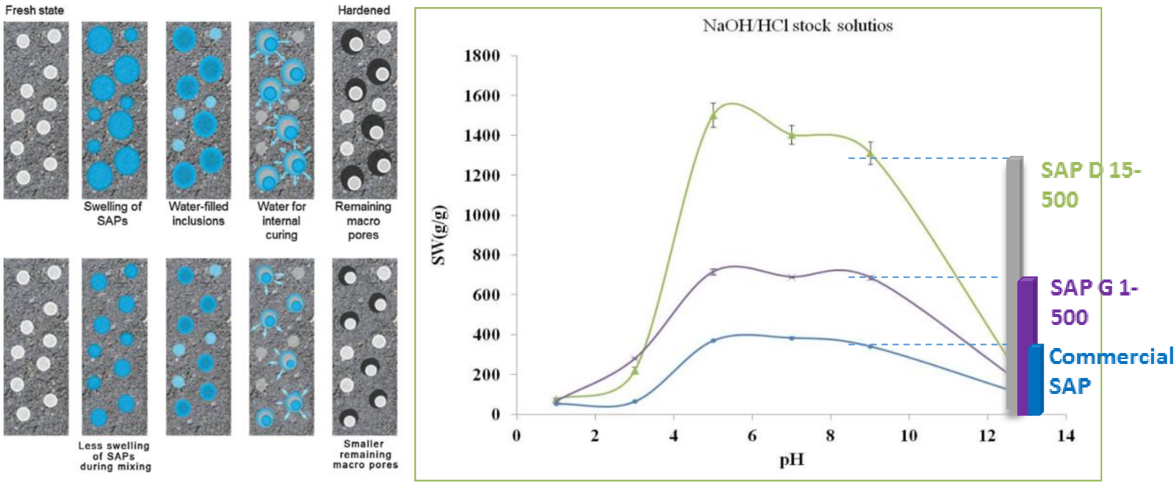

**Figure 8.** Macro-pore formation in mortar by using commercial SAPs (top left) and SAPs with improved pH sensitiveness (bottom left); swelling properties of commercial and in house developed SAPs in NaOH/HCl solutions of varying pH
Left figure reproduced with permission. [83] 2017, Elsevier.

Secondly, upon crack formation and ingress of liquid substances, self-sealing of cracks occurs immediately due to the swelling and blocking effect induced by the SAPs. [72, 77, 84] Snoeck et al. visualized by neutron radiography how SAPs in a cracked mortar specimen can maintain a water head imposed on top. [77] In the work by e.g. Gruyaert et al., [81] water permeability tests, as developed by Tziviloglou et al., [85] on mortar specimens containing SAPs have shown immediate sealing efficiencies of up to 96% (for a mix with 1 mass % SAP relative to the cement content) for crack widths around 0.150 mm. However, the value depends strongly on the SAP content and the type of SAP used. Recently, Hong and Choi proposed a model to quantitatively assess the self-sealing of cracks in cementitious materials in function of crack size and SAP dosage by predicting the reduction ratio of flow rate. [86] While this immediate recovery in water-tightness is temporarily, autogenous healing of the cracks can be stimulated in a longer timeframe due to the release of absorbed water from the SAPs to the matrix during drier periods. The water absorbed by the SAPs can come from intruded water, but can also be extracted from the moisture in the environment.[26, 87] This leads to the formation of new calcium silicate hydrates (when unhydrated cement grains are present) and to the crystallization of calcium carbonate. [8, 12, 26, 88] The healing efficiency by using SAPs depends on the crack width. In [26], it has been shown for mixtures with synthetic microfibres that cracks up to 0.030 mm are able to heal completely at the crack mouth in specimens with and without SAPs, while cracks up to 0.150 mm heal only partly in reference mixtures exposed to wet-dry cycles for 28 days. Interestingly, samples containing SAPs can close cracks completely up to about 0.140 mm. In environments with a relative humidity of more than 90% or 60%, only the samples with SAPs showed visual closure of the cracks, indicating that SAP particles can attract moisture from the environment. [26] Cracks larger than 0.200 mm showed only partial healing. [26] The added fibres help to keep the crack width within an easily healable range (30-50 µm). Also, natural fibres such as flax and hemp can be used to increase the environmental sustainability. [25, 89] The (promoted) autogenous healing was also visualized using X-ray computed microtomography. [90] It was found that the extent of autogenous healing in a cementitious material depends on the crack depth. Only near the crack mouth (0 till 800 µm depth) the crack is closed by calcium carbonate formation in case of wet/dry cycles. In combination with superabsorbent polymers, the extent of healing was more substantial.

The SAPs can be added as particles but can also be synthesized in situ, i.e. after crack appearance. [91] A precursor is hereby injected with initiator and cross-linker. Infrared radiation is used to make the precursor copolymerize. However, this sealing mechanism can only be applied afterwards and hence cannot be considered as real self-healing.

SAPs can have a long-term stability depending on their polymeric backbone. Some polymers show degradation as a function of time and will lose their swelling behavior. [92] However, most (commercial) SAPs have a shelf life of more than 5 years and are able to maintain their properties and swelling capacity. [8] Therefore, the promoted healing capacity remains and is a function of the building blocks still present in the cement matrix. An overall better healing capacity is found in specimens with an age of 1 year and older with SAPs compared to SAP-free reference samples. [8, 93]

Recent work has shown the applicability of the use of SAPs for self-healing concrete. Full-scale concrete elements were tested under lab conditions. [94] The beams containing coated SAPs showed an improved healing of the cracks with a width up to 0.2 mm in comparison to reference beams (without healing agent). Furthermore, no rebar corrosion could be detected by the cast-in multi-reference electrodes for the beams containing the coated SAPs within the measuring period consisting of 4 exposure cycles to NaCl solution (24h exposure per week), while the reference beams showed a clear onset of the corrosion already after the first exposure cycle to NaCl solution. [94] Ongoing research studies the behavior of self-healing beams (containing pH-sensitive superabsorbent polymers or bacterial healing agents) under field conditions. [95] Taking into account the growing trend to use sustainable and cost-efficient admixtures in concrete, natural (proteins like collagen and polysaccharides) and semi-synthetic SAPs (natural backbone grafted with synthetic monomers) will gain importance over the synthetic SAPs (mainly made of petroleum based monomers and synthetic cross linkers). Although these hydrogels are biocompatible and biodegradable, they may feature disadvantages such as low mechanical strength and batch variation. Recently, Mignon et al. modified alginates amongst others for use as self-healing agent in concrete. [96-97] These SAPs show a good stability in high pH cement filtrate solutions, are renewable, have a negligible effect on the compressive strength even upon addition of 1 mass % relative to the cement content and result in a strong sealing capacity comparable to that obtained by commercial SAPs.

### *1.2.4. Use of non-SAP polymer additions*

Polymer-modified concrete (PMC) or polymer Portland cement concrete (PPCC), is according to ACI 548.3R, defined as Portland cement and aggregate combined at the time of mixing with organic polymers that are dispersed or redispersed in water. As the cement hydrates, coalescence of the polymer occurs, resulting in a co-matrix of hydrated cement and polymer film throughout the concrete. [98] According to JCI and RILEM definition, polymer-modified concrete can be included in the category of engineered self-healing materials.

In polymer-cement concretes (PCC) the polymer and mineral binder create an interpenetrating network; the co-operation of these two binders yields the improvement of flexural and tensile strength, adhesion to various substrates and tightness, [99] and may also result into a certain self-healing ability. According to Abd-Emoaty, [98] the process in PCC occurs in the same way as in cement concrete but to a larger extent and over a longer period. The reason of that is the delay of cement hydration caused by “coating” of cement grains by the polymers.

Taking into consideration the required characteristics, like rheological properties, sealing ability and mechanical performance, [7, 38] various polymers were considered as possible self-healing agents in PCC. The self-healing efficiency depends on the polymer type, polymer dosage, type of cement, water-cement ratio, etc. [100] For example, Yuan et al. proposed using ethylene vinyl acetate, EVA, copolymer, which fills and heals the crack after heating up to 150°C. [101]

Some researchers found in 2015 that epoxy resin as a healing agent functioned well. [102-104] The cross-linking of an epoxy resin in the environment of Portland cement paste can proceed without the presence of any hardener – to an extent dependent on accessibility to calcium hydroxide, which is a catalyst for the process (**Figure 9**). [102-103] The added excess of unhardened resin remains initially in the pores of the hardened cement paste. As cracking occurs, the resin is gradually released and fills the microcracks. There the resin enters into contact with the calcium hydroxide, leading to cross-linking and hardening. The microcracks are filled and tightened (**Figure 10**).

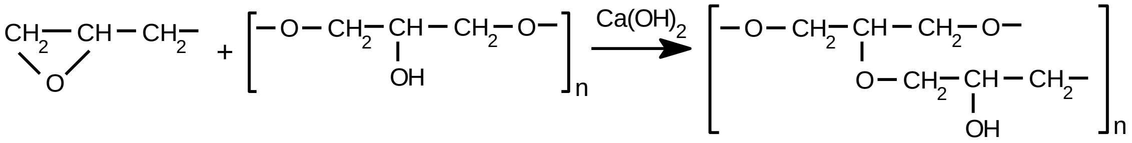

**Figure 9.** Cross-linking of epoxy resin in the presence of calcium hydroxide.

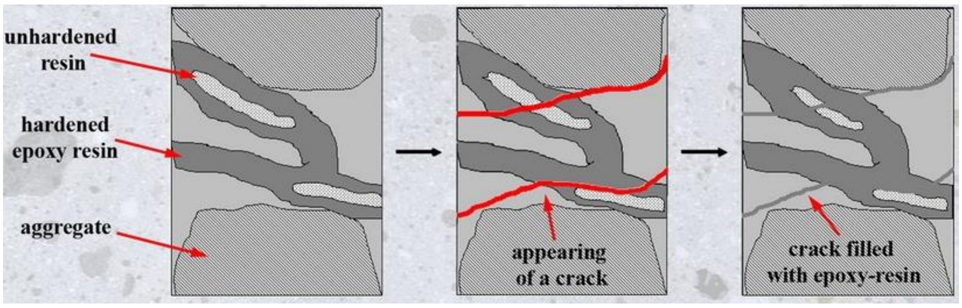

**Figure 10**. Self-repair by modification of concrete using epoxy resin without hardener: initially, part of the resin remains unhardened (left); after microcrack appearance the resin of low viscosity is gradually released due to the action of capillary forces and fills the microcracks (middle); the resin hardens in contact with $Ca(OH)_2$ and tightens the microcrack (right). Reproduced with permission. [104] 2013, De Gruyter.

The results of recent investigations by Łukowski and Adamczewski [104] and Sam et al. [102] have confirmed that the cement composite can obtain some self-repairing ability by modification with epoxy resin without hardener. The self-repair degree (degree of regaining of the initial strength after damaging of the composite microstructure) of the epoxy-cement concrete depends mainly on the polymer/cement ratio, to a lesser degree on the total content of the binder. The maximum value of the self-repair degree reached about 40% in the case of the flexural strength and was observed for a polymer content equal to about 20% by mass of the cement (**Figure 11**).

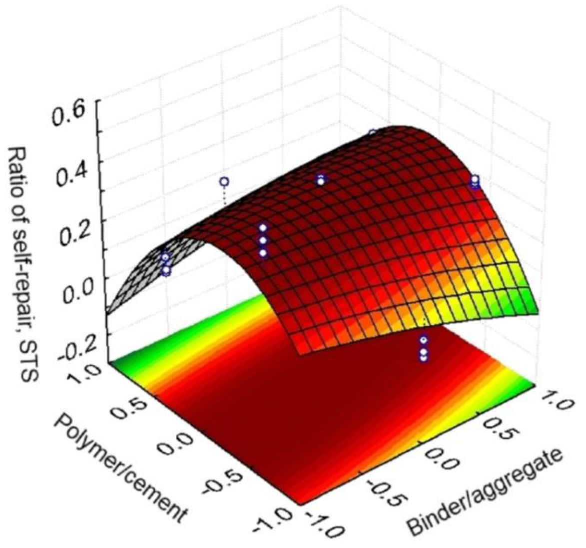

**Figure 11.** Self-repair degree, STS, as a function of polymer/cement (variability range 0.1 to 0.35, in coded values -1 to +1), and binder/aggregate ratio (variability range 0.33 to 0.6, in coded values -1 to +1), where polymer is an epoxy resin in water emulsion, applied without a hardener and binder means cement together with the epoxy resin.
Reproduced with permission. [104] 2013, De Gruyter.

Based on the compressive strength after 28 days, the same researchers noted however that the optimum polymer to cement ratio is lower - maximum 10%. [102-103] The optimum content of polymer in the composite is connected to two limitations. First, some minimum amount of resin is necessary for noticeable self-repairing. However, further resin addition (without a hardener) worsens some of the mechanical properties of the material and eventually the weakening of the microstructure prevails over the effect of the possible self-repair. These reduced mechanical properties can be explained by the presence of unhardened liquid resin in the composite as well as the presence of emulsifiers in the water emulsion of epoxy resin. The emulsifiers may hinder the effective use of water from the emulsion for cement hydration and disturb the catalytic hardening of the resin. Therefore, the mix design should be optimized for reduction of this effect. In view of the previously reviewed findings, it has to be stated that also with reference to the use of non-encapsulated resins as self-healing agents, further investigation is needed to clarify the technological issues and constraints related to their use in concrete as well as to the standard test methods for a comparative assessment of the healing efficiency of the different products available on the market.

Another way of employing polymeric materials for introducing self-healing in concrete structural elements, is the use of shape memory polymer (SMP) tendons to close cracks. [105-106] Shape memory polymer (SMP) materials are able to recover the original shape after damage or deformation upon application. [107] These tendons are cast into a cementitious structural element and electrically activated after cracking occurs. The restrained shrinkage potential of the drawn PET tendons causes a compressive stress to develop within the structural element and this tends to close any cracks that have formed within the cementitious material. The ability of the tendons to maintain a significant post-activation crack closure force is important to the viability of the self-healing system. This issue was investigated by Hazelwood et al. in a series of tests that explored the long-term relaxation of the restrained shrinkage stress within a series of SMP tendons. [108] This stress was monitored for a period of six months and the results showed that the relaxation was limited to 3% of the peak stress in the tendons. The authors concluded that this relatively small relaxation loss was a very positive finding apropos the viability of the self-healing system. The applicability of this approach is limited to macro-sized cracks and depends on the exposure of the concrete to heat.

Later, in an attempt to scale up the technology and develop higher performance tendons, a new type tendon formed from multiple drawn SMP filaments has been developed.[109] Comparisons with commercially-available PET strip suggest that these new tendons have a restrained shrinkage potential twice that of manufactured PET filament samples.

## 2. Encapsulated autonomous self-healing (polymers or minerals)

Autonomic self-healing relies on embedding unconventional engineered additions in the matrix to provide self-healing function as discussed previously. Encapsulation has been the preferred technique for the direct internal delivery of healing agents at the location of damage allowing in situ repair. There are two main approaches in encapsulation of healing agents, discrete and continuous. The main difference lies on the mechanism used to store the healing agent and thus dictates the extension of the damage that can be healed, the repeatability of healing and the recovery rate for each approach. However there are numerous factors to be considered in the design of an encapsulated-based self-healing system, from the development of a capsule system, to integration, mechanical characterisation, triggering and healing evaluation. In this context the following sections review the most recent developments for encapsulated autonomous self-healing pathways, reporting on the progress and future perspectives.

### 2.1. Micro-encapsulation (< 1 mm)

Microencapsulation (diameter $\leq$ 1mm) continues to be a popular technique for the production of autonomous self-healing components for cementitious systems inspired by the ground breaking work of White et al. In this mechanism microcapsules were directly embedded into the matrix and upon crack formation attract propagating cracks, rupturing and releasing the core in the crack volume. [110] The released agent would then react with a dispersed catalyst available in the matrix and heal the crack. The proof of concept for microcapsule based healing in concrete has been demonstrated a number of times. [111-113] In the recent past, a wide range of new and existing production methods, shell compositions and properties and cargo materials has been researched, as detailed in **Table 1.** These trends see approaches to tailor microencapsulation to the specific performance requirements inherent to cementitious matrices. For better control of cargo release recent advances on performance-related microcapsule shells have aimed to enhance durability. The use of double-walled shells combining polyurea-urea-formaldehyde has been demonstrated. [114] Similarly the investigation of more thermally stable materials like polyurea has led to the development of capsules (**Figure 12** (b)) for survivability in elevated temperature environments. [115] A different approach included the production of microcapsules with switchable mechanical properties, [116-118] to ensure survivability during the concrete mixing process. In this context recent collaboration between universities and companies led to the design and production of microcapsules that exhibit ductile ‘rubbery’ behavior when hydrated and then when dried transition to stiff, brittle glass-like behavior (**Figure 12** (a)). [118]

In an effort to quantify mechanical triggering various studies have suggested probabilistic models to determine the likelihood of a capsule or spherical particle being ruptured by a crack.[119-120] Yet although the microcapsules are likely to ‘attract’ propagating cracks, experimental observations have shown that matrix-microcapsule interaction/bonding can determine the fracture mechanism; namely whether it is crack deflection, interface debonding or microcapsule fracture. Thus improving the bond between the microcapsules and cementitious matrix at the interface is an important topic of research to improve the efficiency of the mechanical triggering mechanism. [121-125] Surface modification on phenol formaldehyde [122] and acrylates [124-125] have recently been proposed to alter the hydrophilicity of the shell and thus enhance chemical compatibility and bond strength between matrix and microcapsules. Alternatively inorganic shells, mainly silica-based which are inherently more compatible and can bond with the hydration products in the cementitious matrix, have continued to be researched. [123, 126-127] The release of the encapsulated material can also be triggered by chemical changes in the matrix inducing the disassembly of the capsule shell. A particular matter of concern for concrete is the decrease of alkalinity and depassivation of steel reinforcement caused by the ingress of chlorides and carbon dioxide ($CO_2$). Thus recent advances in the development of microcapsules for chemical triggering have focused on the investigation of pH sensitive shell materials and chloride binding shell and cargo materials to target corrosion induced damage (**Table 1**). [128-131] In particular, polystyrene and ethyl cellulose [130-132] have been proposed as shell materials to envelop corrosion inhibiting/passivation agents through a physical extrusion process. Conversely using a similar mechanical process Xiong et al. developed chloride ion triggered microcapsules functionalising sodium alginate with $Ag^+$ that can bind $Cl^-$ ions leading to collapse of the shell and release of the core material. [133]

Concurrently new and improved production techniques have been employed to tackle the limitations of traditional chemical and physico-chemical microencapsulation approaches. Microfluidics, as a relatively new microencapsulation technique, [134-135] has a lot to offer in this respect in enabling a diverse range of microcapsule shells. Microfluidics is used to produce double emulsions, drops of core material within drops of another fluid, which can be subsequently polymerised to yield fully closed solid-shell microcapsules. [136] The double emulsion methodology allows the production of highly monodisperse microcapsules and precise control over shell thickness. Since a wide range of materials can be used to produce the middle layer, the composition and properties of the shell can be tuned according to the application. [134-135, 137-138] Furthermore, the morphology of the shell can also be adjusted; particularly regarding the cementitious matrix, the hydrophilicity of the shell can be modified to enhance interfacial bonding. [125] A loading efficiency of virtually 100% has been reported and the encapsulation of both aqueous and organic cores. [139] The increased control over the production parameters is possible at production rates of ~1 g/h. However, scale-up platforms for the production of double emulsions have been investigated, including soft lithography, [140] and tandem emulsification, [141] capable of production rates of ~1.5 kg/day. A schematic and a laboratory set up of the production of microcapsules through microfluidics are shown in **Figure 12** (c-d), together with resulting monodispersed and surface functionalised acrylate microcapsules (**Figure 12** (e-f)).

Much of the recent research on cargos (**Table 1**) has continued to focus on the use of adhesive two-part systems requiring the concurrent embedment of a catalyst within the matrix to achieve activation and hardening. Wang et al. [142] suggested a catalyst to microcapsule ratio of 0.5 whilst others [137] have recommended a surplus of catalyst in the system (catalyst to microcapsule ratio of 1.3) to ensure activation of the encapsulated epoxy. These systems are still favourable as they allow faster reaction time and higher degree of mechanical restoration, however the long term stability of reacted organic healing agents in the highly alkaline cementitious matrix is questionable [143] as well as their long term functionality [144]. Nonetheless emerging research favours compatibility and bonding with the mineral substrate of the cementitious matrix, shifting towards cargos that can deliver healing products of such nature; these include encapsulated bacterial spores (see section 3) and mineral cargos such as colloidal silica and sodium silicate. [114, 117-118,145-147] The former can enhance the precipitation of carbonates, while the latter can convert calcium hydroxide to more favourable CSH gel. Yet while these both offer better affinity with the matrix, they generally have a longer healing period and a lower level of mechanical property regain (**Table 1**).

Self-healing performance has continued to be assessed through investigation of the recovery of a range of mechanical and durability properties where the extent of the observed recovery is closely related to capsule fraction, pre-damage level and type of microcapsules used. [148] Relevant results from the literature are summarised in **Table 1**. Mechanical properties included evaluation of various stiffness moduli, fracture energy and compressive and flexural strength while durability parameters included gas and water permeability, chloride diffusion, surface resistivity and capillary absorption. These measurements have been further complemented by monitoring crack mouth and depth healing with time. Nonetheless long-term stability and repeatability of the healing ability has yet not been addressed; although recent studies have been investigating healing on mature specimen (length of curing 2-3 months). [149] Optimum dosages have been considered mainly in terms of durability indicators, [117,150] but depend heavily on the size of microencapsulated agents as well as the proposed healing agent and can differ for different types of microencapsulation suites. The general trends of reported findings indicate that the mechanical recovery rate of damaged specimens is roughly proportional to the dosage of the microcapsules. In addition to self-healing efficiency, the compatibility of these microencapsulation suites with the cementitious matrix, evaluating their effect on fresh and hardened properties of cement paste, mortar and concrete specimens, is of great significance as the properties of cementitious composites containing microcapsules can be very unpredictable. [122] The general trend of reported findings does seem to indicate that the addition of microcapsules reduces mechanical performance in cement paste and mortar. In particular the fraction and size of microcapsules can be seen to have a pronounced effect not only on mechanical properties but also on pore structure and permeability (**Table 1**). However, most researchers seem to identify a critical content below which the effect is negligible or acceptable. [117, 127, 149, 142, 151- 153]

Yet a universal selection of healing agent, microencapsulation technique and content applicable under all conditions doesn’t yet exist. Nevertheless these ‘next generation’ microencapsulation suites can significantly facilitate the adoption of microcapsule-based self-healing cementitious systems in practice. First steps towards that target have already been made with the first large scale application of microcapsules in reinforced concrete panels. [109] A retaining wall panel was constructed with 8% by volume of cement microcapsules [118] and subjected to damage. Crack healing was then monitored over an extended period of 6 months with a range of in-situ and laboratory measurements. The field trials confirmed the feasibility of scaling of the capsules and promising full-scale healing performance over a long-term period. The potential of healing agents to achieve self-healing at a requested level delivered through a targeted and tailored microencapsulation system is reflected on the momentum of recent publications. However, a careful review of these developments also reveals the range of future work that can and need to be performed to minimise the variability in the design parameters, ensure the longevity of the embedded system, advance our understanding of the composite system and abate its application in practice.

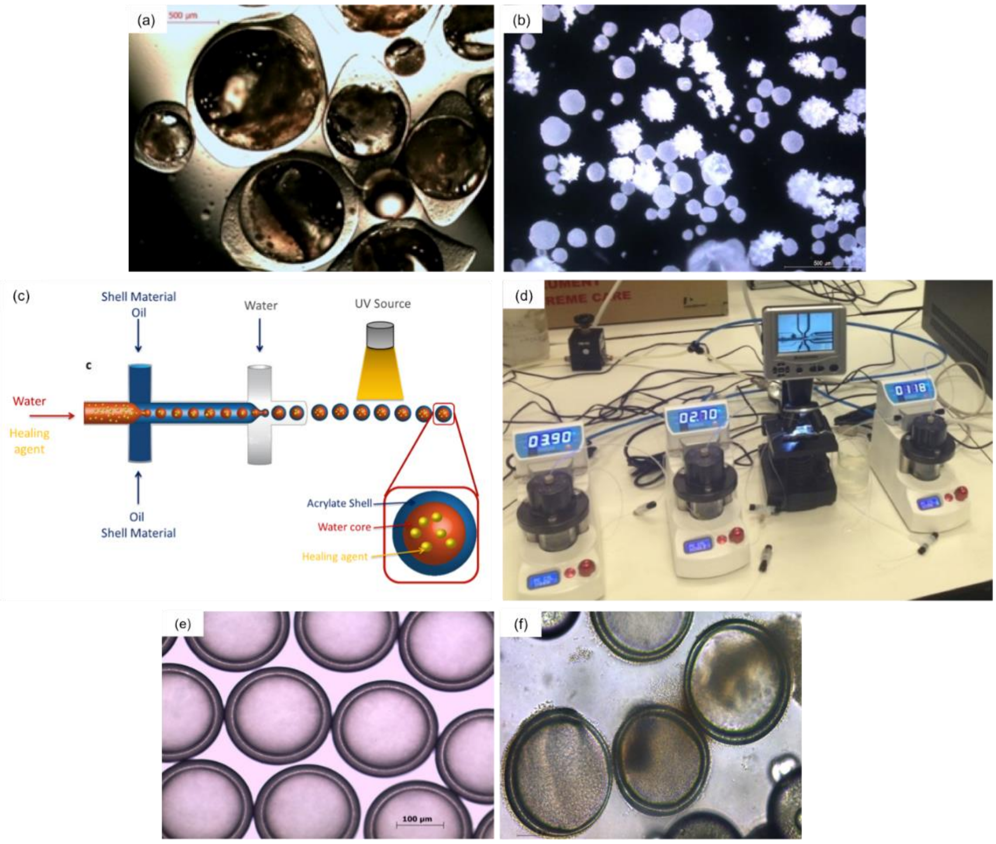

**Figure 12:** Recent research activities in microencapsulation for self-healing in cementitious systems: (a) gum arabic/gelatine shell micro-capsules containing sodium silicate core, [118] (b) polyurea shell microcapsules produced containing semi-crystalline sodium silicate, [145] (c) schematic of the microfluidics process including the photo-polymerisation process, [124] (d) a laboratory setup of double emulsion flow focusing microfluidics platform, [124] (e) optical micrograph of microfluidics produced monodisperse acrylate microcapsules and (f) corresponding surface functionalised acrylate microcapsules. [124]
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Reproduced with permission. [145] 2016, IOP publishing.
Reproduced with permission. [124] 2018, University of Cambridge.

**Table 1.** A summary of microcapsules used in self-healing cementitious materials. Only microcapsules that have been incorporated into a cementitious mix are reviewed. Compatibility with the cementitious matrix is reported as the effect of microcapsule addition on fresh and hardened properties. Self-healing performance is reported in reference to cracked values. '↑' denotes an increase and '↓' a decrease of reviewed properties. 'N/A' refers to data unavailable.

| **Production method** | **Shell** | **Cargo** | **$D_o$ (μm)** | **Addition by weight of cement (%)** | **Compatibility with cementitious matrix** | **Self-healing performance** | **References** |
|---|---|---|---|---|---|---|---|
| Physical triggering | | | | | | | |
| Emulsion polymerisation | UF | Epoxy | ~166 | 3,6,9 | Compressive strength<br>Flexural strength<br>(>3% ↓) | Compressive strength (↑)<br>Flexural strength (↑)<br>Chloride ion permeability (↓) | [121] |
| | | | 100-250 | 2,4,6,8 | Compressive strength (25% ↓)<br>Porosity (↑ with increase in microcapsule content and size) | Crack healing ratios (21-46%)<br>Mechanical recovery (13%↑)<br>$Cl^-$ diffusion (20%↓) | [131,151] |
| | | | ~122 | 3,6,9 | Compressive strength (↓) | N/A | [142] |
| | | | 132, 180, 230 | 0,2,4,6,8 | Compressive strength (5-25% ↓) | $Cl^-$ diffusion (12-20% ↓)<br>Permeability (↓) | [151] |
| | | | ~122 | 0,3,6,9 | Compressive strength (1-14.5% ↓)<br>Dynamic modulus (↓)<br>Pore structure parameters (↑) | Compressive strength (-100%↑)<br>Dynamic modulus (-91%↑)<br>Pore structure parameters (↓) | [142] |
| | | | 150, 205, 243 | 0,3,6 | $Cl^-$ diffusion (↑)<br>Water pressure penetration (↑)<br>Carbonation resistance (↓) with increase in microcapsule content > 3% and size | $Cl^-$ diffusion (30%↓)<br>Porosity (↓) | [125] |
| | | SS | 81-701 | 0.5,1,2.5,5 | E (15%↓) | Stiffness (11% ↑) | [146] |
| | | DCPD | 289-987 | 0.25 | | Stiffness (30% ↑) | |
| | | Calcium nitrate | <100 | 0.25,0.5,1,2 | Compressive strength (↓)<br>Surface resistivity<br>(for 0.25% wt ↓) | Modulus of elasticity (↑)<br>Surface resistivity (↑) | [154,150] |
| | | | ~70 | 0.5,0.75,1,1.25 | Compressive strength (10%↓)<br>Flexural strength (17%↓)<br>E (↓) | N/A | [153] |
| | | MMA | ~1.9 | N/A | N/A | N/A | [155-156] |
| | PU/UF | SS | ~322 | 2.5,5 | N/A | Crack depth (↓)<br>Ultrasonic wave transmission (↓) | [114] |
| | PUF | Epoxy | ~100 | 1,2,4 | N/A | Flexural strength (↑)<br>Damage index (acoustic emissions) (↓) | [157] |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | PUrea | SS | ~130 | 0.8 | Compressive strength (↓)<br>Flexural strength (20%↑)<br>Heat of hydration (28%↓ peak)<br>Setting time (↓)<br>Viscosity (47%↑) | Capillary absorption (45%↓) | [145]<br>THIES Technology Inc |
| | PU | MMA | ~0.3 | N/A | N/A | N/A | [155] |
| | | CS | 30-60 | 1,5 | Compressive strength (↓)<br>Flexural strength (↑)<br>Viscosity (16%↑)<br>Setting time (16%↓)<br>Gas permeability (↓) | Crack healing (43-100%↑)<br>Flexural strength (18%↑)<br>Gas permeability (30%↓) | [156] |
| | | | 60-120 | 1.5 (by concrete) | Compressive strength (-) | Compressive strength (↑)<br>Flexural strength (↑)<br>Capillary absorption (↓) | [147] |
| | PS | Epoxy | 100-150 | 0-2 | N/A | Fracture energy (↑)<br>Stiffness (-)<br>Water absorption (↓) | [158] |
| | PF | N/A | 50-600 | 4 | Compressive strength (32%↓) | Fracture energy (↑)<br>Permeability (↓) | [122] |
| | MF | Epoxy | 10-1000 | 1,2,4 | N/A | Flexural strength (↑) | [148] |
| | M | Bacterial spores | 1-5 | 1,2,3,4,5 | Compressive strength (15-34%↓)<br>Tensile strength (↓)<br>MIP (change in pore distribution)<br>Heat of hydration (-)<br>Setting time (↑)<br>Water absorption (48%↓) | Crack area healing (48-80%↑)<br>Permeability (↓) | [116] |
| Sol-gel | Silica | Epoxy | 5-180 | N/A | N/A | N/A | [126] |
| | | | | 5,10 | Compressive strength (6-30%↓)<br>Flexural strength (15-55%↓)<br>Porosity (-)<br>Sorptivity coefficient (↓) | Sorptivity coefficient (↓) | [127,159] |
| | | MMA | ~3.5 | N/A | N/A | N/A | [155-156] |
| Complex Coacervation | Gum Arabic/ Gelatine | SS emulsion in oil (1:1) | 290-700 | 0.8,1.6,2.3,3.1,4.6,5,6 | Compressive strength (17-27%↓ for >1.6% wt),<br>Flexural strength (↑)<br>Fracture toughness (23%↑)<br>E, Heat of hydration, Setting time (-)<br>Viscosity (11-200%↑) | Crack mouth healing (20-77%↑)<br>Crack depth (↓)<br>Capillary absorption (54%↓) | [117-118]<br>Lambson Ltd |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Extrusion | Alginate | Bacterial spores | ~1000 | N/A | N/A | N/A | [160] |
| Extrusion/ Photo-polymerisation | Modified alginate | Bacterial spores | 20-100 | 0.5,1 | Workability (↓)<br>Compressive strength (16.2%-23.4%↓)<br>Tensile strength (15.6%-30%↓) | N/A | [161] |
| Spray drying | PVA | CSA pellet | ~500 | 10 | Length change test (-) | Dynamic modulus of elasticity (90%↑)<br>Water passing test (↓) | [162] |
| Microfluidics/ Photo-polymerisation | Acrylate | Water | ~88 | 10 | N/A | N/A | [124] |
| | | CS, SS, Oil, CS, SS in oil | 80-120 | N/A | N/A | N/A | [124-125] |
| Chemical triggering | | | | | | | |
| Emulsion polymerisation | PS | SF | 400-1200 | N/A | N/A | pH responsive release | [128-129] |
| Extrusion | EC | CH | 300-700 | N/A | N/A | pH responsive release Passivation stabilisation (↑) | [130] |
| | | MFP | 100-700 | 0, 3,5 | N/A | pH responsive release<br>Corrosion rates (↓) | [128-129, 132] |
| | | | | 5 | N/A | | |
| | | $NaNO_2$ | 200-700 | 5 | N/A | | |
| | Alginate | $Ag^+$ | 2400-2500 | 10 | N/A | $Cl^-$ triggered binding<br>Corrosion inhibition | [133] |

CH: calcium hydroxide ($Ca(OH)_2$), CS: colloidal silica, CSA: calcium sulfoaluminate, DCPD: dicyclopentadiene, EC: ethylene cellulose, M: melamine, MF: melamine formaldehyde, MFP: monofluorophosphate, PF: phenol formaldehyde, PS: polystyrene, PU: poly-urethane, PUrea: poly-urea, PVA: polyvinyl alcohol, SF: sodium fluorophosphates ($Na_2PO_3F$), SS: sodium silicate ($NaSiO_3$), UF: urea formaldehyde

## 2.2. Macro-encapsulation

One of the earliest studies involving macro-encapsulation was carried out by Dry who proposed polypropylene and glass fibers with mono or multi-component methyl methacrylate core for concrete cracks repairing. [163-165] The choice of the fibers was motivated by the combination of mechanical reinforcement, together with crack sealing, and an economical encapsulation method. Furthermore, this solution was preferred, compared to embedded microcapsules, because it offered the advantage of being able to store a larger amount of repairing agent and to potentially achieve multiple healings. A final aim was to prevent adhesive degradation over time. The release of the healing agent was activated by crack formation, which results in breakage of the embedded brittle fibers. Li et al. used 50 μL hollow glass fibers (1.0 mm outer diameter, 0.8 mm inner diameter and 100 mm in length) filled with superglue (ethyl cyanoacrylate) and sealed at both ends with silicone. [144] Eight out of nine specimens showed recovery of stiffness capacity after repairing. Similar work was conducted by Mihashi et al., [166] with encapsulated alkali-silica solutions and by Joseph et al., [167] who experimented 3 mm external diameter and 100 mm length tubes filled with low viscosity ethyl cyanoacrylate. In both works hollow tubes were placed inside a cementitious matrix with one end linked to the supply of healing agent and the other end sealed with wax. Joseph et al. observed higher post-crack stiffness, peak load and ductility after healing compared to reference samples. [167] In many other studies, hollow glass tubes having an internal diameter from 0.8 mm to 4 mm were successfully used as encapsulation devices. [7, 168-171] A system of concentric glass macrocapsules was also proposed to envelope several expansive minerals (outer capsule) and water (inner capsule) by Qureshi et al. [172] Samples immersed in water yielded a sealing efficiency up to 95% and 25% strength recovery in 28 days.

However, glass capsules may have a negative effect on concrete durability, because of the possible onset of undesired alkali-silica-reactions. To avoid this drawback, ceramic capsules were successfully experimented, [2] as well as spherical or cylindrical polymeric capsules [7, 173, 174]. Nishiwaki et al. proposed a self-healing self-diagnosis polymeric system: when cracked, an embedded ethylene vinyl acetate (EVA) pipe (3.4 mm outer diameter, 2.0 mm inner diameter) selectively melts due to an increase of its resistance and releases the healing agent (epoxy resin) in the crack. [175] Then, fractures up to 2.5 mm in width are repaired.

Polymeric capsules are potentially easier to produce, due to lower processing temperatures, and the possibility for integrated extrusion, filling, and sealing steps. In the case of cylindrical capsules the diameters range from 0.8 mm up to 5 mm, to ensure that the capillary attractive force of the crack and the gravitational force on the fluid mass are sufficient to overcome the capillary resistive force of the cylindrical capsules and the negative pressure forces caused by the sealed ends. [7, 81, 167, 173] In other words, the crack width of the matrix should be less than the inner diameter of the capsules. [144] Spherical macrocapsules do not present this inconvenient property. Recently, a study has been performed on cylindrical polymeric capsules (5 cm long) (**Figure 13**). The extruded capsules were made of polystyrene (PS), polylactic acid (PLA), polymethyl methacrylate (PMMA, labelled PMMA_1 and PMMA_2 for low and high molecular weight, respectively) and a blend of PMMA_1 with 20% polyethyleneglycol monomethylether (PEG). [176] External diameters ranged from 6.1 to 8.4 mm and wall thicknesses were in the range 0.26 - 1.19 mm. Sand blasting was used to improve cement paste adhesion. The crack width needed to rupture the PMMA_1 capsules depended on the wall thickness, as shown in **Figure 13D**. PMMA_2, PS, PLA and PMMA_1-PEG capsules broke for very large cracks only. Subsequent real-scale tests revealed that the resistance of cracked concrete against chloride could be increased for concrete with mixed-in PMMA or glass capsules filled with water repellent agent. [177] Glass capsules provided better crack sealing compared to PMMA capsules as a result of the more uniform distribution in the concrete beam, while the PMMA capsules tended to float.

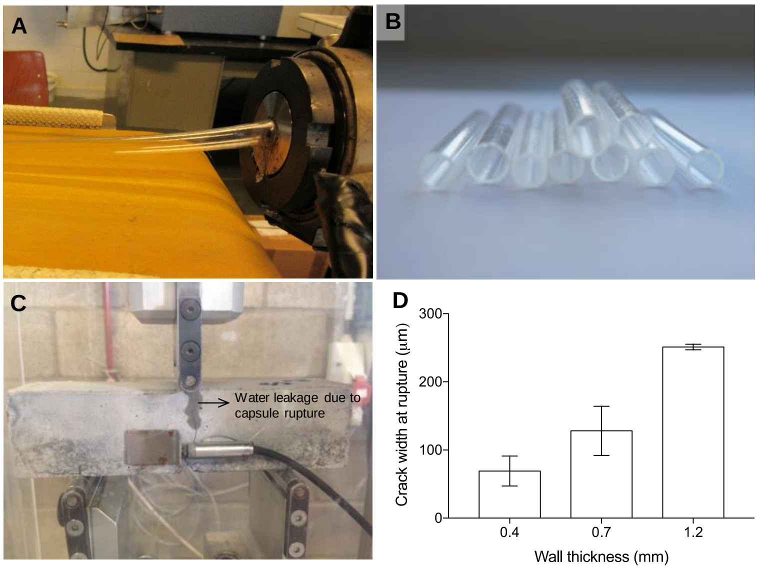

**Figure 13.** Capsule extrusion using laboratory-scale extruder (A); extruded poly(methyl methacrylate) macrocapsues (B); determination of crack width at rupture by 3-point-bending test (C) and crack width at rupture of extruded PMMA capsules in function of wall thickness.

Cementitious hollow tubes (CHT) having different internal diameters (2 mm and 7.5 mm) and a length of 4-5 cm  were also produced by extrusion and used as containers and releasing devices for sodium silicate and potassium silicate solutions by Formia et al. [178-179] When tubes with a bigger diameter were used, load recovery indices up to nearly 70% and stiffness recovery indices up to 50% were reached, even in specimens presenting large cracks (>1 mm, **Figure 14**). Moreover, multiple healing seemed possible.

**Figure 14.** Release of sodium silicate after pre-cracking (wet zone around the crack).

Given that aggregates are the main constituent of concrete, they have been used to host self-healing agents. Thus, expanded clay lightweight aggregates (LWA) were proposed as 'containers' for the healing agent in replacement of part of regular aggregates. [180-181] Sisomphon et al. impregnated LWA with a sodium-monofluorophosphate solution under vacuum to produce an effective self-healing system in blast furnace slag cement mortars. [180] A cement paste layer was used as an external coating. Recently, Alghamri et al. impregnated LWA having a diameter range of 4–8 mm with a sodium silicate solution as a potential solution for self-healing concrete. [181] After impregnation, LWA were sprayed with a polyvinyl alcohol solution (PVA, with an average molecular weight of 146,000-186,000 g/mol) and dried with hot air. Samples pre-cracked up to 300 µm crack width at 7 days were healed for 28 days in water and showed about 80% recovery of the pre-cracking strength, as well as a 50% reduction in the sorptivity index compared to the control cracked specimens.

### 2.3. Vascular

The vascular healing concept in concrete takes a biomimetic approach to self-healing. Examples of such vascular network systems include the human cardiovascular system, that transports blood around the body, and the plant vascular tissue system which, via xylem and phloem networks, transports food, water and minerals. In a similar manner, vascular networks in concrete can deliver liquid healing agents to damage sites. When this healing agent is supplied from an external source there is theoretically no limit to the volume of damaged material that can be repaired. The early work by Dry used long thin glass channels embedded within concrete. [164] This self-healing system was subsequently scaled up and used in a trial bridge deck. [182] One challenge that prevented wide scale use of this method was the difficulty of casting concrete with these very brittle materials present. Recent work has focused on overcoming some of these challenges. A more comprehensive review of this early work on vascular networks is given by de Rooij et al. [6]

The major advantage of the vascular method over the encapsulation approach, is that healing agent can be continually supplied. [183] Indeed, different healing agents can be supplied at different times to treat various types of damages in concrete. Furthermore, the healing agent can be supplied under pressure to ensure that it reaches the required damage zones, [184] similar to the concept of injecting epoxy when repairing cracks in concrete. Various forms of vascular networks have been used in concrete. The simplest form comprises a one-dimensional channel, of which both ends can be accessed from the concrete surface. [120, 166, 185-186] More complex two and three dimensional channel networks have been created in concrete to provide multiple and alternative paths for healing agent to be transported to damage zones. Such forms have been achieved by using multi-flow junction nodes within the network. [184]

Several different ways to create channels in concrete have been developed. One approach is to embed capillary tubes in concrete, which are strong enough to withstand mixing and casting but brittle enough to fracture when the concrete cracks. [12, 185-186] Channels have also been made by placing solid bars in moulds or shutters prior to casting and then removing them after the concrete has set to leave hollow voids. [187] Building on this concept, a novel method of creating channels was developed by Davies et al., [184] whereby shrinkable polyolefin tubes or polyurethane tubes were embedded in concrete and removed after casting. This method introduces a degree of flexibility in positioning the channels around the steel reinforcement and enables to remove the tubes several days after casting to leave a hollow network inside the concrete. Recent investigations by Minnebo et al. explored the use of polymethylmethacrylate, starch, inorganic phosphate cement and alumina for the material of the tubular channels. [188] A somewhat different approach to providing multiple flow paths has been developed by Sangadji and Schlangen, [189] who embedded porous concrete pipes in concrete specimens. This has the advantage of creating a very large number of flow paths for healing agent, although the flow is more diffuse than in a single defined channel and therefore requires significantly more healing agent to achieve the same healing efficiency.

Several different components for the vascular network have been prototyped using 3D printing. Tubular channels can be made using the printed polylactide material but the lengths are typically restricted to the size of the 3D printer. A 3D vascular network distribution piece was created by Minnebo et al. which allowed one inlet to be connected to several channels embedded in the concrete. [188] A 3D joint was developed by Davies et al., [184] which allowed a crossing matrix of tubes, upon removal of tubes, to leave a 2D interconnected vascular network. An example of such a 2D vascular network embedded within a 600mm square slab with healing agent supplied is presented in **Figure 15**. It can be shown that a 2D vascular network having multiple points of access is beneficial to be able to prime the system, remove the air, and allow healing agent to migrate to all regions of the network. [184]

The choice of healing agent to be used in a vascular network is important and remains a topic of research. [6, 164, 190] The ideal properties for such a healing agent include a low viscosity liquid which can flow easily or be pumped into the network, be able to penetrate small cracks taking advantage of the capillary forces developed, [190] to be supplied but then flushed out using air or water to preserve the repeatable use of the network, to target water tightness or strength recovery. [184] For example, the concept of improving the water tightness of construction joints using an internal channel supplied with waterproofing agent is already being used commercially. [191]

The position of the vascular network in the concrete structure, relative to the steel reinforcement, can also act as a crack inducer to provide a known target area for healing. [184] A perceived disadvantage of having a vascular network in concrete, if left open to the atmosphere, is that it could provide a preferential pathway for deleterious materials to bypass the concrete cover protection layer and compromise the durability of concrete structures.

The proof of concept for including a vascular network in concrete has been demonstrated a number of times. [6, 164] The versatility of the vascular network concept could prove to be the ideal solution to the most difficult challenges of overcoming water ingress and cracking prevalent in concrete. [192] However, there remains a challenge to develop large concrete structures with vascular network systems that can initiate healing without human intervention. Before this can be achieved more work is needed on healing agents, their storage, delivery systems and on methods for remotely activating vascular networks.

**Figure 15.** 2D vascular network releasing sodium silicate in a 600mm square concrete slab.

## 3. Self-healing bio-concrete

The production of calcium carbonate as a side effect of microbiological activity [5] can be another mechanism to "engineer" the self-healing capacity of concrete. It has potential for long-lasting and active crack repair, at the same time representing a potentially environmentally friendly method. Calcium carbonate ($CaCO_3$), or limestone, provides efficient bonding capacity and compatibility with the existing concrete compositions. Calcium carbonate can actually be part of the concrete mix design, or be chemically produced inside the concrete matrix due to carbonation of present calcium hydroxide (Portlandite) minerals. Limestone formed inside the matrix of concrete can result in densification of the matrix through filling of pores and can contribute to self-healing of cracks, decreasing its (water) permeability and leading to a regain of lost strength. Most bacteria can induce the precipitation of $CaCO_3$ if given suitable conditions. [193] However, different bacteria following different metabolic pathways for precipitation of bacterial $CaCO_3$ have different carbonatogenesity. Furthermore, several external factors affect the precipitation efficiency and provoke a different carbonate yield by the same bacterial strain. It is likely that a faster healing occurs in a wet/dry environment . [194] Also, the control of crack width is an important factor in order to achieve faster and efficient healing by a biological action. [195]

In the following sections different microbial metabolic pathways potentially resulting in precipitation of calcium carbonate and therefore of potential interest for application in self-healing concrete are reviewed.

### 3.1. Selection of micro-organisms

#### *3.1.1. Ureolytic bacteria*

The alkali-tolerant ureolytic strains have been commonly investigated for application on or in cementitious materials. These bacteria can decompose urea into ammonium/ammonia and carbonate ions (Equation 2). If sufficient $Ca^{2+}$ ions are present in the surroundings, $CaCO_3$ can be formed according to Equation 3.

$$\mathrm{CO(NH_2)_2} + \mathrm{2H_2O} \xrightarrow{\text{Bacterial urease}} \mathrm{2NH_4^+} + \mathrm{CO_3^{2-}} \qquad (2)$$

$$\mathrm{Ca^{2+}} + \mathrm{CO_3^{2-}} \rightarrow \mathrm{CaCO_3} \qquad (3)$$

*Sporosarcina pasteurii* (also named *Bacillus pasteurii*), *Sporosarcina ureae*, *Bacillus sphaericus* and *Bacillus megaterium* belong to this group. They have been used in a number of studies for waterproofing and improving strength and durability aspects of porous and cracked concrete, as reviewed in 2010 by De Muynck et al., [196] in 2013 by Pacheco-Torgal and Labrincha, [197] Phillips et al., [198] and Van Tittelboom and De Belie, [7] in 2014 by Sarayu et al., [199] in 2015 by Wong, [200] and recently in 2017 by Joshi et al., [201] Vijay et al., [202] Souradeep et al., [203] Han and Xing, [204] and exhaustively by Al-Salloum et al., [205] (the latter review covering 255 literature references) and several recent reports [206-208] .

Theoretically, 1 mol $CaCO_3$ can be formed if 1 mol urea is supplied. However, the fact that the bio-chemical reaction process is controlled by the microbially generated urease enzyme, causes the carbonate productivity to rely on the presence of this enzyme. The bacterial ureolytic activity is therefore more important than the concentration of the reactants as in a normal chemical reaction. Without this enzyme as catalyst, the urea hydrolysis is an extremely slow process ($3\times10^{-10}$ $s^{-1}$); on the contrary the urease catalyzed urea hydrolysis is quite fast ($3\times10^{4}$ $s^{-1}$). Thus the enzyme can provoke an increase in the rate of urea hydrolysis by a factor of $10^{14}$. Wang et al. reported a urease activity of around 40 mM urea hydrolyzed.OD$^{-1}$.h$^{-1}$ (OD = optical density) for *Bacillus sphaericus* under optimal conditions ($10^8$ cells mL$^{-1}$, 28°C, 1M urea, 20g L$^{-1}$ yeast extract, and 1M $Ca^{2+}$). [209] Hence *B. sphaericus* cells could precipitate within one day 60 g $CaCO_3$ L$^{-1}$. Without yeast extract, 800 mM urea were decomposed within 3 days, equivalent to 26 g $CaCO_3$ L$^{-1}$.d$^{-1}$. [210] For a certain amount of bacteria, an inhibitory effect was seen when the amount of urea exceeds a certain limit. Wang et al. found in their experiments an upper limit of 1.5M and 2M urea for $10^7$ and $2\times10^7$ cellsmL$^{-1}$, respectively. $Ca^{2+}$ is on the one hand needed for sufficient $CaCO_3$ precipitation, but on the other hand bacteria need only little $Ca^{2+}$ and high concentrations can become toxic. [211] The presence of 0.9M $Ca^{2+}$ did not hinder bacterial activities for a concentration of $10^8$ cells mL$^{-1}$, while at a lower bacterial concentration ($10^7$ cells/mL), only 0.5M $Ca^{2+}$ could be added to maintain significant urea decomposition. [211] Also the temperature is an important factor governing precipitation efficiency, with lower temperatures (10°C) leading to a significantly reduced $CaCO_3$ precipitation rate (5 g $CaCO_3$ L$^{-1}$.d$^{-1}$ in the tests of Wang et al. [211] For self-healing applications, often the dormant bacterial spores are used to enhance the survival inside the cementitious matrix. However, *B. sphaericus* spores were shown to have a slower $CaCO_3$ precipitation than vegetative cells, since spores first need to germinate before their precipitation activities can start. [211] At 20°C, *B. sphaericus* spores ($10^8$ spores mL$^{-1}$) could decompose 20g/L urea within one day (equivalent to 10 g L$^{-1}$.d$^{-1}$ $CaCO_3$), while $10^7$ spores mL$^{-1}$ needed 3 days to decompose the same amount of urea.

### *3.1.2. Denitrifying bacteria*

Bacterially induced $CaCO_3$ precipitation through nitrate reduction by different strains such as *Pseudomonas denitrificans* and *Castellaniella denitrificans* has been investigated for soil consolidation. [212-213] Recently, resilient denitrifiers have been used for concrete self-healing due to their suitability to function under oxygen limited conditions. [214] Bacterial urea hydrolysis and aerobic oxidation of organic carbon require oxygen to initiate bacterial activity (spore germination) or as final electron acceptor to initiate and to keep the microbial activity, which can be a restricting factor for deep crack healing. Under oxygen limited conditions, denitrifiers can use nitrate ($NO_3^-$) as an alternative electron acceptor for oxidation of organic carbon and generate $CO_3^{2-}$ and $HCO_3^-$ ions, which are necessary for $CaCO_3$ precipitation (Equation 4). Although precipitation yields are generally lower than for the ureolytic pathway, a $CaCO_3$ precipitation of 7g $CaCO_3$ $g^{-1}$ $NO_3$-N per day could be achieved by *Diaphorobacter nitroreducens.* [215] Furthermore, the resilience of *D. nitroreducens* enabled repetitive $CaCO_3$ precipitation with a constant precipitation rate of 0.72~1.2g $CaCO_3$ $L^{-1}.d^{-1}$.

$$5HCOO^- + 2NO_3^- \rightarrow N_2 + 3HCO_3^- + 2CO_3^{2-} + H_2O \qquad (4)$$

The approach of a self-healing mechanism, based on production of bacterial calcium carbonate, requires the following essential parameters: an optimum environment, adequate pH value and nutritive requirements for the chosen bacteria cells. Concerning the nutrient source for $NO_3^-$ reducing bacteria commercial concrete admixtures as calcium formate $Ca(HCOO)_2$ and calcium nitrate $Ca(NO_3)_2$ could serve as good candidates. It was shown [216] that the highest crack width healed in mortar specimens immersed in water, by protected *Diaphorobacter nitroreducens* and *Pseudomonas aeruginosa* was 370 ± 20 mm in 28 days and 480 ± 16 mm in 56 days. An example of the crack healing potential versus the reference and control samples is shown in **Figure 16**. Water tightness regain up to 85% was achieved at the end of 56 days for 465 ± 21 mm crack width.

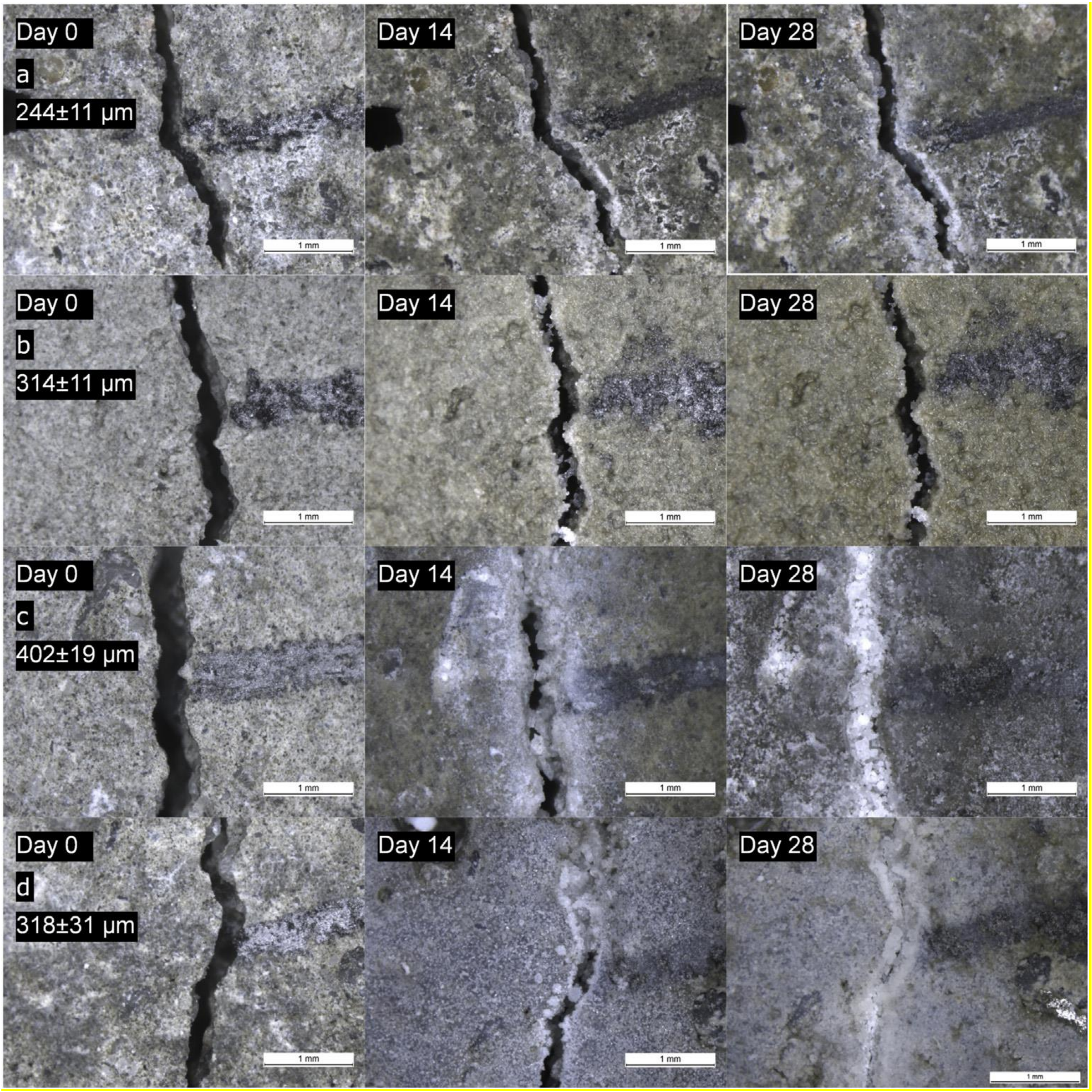

**Figure 16.** Photomicrographs showing biweekly evolution of cracks during 28 days of water immersion: (a) reference mortar; (b) abiotic control containing only nutrients; (c) mortar containing *Diaphorobacter nitroreducens* loaded expanded clay particles; (d) mortar containing *Pseudomonas aeruginosa* loaded expanded clay particles (given values represent the average width of the shown crack ± standard deviation).
Reproduced with permission. [216] 2016, Elsevier.

Nitrate reduction could also lead to the production of $NO_2^-$ which is known as a corrosion inhibitor (Equation 5): [217]

$$2HCOO^- + 2NO_3^- + 2H^+ \rightarrow 2CO_2 + 2H_2O + 2NO_2^- \qquad (5)$$

In alkaline conditions (pH ~ 9), microbial $NO_2^-$ reduction is mostly suppressed by high rate $NO_3^-$ reduction causing $NO_2^-$ to accumulate, which is called partial/incomplete denitrification. Nitrite precedes $Cl^-$ attack on ferrous oxides, the weakest points inside the passive ferric oxide layer, and rapidly oxidizes the ferrous ions to ferric oxide at the corrosion site which suppresses the corrosion. Studies on $NO_2^-$ for corrosion inhibition have revealed that the optimum corrosion inhibition could be achieved when the $[NO_2^-]$:$[Cl^-]$ ratio was in the range of 0.34-1. [218] Therefore, biological $NO_3^-$ reduction has significant potential to inhibit corrosion in concrete environment. It was shown that vegetative axenic nitrate reducing and $CaCO_3$ precipitating bacteria, *Pseudomonas aeruginosa* and *Diaphorobacter nitroreducens*, could survive mortar environment if protected by either diatomaceous earth, expanded clay or granular activated carbon.[217] The tested cultures tended to accumulate nitrite at alkaline pH conditions. Microbial produced $NO_2^-$ could inhibit steel corrosion up to a certain extent in corrosive electrolyte solution (0.05 M $Cl^-$, pH 9) and the controlling parameter was $[NO_2^-]$:$[Cl^-]$ ratio. [217] Pitting corrosion occurred around −100 mV when $[NO_2^-]$:$[Cl^-]$ ratio was below 1.

### *3.1.3. Aerobic heterotrophic bacteria*

The metabolic conversion of organic compounds by microorganisms under aerobic (in the presence of oxygen) conditions can also result in the precipitation calcium carbonate. Whether precipitation actually occurs depends largely on the chemistry of the medium (environment) the microorganisms are in. Simply put, typical requirement for precipitation of calcium carbonate to occur is that the local ion concentration product of calcium ($Ca^{2+}$) and carbonate ($CO_3^{2-}$) ions exceeds the solubility product of calcium carbonate (in form of either calcite, aragonite, or vaterite). In principle, the higher the ion concentration product, as referred to the saturation state, the higher the calcium carbonate precipitation rate. However, in practice, several physico-chemical conditions can reduce or even inhibit calcium carbonate from precipitating. E.g. precipitation nuclei for initiation of calcium carbonate crystal formation are required and certain chemical compounds can form complexes with either the calcium or the carbonate ions, reducing their reactivity or 'activity' in geochemical terminology. [219] While aerobic degradation of organic compounds does not directly affect the concentration of calcium ions, it does increase the dissolved inorganic carbon concentration (DIC: $CO_2$ + $HCO_3^-$ + $CO_3^{2-}$), and particularly under alkaline conditions the carbonate ion concentration. Therefore, if calcium ions are available, metabolic conversion of organic compounds under alkaline conditions will increase the likelihood and rate of calcium carbonate precipitation. [220]

Jonkers and colleagues developed since 2006 in a series of studies a bacterial spore and an organic compound based healing agent for providing autonomous healing potential to concrete under aerobic conditions (see [221-222] and references therein, and [160,223-227]). The specific healing agent contains organic compounds in the form of calcium salts of fatty acids such as calcium formate, calcium acetate, calcium glutamate, calcium propionate and calcium lactate or lactate-derivatives. [228] In latter study it was found that upon addition of a lactate-derived bacteria-based healing agent, surface water absorption of mortar specimen was decreased in Ordinary Portland Cement (OPC) based (CEM I) specimen but not (increased) in Blast Furnace Slag cement-based (CEMIIIb) specimen. [228]

The bacteria, also part of the healing agent, are present in form of metabolically virtually inactive spores which survive incorporation in the highly alkaline concrete matrix, and those typically used are gram positive alkali resistant members of the genus *Bacillus* such as *B. cohnii*, *B. pseudofirmus* and phylogenetically related facultative aerobic strains. The organic calcium salts can be metabolically converted by the crack-ingress water and activated and germinated bacterial spores (active vegetative cells) to calcium carbonate and carbon dioxide as given in the following biochemical reaction for aerobic metabolic degradation of calcium lactate (Equation 6): [229]

$$CaC_6H_{10}O_6 + 6O_2 \text{-->} CaCO_3 + 5CO_2 + 5H_2O \qquad (6)$$

The metabolically produced carbon dioxide can react further with the alkalinity provided by the concrete matrix in the form of calcium hydroxide (Portlandite minerals) to produce more calcium carbonate (Equation 7): [230]

$$5CO_2 + 5Ca(OH)_2 \text{-->} 5CaCO_3 + 5H_2O \qquad (7)$$

Advantage of the carbon dioxide produced by metabolic degradation of organic compounds (reaction 6) is that it prevents soluble Portlandite minerals from leaching out of immersed concrete in case of crack formation as limestone produced (reaction 7) is much less soluble. This enhanced biological carbonation process which occurs on the crack surfaces has the potential to bridge and seal cracks as long as sufficient alkalinity (in form of calcium hydroxide) is provided by the concrete matrix. [230]

In two recent studies the effect of organic calcium salts, which can act as calcium carbonate mineral precursor compounds (calcium and sodium gluconate, calcium acetate and calcium lactate), were investigated for potential to heal cracks in mortar specimens, and it was found that calcium gluconate and calcium lactate enhance the self-healing kinetics for large cracks, [231] and that compressive strength of mortar cubes increased with 8% for calcium lactate and with 13.4% for calcium acetate [232].

Characteristic of the metabolic aerobic degradation mechanism of organic compounds is that the biochemical reaction depends on the availability of oxygen and, consequently, that limitation of its availability will decrease the rate of calcium carbonate precipitation. However, on the other hand, absence of oxygen will reduce the rate and risk of corrosion of the steel reinforcing bars embedded in the concrete and presence of active oxygen respiring microorganisms will therefore potentially prolong the service life of steel reinforced concrete constructions in corrosion sensitive environments.

Nevertheless, in a series of recent studies the potential of oxygen releasing compounds, typically peroxides, as part of concrete healing agent formulations were investigated for their potential to increase calcium carbonate precipitation yield by aerobic bacteria under oxygen-limiting conditions. While calcium peroxide and zinc peroxide appeared inhibitory, urea-hydrogen peroxide and magnesium peroxide were found to stimulate calcium carbonate precipitation in one study, [233] Zhang et al. found that calcium peroxidase tablets improved calcium precipitation by bacterial strain H4 at a dosage range of 7.5-12.5 g L$^{-1}$. [234 -235] Another limitation for microbially mediated calcium carbonate precipitation rates might be low environmental temperatures (underground, (deep) sea etc.) as in general microbial processes dramatically slow down when temperatures reach the freezing point. Therefore Palin et al. developed a bacteria-based self-healing cementitious composite for application in low-temperature marine environments and found a crack-healing capacity of 95% for 0.4 mm and 93% for 0.6 mm wide cracks respectively upon 56 days of immersion of this composite in seawater at 8°C. [236]

### *3.1.4. Pure cultures vs. mixed cultures*

Silva et al. calculated an operational expense cost (OPEX) of more than 400 €/kg of bio-agent for the production of axenic ureolytic spores, a cost that was highly affected by the need for sterile production conditions. [237] Non-axenic (non-sterile) production of ureolytic bacterial spores would allow to reduce production costs. Hence a new selection process was developed to obtain an efficient ureolytic microbial community starting from a side stream from vegetable processing. [238] This mixed culture was called "Cyclic EnRiched Ureolytic Powder" or CERUP, or later also 'Mixed Ureolytic Culture' or MUC. The OPEX cost of CERUP was about 40 times lower than the OPEX cost of an axenic *B. sphaericus* culture. CERUP was obtained by applying thermal cycles up to maximum temperatures of 60-70 °C for a period of 2 h. In these conditions, some spore forming bacterial strains have the ability to sporulate fast enough to allow them to survive. In parallel, considerable amounts of urea were added, to stimulate mainly the ureolytic bacteria. Ureolytic activity and calcium carbonate precipitation capability of CERUP produced in 5 L and 50 L reactors were proven to be as good as the benchmark *Bacillus sphaericus* (20 g urea/L decomposed in 24h). Additionally, the bacterial cultures were automatically encapsulated by remaining salts, so that they can protect themselves from harsh conditions. Incorporation of CERUP in concrete at 0.5% or 1% relative to the cement content provided efficient self-healing of cracks.

Similarly, special granules called 'activated compact denitrifying core' (ACDC) were cultivated by Ersan et al. [216, 239] It was estimated that the OPEX cost to obtain ACDC would be around 17.4 Euro/kg ACDC. ACDC is a denitrifying microbial community protected by various bacterial partners and obtained in a sequential batch reactor operated with anoxic/aerobic period sequence. Selective stress conditions were applied and a minimal nutrient solution (COD:N – 5:1) was used 4 times/day as feed (with COD: chemical oxygen demand). The initial pH of the feed solution was set between 9-9.5 by using concentrated NaOH solution (10 M). ACDC granules were harvested from the reactor after 2 months and subsequently dried. The granules consisted of 70 % bacteria and 30 % inorganic salts. Ersan et al. added, without any further protection, ACDC granules (0.5 – 2 mm) to mortar (0.5 w/w cement). $Ca(NO_3)_2$ and $Ca(HCOO)_2$ were added as nutrients. [239] After crack creation in 28 days old mortar specimens and immersion in water for 28 days, effective crack closure up to 0.5 mm was achieved. Weekly $NO_x$ analysis revealed that 92±2 % of the available $NO_3^-$ was consumed by the bacteria. Another set of specimens was cracked after 6 months curing. It was proven by microscopic analysis that also cracks occurring in specimens cured for 6 months were healed by mineral formation. In ACDC containing specimens larger cracks were healed in comparison with control specimens and capillary water absorption was reduced up to 70 %. Additionally, the ACDC produced 57 mM $NO_2$ in 1 week, which induced passivation of plain steel in corrosive solutions containing 0.05 M NaCl. [216]

Microbial consortia capable of microbially induced carbonate precipitation (MICP) under aerobic, anaerobic, or facultative anaerobic conditions were investigated by Zhang et al. and in this study it was found that aerobic consortia performed better with respect to crack-healing in comparison to the other two consortia types, however, all three consortia could completely heal selected cracks within a period of 28 days incubation. [240]

### 3.2. Protection of micro-organisms

There are some limitation factors for application of bacteria in self-healing concrete: high pH values in concrete (pH ~ 13), dense matrix (with small pores) and unsuitable humidity conditions. To overcome these obstacles, several bacteria protection methods have been developed: encapsulation techniques, immobilization of bacteria within porous carriers and self-immobilization/self-protection.

### *3.2.1. Micro-encapsulation*

Most bacteria-based self-healing concrete systems require spores to be immobilised, by encapsulation, prior to their addition to concrete due to concerns about their viability in hydrating concrete. The key aspects related to the micro-encapsulation of self-healing compounds have been discussed in Section 1.2.1 and much of the technology discussed in that section can be translated to micro-encapsulation of bacterial spores. Whilst it has to be recognised that some synthetic polymers are deleterious to bacteria, [204] the well documented resilience of endospores (particularly those of the *Bacillus* genus) to adverse conditions is such that micro-encapsulation of spores should in general cause few problems. Indeed, the micro-encapsulation of spores is potentially much simpler than the micro-encapsulation of polymers or minerals because spores are inert, solid and non-soluble in water.

The encapsulation of spores has been proven using commercial encapsulation methods including: (i) encapsulation of *B. sphaericus* in melamine-based microcapsules [116] and (ii) encapsulation of *B. pseudofirmus* and *B. subtilis* in synthesised gelatin/acacia gum microcapsules using complex coacervation. [241] In both cases the microcapsules formed were initially soft and flexible but transitioned to a more brittle, stiff state after drying. This transition enabled the microcapsules to survive the wet mixing process but rupture successfully upon crack formation. Elsewhere a system has been developed in which microcrystalline cellulose (MCC) is mixed with spores of *B. pseudofirmus* and encapsulated in a shell of ethyl cellulose. As with other micro-encapsulation techniques it was demonstrated that the spores survived the mixing process and that some of the microcapsules fracture upon formation of a crack [242]. The survival, viability and calcium carbonate precipitating capability of spores after encapsulation has been verified in all cases.

Whilst the micro-encapsulation of spores for use in self-healing concrete has been established there has been less progress on the encapsulation of the nutrients (urea, yeast extract and calcium precursors) required for bacteria-based self-healing, mainly because water-soluble materials can easily escape into the external phases during encapsulation. For encapsulation by complex coacervation this problem of escaping actives is two-fold with regards to the calcium-based precursor as: (i) it can affect the pH of the system, a key parameter for wall deposition, and (ii) the calcium ions can disrupt the complexation of the two wall material polymers. However, some success in encapsulating yeast extract and calcium acetate by complex coacervation by first dissolving them in a water phase with gelatine, which act as an emulsion stabiliser, has been achieved. [241] Further work to optimise this process is on-going.

### *3.2.2. Impregnation in porous granules*

Several researchers immobilized *Bacillus sphaericus Bacillius subtillis, Sporosarcina pasteurii* or *Diaphorobacter nitroreducens* and their respective nutrients in lightweight aggregates (LWA), for example, biochar, diatomaceous earth, metakaolin, expanded clay, expanded shale, expanded perlite, granular activated carbon, zeolite, ceramsite, etc. prior to addition to the concrete mixture. [85, 194, 224, 243-249] The loading procedure typically consists of impregnating the LWA at room temperature or under vacuum with a solution containing the bacterial spores and nutrients, either together or separately, followed by drying. In some researches separate encapsulation was used to increase the capability of self-healing. [194] Commonly, LWA particles have been coated with a single or dual layer of sodium silicate solution and cement powder to prevent leaching of the spores and nutrients into the mortar. The functionality of these healing agents was demonstrated by showing metabolic activity of the activated bacterial spores by oxygen consumption measurements (for aerobic bacterial strains), or by regain of material functionality in form of regain of water tightness.

The results indicated that although diatomaceous earth provided protection for $NO_3^-$ reducing vegetative strains, it significantly decreased the setting time when combined with the respective nutrients, $Ca(HCOO)_2$ and $Ca(NO_3)_2$, necessary for self-healing. Therefore, diatomaceous earth was suggested not to be used as a protective carrier for denitrifying microorganisms in the development of self-healing concrete, [215, 243] while it was experimentally proven to be useful for immobilisation of ureolytic bacteria [250].

Use of pre-wetted lightweight aggregates as internal nutrient reservoirs could be a promising approach to promote self-healing of internal cracks in bio-mortar/concrete, particularly for mixes that require low w/cm for special applications. [246]

It was shown that crack healing could be achieved when coated expanded perlite was used as a 20% replacement of aggregate, provided a suitable ratio of spores to calcium acetate was achieved. [194]

Optimisation of the self-healing performance should be considered in terms of the number of bacterial spores required, the concentration and composition of nutrients and precursors, and which system (one or two-component) would be likely to efficiently produce self-healing in concrete.

Although a proof of concept was shown for healing agent components contained in LWA, the application range may be limited because of the incorporation of quite large volumes of expanded minerals, which affects the mixture design and reduces the concrete strength. In order to extend the applicability range, the volume of added healing agent was reduced by increasing the content of efficient healing agent constituent in particles. A way of producing scalable particles almost fully consisting of active ingredients is by roller compacting spore powders to sheets, with subsequent milling to flakes that are in the size range of the sand fraction (1–4 mm). [85,251] A typical property of these flakes is solubility in water, which is beneficial for matrix cracking and water ingress, dispersing the healing agent in the crack volume. Partial particle dissolution during concrete mixing can be prevented by application of a protective barrier around the soluble particle, in the form of a coating. The coating material can be inorganic (e.g. cement paste or geopolymer) or organic (e.g. calcium cross-linked polyvinyl alcohol alginate or lactic acid derivatives).

In a recent study magnetic iron oxide nanoparticles were used for immobilization and protection of *Bacillus* cells (**Figure 17**). In this study it was shown that precipitation of calcium carbonate by immobilized bacteria resulted in significantly improved crack healing behavior of the cracked concrete matrix in comparison to control specimen. [252, 253]

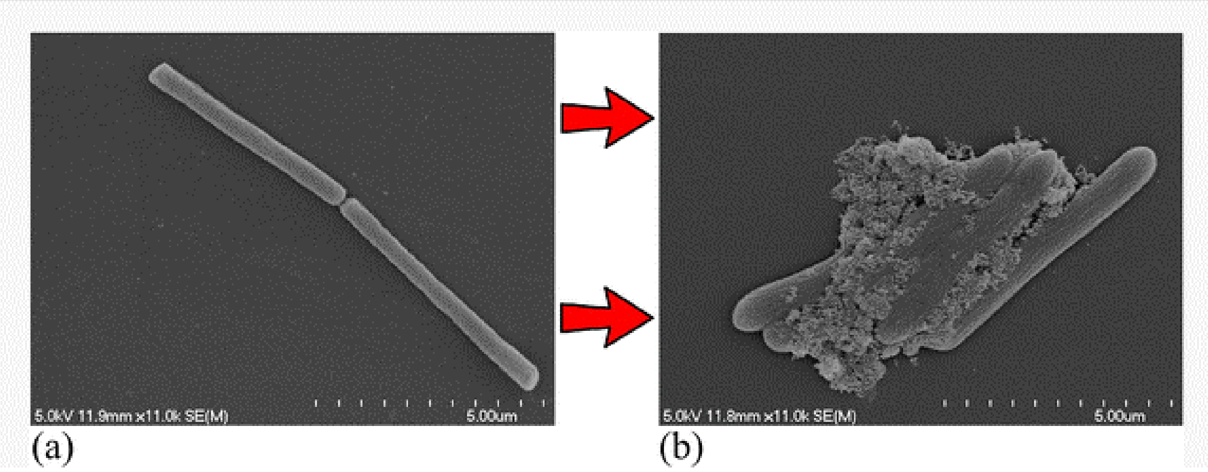

**Figure 17.** SEM micrographs of (a) bacterial cells and (b) decorated cells with iron oxide nanoparticles indicating the successful attachment of nanoparticles to the cell surface. Reproduced with permission.[252] 2018, Springer.

### *3.2.3. Encapsulation in hydrogels*

The use of bio-hydrogels consisting of spores encapsulated within hydrophilic polymer gels has been investigated recently. The bio-hydrogels were formed by incorporating a spore suspension into the polymer solution prior to synthesis. Bio-hydrogels investigated by Wang et al. incorporated approximately $10^8$ spores of *Bacillus sphaericus* per g of synthetic hydrogel. [254-255] The viability of the spores was not decreased after encapsulation. The hydrogel had a good cell entrapping capacity, and could keep more than 90% of the encapsulated spores from releasing during the mixing process. When used in self-healing concrete (at a dosage of 5% by mass of cement), they showed to be a promising carrier due to their ability to both protect spores during mixing and casting, and then their ability to swell and act as a water reservoir for spore germination and bacterial activity once cracking occurs. Indeed, in normal humidity conditions, hydrogels can absorb moisture and retain it for bacterial use, which is beneficial for realistic self-healing. The maximum crack width healed was about 0.5 mm in 7 days in the specimens with bio-hydrogels compared with 0–0.3 mm in the ones with non-bio hydrogels. [254-255] The healing ratios in the specimens with bio-hydrogels were in the range from 70 % to 100% for cracks smaller than 0.3 mm, which is more than 50 % higher than for the ones with pure hydrogel and the total volume ratio of the healing product in the specimens with bio-hydrogels amounted to 2.2 %, which was about 60 % higher than for the ones with pure hydrogel (1.37 %).

Wang et al. have also considered a modified-alginate bio-hydrogel containing around 4 x $10^9$ spores per g of hydrogel. [161] Palin et al. applied alginate beads to encapsulate spores of an undisclosed bacterium. [160] The beads consisted of calcium alginate and mineral precursors and were produced by pumping drop wise a precursor solution of magnesium acetate, yeast extract and 7 x $10^8$ of unidentified bacteria spores per litre into a calcium acetate solution. As with the previously mentioned bio-hydrogels, the resulting beads provided considerable crack healing potential due to a combination of calcite precipitation and swelling of the bead due to interactions between water and the hydrophilic groups of the alginate.

## 4. Outlook and drawbacks

While concrete contains inherent self-healing properties, this autogenous healing mechanism is only efficient for small cracks. The phenomenon itself has been well studied, but still no consensus is found regarding the maximum healable crack sizes: mostly values of 10 to 100 µm are mentioned, sometimes up to 200 µm, and only in the presence of water. Nevertheless, it is clear that autogenous healing is difficult to predict and can hardly be relied upon. Therefore, concrete has been engineered to stimulate autogenous healing or specific self-healing mechanisms have been introduced.

Stimulated autogenous healing is limited by the presence of reagents in the concrete matrix, such as unreacted binder particles. Hence, the maximum healable crack width will not increase much in comparison with pure autogenous healing. Addition of fibres can help to keep the crack widths below the maximum healable width and improve the self-healing efficiency. An advantage of these stimulating systems is that they could be provided to the concrete manufacturers at a lower cost than the encapsulated systems, and that the producers are familiar with the use of similar additions and admixtures.

Still, according to the available literature, introduction of mineral additions or crystalline admixtures (CA) into the concrete matrix may either enhance or reduce the self-healing efficiency, or have no effect. This largely depends on the mix design (e.g. a more positive effect can be seen for CA in HPFRC) and healing conditions (e.g. mineral additions may enhance CSH formation by continuing binder hydration in submersed conditions, but reduce calcium carbonate precipitation in the cracks during wet-dry cycles). Generally, the healing will remain a reasonable slow process, needing several weeks up to several months to heal cracks of up to 200 µm in width. Further stimulation of the chemical reactions by alkaline activators brings along the problem of supply of these activators to the material and encapsulation would increase the cost to the same level as for the autonomous healing systems. Also the use of fibres to limit crack widths will increase the costs and will only be applicable for specific concrete applications. Natural fibres could provide an interesting and more sustainable alternative to the steel or polymeric fibres, with the added benefit of water storage capacity which will enhance self-healing. Superabsorbent polymers (SAPs) attract more and more attention lately, since they can provide a three-level approach that combines crack mitigation due to internal curing in fresh concrete, immediate crack sealing upon water ingress in hardened concrete, and subsequent promotion of self-healing. Additionally, they make self-healing less dependent on the presence of liquid water, since healing in humid air has also been proven in mortar with SAPs (although with reduced efficiency). Further efforts are needed to define the best SAP or combination of SAPs to obtain these three effects simultaneously at a reasonable cost, and with limited negative effect on the concrete mechanical properties. Here, it is expected that due to sustainability concerns, the natural and semi-synthetic SAPs will gain importance. Polymer modified concrete (PMC) on the other hand, is more like a niche product with higher price, and hence the introduction of self-healing PMC will be restricted to the same markets, for repair mortars or for cases where resistance against (acidic) liquids and abrasion is an issue. Whereas a long-term preservation of the self-healing efficiency is expected for the mineral, crystalline and SAP-based systems, it would be an issue for self-healing PMC, since the shelf-life of e.g. epoxy resin is usually between 1-3 years. Although studies on healing efficiency at later ages are largely lacking, it would be expected that the liquid polymer starts to harden in the matrix if it has not been needed for self-healing action before that age.

With the purpose of increasing the maximum healable crack widths and promoting the healing of the internal cracks, autonomous self-healing systems have been designed. These include micro- and macro-encapsulated polymers or minerals, and bacteria based systems (encapsulated or not). For encapsulation, a whole range of shell materials have been investigated and tailored for use in cementitious matrices. Important progress has been made regarding switchable properties (from rubbery behaviour in fresh concrete to brittle behaviour in hardened concrete), improved bond with the cementitious matrix, and chemical triggering mechanisms. Since encapsulated systems usually negatively affect the mechanical properties of concrete, optimum dosages have been proposed that balance mechanical properties with healing effect (usually 0.5 to 10% by weight of cement). Although mostly the healing of cracks up to 300 µm in width has been investigated, some researchers have shown that cracks of more than 1 mm can be healed for specific self-healing systems. A point of concern is the long-term stability of encapsulated polymeric healing agents, due to their limited pot-life and the additional fact that the capsule shells cannot be considered to be completely impermeable to the highly alkaline concrete pore solution. Therefore, several researchers made a shift towards encapsulation of mineral cargos or bacterial spores. Still, long-term stability and repeatability of the healing ability has not yet been properly addressed and should be a focus of future work. This long-term stability may be less an issue for the vascular systems, where the healing agent is only injected in the system at the moment of crack induction. However, there remains the challenge to develop vascular networks for large concrete structures and to remotely activate them.

The bacteria mediated mechanisms for self-healing of cracked and porous concrete surely have their limitations as well. From a performance point of view, aerobic oxidation and denitrification have a disadvantage in terms of $CaCO_3$ precipitation yields, when compared to the ureolytic pathway. However, from an environmental point of view, urea hydrolysis has the disadvantage of producing ammonia as a by-product. Denitrification can be advantageous when the necessary nutrients are considered. Yeast extract, urea, calcium lactate and calcium glutamate used for urea hydrolysis or aerobic respiration, are organic compounds which may negatively affect concrete properties. In the case of denitrification, commercial concrete admixtures like calcium formate and calcium nitrate can serve as nutrient source for $NO_3^-$

reducing bacteria without negative effect. Self-healing strategies using aerobic oxidation or ureolytic bacteria lack the preventive action to avoid exposure of the steel surface to corrosive substances during the healing period, which usually takes several weeks. However, recent proof-of-concept studies show that is possible to achieve nitrite production and hence corrosion inhibition simultaneous with crack healing by using $NO_3^-$ reducing bacteria. On the other hand, absence of oxygen will reduce the rate and risk of corrosion of the steel reinforcing bars and presence of active oxygen respiring microorganisms will therefore also potentially prolong the service life of steel reinforced concrete constructions.

For (stimulated) autogenous and bacterial self-healing systems, the calcium carbonate (limestone) formed within the cracks mainly seals cracks but hardly regains lost strength. Moreover, limestone is rather soluble under acidic conditions and will therefore not result in durable sealing of cracks when in contact with low pH conditions. Another drawback of limestone is that it shows rather brittle behavior and the mechanism of microbial limestone formation is therefore less suitable for durable sealing of cracks in concrete subjected to dynamic loading conditions as this will result in repetitive opening of cracks. To overcome these drawbacks, a more acid resistant, stronger, and/or more elastic (low E-modulus) material would be required. Optional materials would be minerals like hydroxyapatite (calcium phosphates) as these are stronger and more acid resistant, or bio organic-mineral composites like nacre which are not only stronger but also more elastic in comparison to calcium carbonate based minerals. [256] Further research should also focus on low cost fermentation and drying processes to obtain bacteria from industrial by-products, together with low cost production strategies and protection mechanisms. Although presently more than 200 studies reported on improved durability aspects of concrete due to bacteria-mediated limestone formation [see references in this review and in Al-Salloum Y. et al. [205]] virtually all are based on laboratory studies what calls for outdoor applications to show that bacteria-mediated limestone formation is a relevant mechanism that could increase concrete structure durability.

Actually, all self-healing systems should improve durability-related properties, and further research should be focused on long-term durability of the healed structures, e.g. resistance to corrosion, freeze/thaw and salt crystallization. In depth Life Cycle Assessment (LCA) studies are required to show that self-healing concrete is more sustainable and is over the service life of the structure more economical than a traditional concrete which needs more inspection and repair.

## 5. Conclusions

This review examined the current knowledge relevant to the development of self-healing concrete reporting on the progress and future perspectives of different healing pathways. Autogenous healing of concrete and mortar is not reliable and limited to crack widths of around 100 µm. It can be significantly enhanced when the concrete mix is engineered by addition of certain minerals, crystalline admixtures, fibres, hydrogels, polymers or bacteria, which may be added as such or after encapsulation. Since certain self-healing additives, such as mineral additions or hydrogels, only improve or stimulate the intrinsic self-healing properties of concrete, full crack healing can only be obtained if cracks widths are limited to a few hundreds of micrometers. If larger cracks need to be healed, additional crack healing material can be supplied by bacterial precipitation mechanisms or by encapsulated polymeric agents. Whereas the calcium carbonate deposited by (stimulated) autogenous healing or by bacteria in the crack is a brittle material and hence mainly useful for healing of static cracks, polymeric healing agents can show a larger degree of elasticity which may allow to keep even a dynamic crack sealed.

Another concern is the shelf-life of the self-healing functionality. Most polymeric healing agents, even when stored in perfectly sealed conditions, have a shelf-life of only about one year. Moisture curing polymers, such as polyurethane, may cure prematurely when capsules are not entirely watertight. Mineral healing agents and bacterial spores may show a higher shelf-life.

A challenge for upscaling of the healing mechanisms from lab scale (where tests are usually performed on mortar specimens) towards real-life concrete applications, is to maintain a high self-healing efficiency. When keeping the dosage of the additives constant relative to the cement weight, the move from mortar to concrete results in a significant dilution of the additives. However, when keeping the same dosage in proportion to the total volume, an unacceptable strength decrease and high costs due to high healing agent dosage may result.

Furthermore, the efficiency of self-healing still needs to be further proven under real environmental conditions, this means at non-ideal curing temperatures, at high salt concentrations (like in marine environment), at later ages of the concrete, under sustained stresses, repeated cracking and healing cycles etc. The design of appropriate monitoring techniques to follow up the self-healing efficiency over the lifetime of a concrete element as well as reproducible standard test methods to evaluate the healing efficiency is hereby of utmost importance.

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## Biographies

**Nele De Belie** received her PhD from Ghent University in 1997. After three years postdoctoral research at KU Leuven with 6 month research stays in Copenhagen and Auckland, she moved back to Ghent for a professor position. She is currently the head of the Concrete and Environment group with main research interests in the areas of concrete durability and sustainability, concrete with industrial by-products and self-healing concrete.

**Elke Gruyaert** received her PhD from Ghent University in 2011. During her post-doctoral research (2011-2017) she was involved in research activities related to self-healing and ‘green’ concrete. Recently, she has been appointed as professor at KULeuven in the field of Concrete Technology and Concrete Durability.

**Henk Jonkers** obtained his PhD degree from Groningen University in 1999. After seven years working as research scientist at the Max-Planck-Institute for Marine Microbiology in Bremen he moved to Delft University of Technology where he is currently chairing as associate professor the Sustainability group within the Materials & Environment section. His main research concerns development of bio-based-, self-healing-, and sustainable construction materials.

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