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X-ray computed microtomography to study autogenous healing of cementitious materials promoted by superabsorbent polymers

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ABSTRACT

Autogenous healing of cracks may offer a solution for brittle cementitious materials. In this study, the healing building blocks are available through the well-designed ultra-ductile microfibre-reinforced mixture with a low water-to-binder ratio and water is available through the inclusion of superabsorbent polymers. As visual inspection demonstrates that the crack is completely closed at the surface, one may ask whether this healing also is present in the interior of the crack. X-ray computed microtomography was therefore used to study the extent of autogenous healing in cracked cylindrical specimens. 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 800–1000 μm) 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. For mixtures containing superabsorbent polymers there was even partial healing in the interior of the crack when stored at a relative humidity of 60% or more than 90%. Energy-dispersive spectroscopy combined with microscopic analysis showed that the healing products were mainly calcium carbonate. The smart cementitious material with superabsorbent polymers is thus an excellent material to use in future building applications as the healing capacity is improved.

1. Introduction

Self-healing is a hot topic nowadays [1]. Recent reviews on self-healing cementitious materials in general [2–4] and self-healing in strain-hardening cementitious materials [5,6] have been published. Autogenous healing was already studied in the mid twentieth century. There it was concluded that the main healing mechanism at the surface was calcium carbonate ($CaCO_3$) [7] and calcium hydroxide ($Ca(OH)_2$) precipitation and that no amorphous hydrated products of cement were found. At 95% relative humidity (RH), there was no healing visible and it was concluded that the presence of water as curing medium was essential [8]. In a humid environment, so without the presence of water, the material indeed does not show any form of healing [9].

The studied material in this research is an ultra-ductile fibre-reinforced cementitious material optimized through the use of micromechanics in order to attain high tensile ductility and tight micro-cracks at moderate fibre contents (2 v% or less) [9–17]. The extreme strain capacity of this material (beyond 3%) is several hundred times that of traditional concrete and its toughness is similar to that of aluminium alloys [18]. Due to the use of microfibres, the crack widths are restrained within the healable range (30–50 μm for complete healing after wet/dry cycles, smaller than the 150 μm criterion for no healing [9,19–22]). Autogenous healing has been demonstrated in these strain-hardening cementitious materials and the healing products were mainly $CaCO_3$, $Ca(OH)_2$ [23,24] and calcium silicate hydrates (CSH) [25]. Autogenous healing of these cementitious materials can provide a solution of the cracking problems found in building constructions and it is a potential solution for obtaining a sustainable concrete infrastructure. But the healing is limited (as water needs to be present) and needs to be stimulated.

The obtained autogenous healing can be improved by adding superabsorbent polymer (SAP) particles [20,21,26]. The SAP particles have the ability to absorb a significant amount of fluid from the surrounding environment (up to 500 times their own weight) and

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to retain the liquid within their structure without dissolving. First, they were used in concrete to mitigate autogenous shrinkage [27–30]. They can be used for self-sealing purposes as their swelling action may block the crack from intruding fluids [31–33]. By absorbing fluids from the surroundings after crack formation, water is available for healing as well. Even complete healing was possible as formation of new cracks was noticed upon reloading some samples containing SAP [20]. Specimens with SAPs are even able to regain some of their mechanical properties after being preloaded/pre-cracked and reloaded under four-point-bending (up to 75–100% regain in mechanical properties) [34]. In an environment with a relative humidity of more than 60%, only samples with SAP showed partial healing, as moisture was extracted from the environment [20].

The mechanism of further hydration and calcium carbonate crystallization may seal a crack at first and can result in the regain of mechanical properties. The regain is mostly measured by means of repeating mechanical tests and comparing the strength before and after healing, and the closure of cracks is studied quantitatively by means of light microscopy at the crack surface. But, almost no results of the healing inside a specimen can be given by such a microscopic test, unless you destroy the sample. Thin sections for example need sawing of the specimen, possibly damaging the formed crystals in the crack. Characterization of the healing only from the surface is not sufficient to evaluate or verify the extent of healing throughout the entire specimen. This information, however, is very important to give insight in the extent of healing and its effectiveness, as the healing efficiency relies on the amount and distribution of the formed healing products. Therefore, one needs to quantify the amount in the whole specimen, in three dimensions, but without disturbing the formed healing products. High-resolution X-ray computed microtomography (X-ray μCT) becomes therefore useful. It is a non-destructive technique which generates three-dimensional images by combining a series of cross-sectional micrographs. Those micrographs are based on the attenuation of X-rays at different positions and depend on the atomic number and density of the material [35]. The total amount and the distribution of the healing products in the cementitious matrix can hereby be investigated without disturbing the formed hydration products inside the crack. In addition, because X-ray μCT is non-destructive, the internal structure of the same sample can be compared and analysed before and after healing.

An X-ray study already proved bio-deposition [36] and bacterial-based self-healing and provided a nice quantification of the amount of healing products [37,38]. This bacterial healing occurs to a higher extent compared to autogenous healing as its mechanism not only depends on the available reagents in the cementitious matrix, but it is a result of the bacterial metabolism. Sealing by precipitation in high-strength low-permeability concrete was already studied by means of micro-focus X-ray CT [39]. It was found that precipitation occurred only near the exterior (at the surface) of the specimen and only the first 0 till 50–200 μm of the cracks (crack width of 100 μm) was filled with precipitation. However, the test specimens were stored in seawater. The observed precipitation could thus also be the result of a combination of autogenous healing and salt formation. A recent μCT study [40] gave results on the healing properties of strain-hardening materials. It was found that the extent and rate of healing strongly depended on the initial surface crack width. Also, the region of a crack close to the surface (from 0 to 50–150 μm below the surface) could be sealed quickly with crystalline precipitates. At greater depths, the healing process takes longer and is more likely due to continued hydration and puzzolanic reactions. The study was done on V-shaped cracks after performing four-point-bending tests and Fan & Li studied two average crack widths (31 μm and 102 μm) under wet/dry cycles (24 h in water and 24 h at 50% RH). For the 102 μm average crack, the total crack volume decreased 2.4%, 7.2% and 10.8% after 1, 5 and 10 wet/dry cycles, respectively. In the 31 μm average crack, this was 13.2%, 55.3% and 73.1%, respectively. Smaller cracks are able to close by autogenous healing. For the large crack, 30% of the crack was healed in the region from the surface to 50–150 μm below the top surface. Beyond this shallow region, the extent of healing had a dramatic drop.

The aim of this research is to demonstrate the effective use of superabsorbent polymers to stimulate autogenous healing. The self-healing efficiency was studied in the interior of the specimen by means of X-ray μCT and the healing products were visualized three-dimensionally. The amount of healing within the cracks was quantified as a function of the distance from the surface. The formed healing products were additionally studied by means of scanning electron microscopy and energy-dispersive X-ray spectroscopy for elemental mapping/analysis.

2. Materials and methods

2.1. Materials

The strain-hardening cementitious mixtures contained CEM I 52.5 N (Holcim, Belgium), Class F fly ash (OBBC, Belgium), silica sand (D50 = 170 μm; Sibelco, Belgium), water, polycarboxylate superplasticizer (Glenium 51, conc. 35%; BASF, Germany), and Polyvinyl-Alcohol (PVA) fibres (2 v%; 15 dtex; 8 mm cutting length; 12 cN/dtex tenacity; Kuraray, Japan). The mixture composition, based on [14], is given in Table 1. In the mixture containing SAP, one mass-percentage (1 m%) of cement weight of SAP was added on top of the used mixture without SAPs.

In Snoeck et al. [20,34] it was concluded that increasing the amount of SAP from 0.5 m% to 1 m% also increased the regain in strength. The latter is also the best amount considering self-sealing [31] and this amount was therefore used in this research. The amount of SAPs added in this research is relatively high (1 m%), as those amounts are mostly used to receive self-sealing and self-healing rather than to mitigate autogenous shrinkage (typical amounts of 0.3–0.4 m%).

The type of SAP (BASF, Germany) used, was a cross-linked potassium salt polyacrylate. The SAP was produced through bulk polymerization and consisted of irregularly shaped particles (476.6 ± 52.9 μm). The size is ideal to promote self-sealing [31] and self-healing [20]. To assess the sealing capacity of the SAP, the swelling capacity was calculated from the volume increase between the vacuum dried state and the saturated state of the SAP. A test fluid was added to vacuum dried SAP particles and the whole was filtered after one day. The amount of filtered fluid was recorded. To ensure there was no influence of the filter paper, the latter was saturated with the fluid prior to filtration. The difference in mass of test fluid is the amount of test fluid absorbed by the SAP. By dividing this value by the initial mass of the SAP, the absorption capacity was determined. These measurements were performed with de-ionized water and filtered cement slurry (obtained by mixing 10 g CEM I 52.5 N in 100 g of de-ionized water) [20,34]. The absorption capacity was 283 ± 2 g de-ionized water/g SAP and 58 ± 2 g filtered cement slurry/g SAP. The SAP particles were able to extract 28.1%, 84.0% and 394.1% of their weight in moisture from the air in an environment with 60, 90 and 98% RH, respectively. The latter was determined by using dynamic vapour sorption (DVS) in which the relative humidity can be changed in a controlled nitrogen environment while measuring the weight of the sample [41].