REPEATED AUTOGENOUS HEALING IN CEMENTITIOUS COMPOSITES WITH MICROFIBRES AND SUPERABSORBENT POLYMERS

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Abstract
Cementitious materials are sensitive to crack formation and it would be beneficial if the material could reach again the original strength. Autogenous healing is an already-present feature in cementitious materials, but it is an inferior mechanism as it can only heal cracks up to 50 µm in the presence of water. Therefore, a cementitious material with synthetic microfibres and superabsorbent polymers (SAPs) is proposed. The microfibres will cause multiple crack formation and will result in a vast amount of small healable cracks. If superabsorbent polymers (SAPs) are also included, the self-healing can be promoted as SAPs are able to extract moisture from the environment and to provide it to the cementitious matrix for autogenous healing. But, if the building blocks are exhausted due to a first healing cycle, healing at second reloading may be less efficient. A crack can thus possibly heal only once. In this study, the ability of (promoted) autogenous healing to repeat itself is investigated by comparing the mechanical properties after performing repeated four-point-bending tests. Specimens are able to heal and to regain some of the mechanical properties after being preloaded and pre-cracked under four-point-bending. Even if those healed samples are reloaded for a second time, there is some regain in mechanical properties. If SAPs are added, there is even healing in an environment without liquid water (relative humidity of more than 90%), also in repeated healing actions. The cementitious composite with microfibres and SAPs thus shows partial repeatability of self-healing.

Keywords
Self-healing, four-point-bending, durability, hydrogels, CaCO₃
1 INTRODUCTION

Cracks occur in concrete due to its low tensile strength. These cracks have a negative effect on the durability of the structure because harmful substances may enter and deteriorate the concrete. This results in repair works which are labour-intensive and expensive. Concrete, however, has the ability to heal itself by closing small cracks, referred to as autogenous healing.

Two mechanisms are mainly responsible for this form of passive healing: the continued hydration of unhydrated cement grains and the precipitation of calcium carbonate (CaCO$_3$) [1, 2]. In the last case, CO$_2$ dissolves in water to react with Ca$^{2+}$ ions present in the mortar matrix (Fig. 1). A detailed study on the autogenous healing of cracks in concrete was performed by Edvardsen [3]. She found a reduced permeability in time due to autogenous healing and performed an intensive study on the laws which govern the nucleation and crystal growth processes. The decrease in permeability demonstrates the potential of the autogenous healing as there is less intrusion of durability-decreasing substances.

![Diagram of autogenous healing mechanism](image)

(a) (b)

Figure 1: Autogenous healing mechanism by further hydration (a) and calcium carbonate crystallization (b). Figure redrafted after ter Heide [4].

A small crack, with a crack width smaller than 50 $\mu$m, is needed for high-strength concrete to be able to heal the crack completely. If not, the products available in the mortar mix are consumed before the crack is effectively closed. The wanted cracking behaviour is obtained by adding microfibers to the mortar mix, typically 2 vol%. This results in a concrete with a high tensile ductility, strain hardening and small crack widths in the range of 20–80 $\mu$m [5, 6]. Cracks smaller than 50 $\mu$m show complete healing and cracks up to 150 $\mu$m show partial healing [5]. Without the presence of water, the composite does not heal. Recent studies aimed at a crack width of maximum 30 $\mu$m to ensure a complete healing of the crack by means of autogenous healing [7].

The self-healing capability of concrete can be improved by adding superabsorbent polymers (SAPs). SAPs have the ability to absorb and retain a vast amount of liquid without dissolving (Fig. 2). The use of SAPs to promote the self-healing is dual. SAP-particles swell during the mixing process and shrink during the hardening of the concrete, leaving behind macropores [7, 8]. These macropores act as initial flaws and promote multiple cracking. Secondly, SAP-particles are very useful during the self-healing as they absorb water during wet periods and slowly release it during dry periods. Water is thus continuously available for
the self-healing process [7] and the composite showed a complete regain in mechanical properties, with healing of cracks up to 130 μm. Also, as the SAPs swell, they will initially seal a crack from intruding fluids, thus increasing the durability [9]. In this way, a smart cementitious material which is reliable and independent from external conditions is acquired.

Figure 2: Visualization of a dry and saturated superabsorbent polymer particle.

If we consider Fig. 3a, the durability performance of a construction is higher than the required performance. But, if there is excessive loading and/or cracking, this durability parameter may shift to lower values and degradation may occur. If one does not notice the failure and does not repair, the construction may decline. The dashed curve shows the costs. The costs will increase stepwise in time due to manual repair and maintenance monitoring [10].

Figure 3: Durability performance and costs as a function of time for manual repair (a), and for a self-healing material (b). Figure redrafted after van Breugel [10].

If we would use an ideal self-healing material, the durability would be guaranteed (Fig. 3b). But, in case of autogenous healing, the amount of available building blocks is consumed in time, thus limiting the possibility of renewed crack healing. So, the question rose whether this autogenous healing could be repeated. What will happen when autogenously healed specimens are subjected to cracking again? In this paper, the possibility of a repeated autogenous healing is investigated by performing four-point-bending tests on self-healing materials.
2 MATERIALS AND METHODS

2.1 Materials
The mortar mixtures contain 608 kg/m³ CEM I 52.5 N, 608 kg/m³ Class F fly ash, 426 kg/m³ silica sand (D_{50} = 170 μm; Sibelco, Belgium), 365 kg/m³ water, a polycarboxylate superplasticizer (Glenium 51, conc. 35%), 2 vol% of Polyvinyl-Alcohol (PVA) fibres (Kuraray, Japan), and a varying amount of SAP expressed as mass-% (m%) of cement weight. Two types of SAP from BASF were used: SAP A being a copolymer of acrylamide and sodium acrylate (particle size 100.0 ± 21.5 μm); SAP B, a crosslinked potassium salt polyacrylate (476.6 ± 52.9 μm).

To assess the swelling capacity of SAP, the swelling capacity was calculated from the volume increase between the vacuum dried state and the saturated state. A 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 measurements were performed with de-ionized water and filtered cement slurry (obtained by mixing 10 g CEM 1 in 100 g of de-ionized water). The absorption capacity is 305 ± 4 g de-ionized water/g SAP A, 283 ± 2 g de-ionized water/g SAP B, 61 ± 1 g filtered cement slurry/g SAP A and 58 ± 2 g filtered cement slurry/g SAP B. The SAP particles are also able to extract 4 times their weight in moisture from an environment at 98% RH.

2.2 Methods
2.2.1 Mixing, casting and storage procedures
First, the solid components (cement, fly ash and SAPs) were equally distributed with a mortar mixer. Then, water and superplasticizer (30 s at 140 rpm) were added. Silica sand was added for the next 30 s at 140 rpm. To ensure a homogeneous dispersion of all components, the speed was increased for the following 30 s to 285 rpm. The edges of the bowl were scraped and the there was a total resting period of 90 s. Next, at a speed of 140 rpm, microfibres were slowly added during 30 s. The final step was mixing for 60 s at 285 rpm.

A comparison of the flow value of mixtures with and without SAPs was used to reflect the absorption by the SAPs in the mortar mixture [11]. The material was hereby spread by jolting a plate 15 times. The amount of additional mixing water was increased several times in several mixes with the same amount of SAPs until the flow value corresponded to the flow value of the same mixture without SAPs.

Moulds were filled and the samples were compacted by jolting a plate 60 times. The samples were demoulded after 24 h and were stored at a relative humidity of 95 ± 5% and 20 ± 2°C until the age of 28 days. Series used for four-point bending tests (Table 1), consisted of minimum three 160 × 40 × 10 mm³ samples with 2 vol% of microfibres.

2.2.2 Four-point-bending and curing conditions
Cracks were created in the specimens by a four-point-bending test at the age of 28 days. A servo hydraulic testing system (Walter+Bai DB 250/15) ensured a displacement-controlled test (0.0015 mm/s to imitate a quasi-static load). The strain at the bottom side of the specimen was limited to 1%. This strain is lower than the maximum strain, so the service cracks could be studied. After cracking, the samples were cured at 20 ± 2°C by applying wet/dry cycles (alternatively stored in water for 12 h, and at a relative humidity (RH) of 60% for 12 h), or by placing them in a room with a RH > 90% or RH = 60%.
Table 1: Explanation of the different samples codes.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$m%$ [%]</th>
<th>SAP type</th>
<th>Curing</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 60</td>
<td>0</td>
<td>-</td>
<td>RH = 60%</td>
</tr>
<tr>
<td>0 - 90</td>
<td>0</td>
<td>-</td>
<td>RH &gt; 90%</td>
</tr>
<tr>
<td>0 - wd</td>
<td>0</td>
<td>-</td>
<td>wet/dry</td>
</tr>
<tr>
<td>0.5A - 60</td>
<td>0.5</td>
<td>A</td>
<td>RH = 60%</td>
</tr>
<tr>
<td>0.5A - 90</td>
<td>0.5</td>
<td>A</td>
<td>RH &gt; 90%</td>
</tr>
<tr>
<td>0.5A - wd</td>
<td>0.5</td>
<td>A</td>
<td>wet/dry</td>
</tr>
<tr>
<td>0.5B - 60</td>
<td>0.5</td>
<td>B</td>
<td>RH = 60%</td>
</tr>
<tr>
<td>0.5B - 90</td>
<td>0.5</td>
<td>B</td>
<td>RH &gt; 90%</td>
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<tr>
<td>0.5B - wd</td>
<td>0.5</td>
<td>B</td>
<td>wet/dry</td>
</tr>
<tr>
<td>1B - 60</td>
<td>1</td>
<td>B</td>
<td>RH = 60%</td>
</tr>
<tr>
<td>1B - 90</td>
<td>1</td>
<td>B</td>
<td>RH &gt; 90%</td>
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<tr>
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<td>B</td>
<td>wet/dry</td>
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After a period of 28 days, the specimens were reloaded in four-point-bending and the mechanical properties obtained during the first and second loading cycle were compared. These are the first-cracking-strength and the regain in first-cracking-strength. The first-cracking-strength is obtained just before the first drop in stress due to an unstable extension in the matrix fibre tunnel. Again, the strain was limited to 1%. After another 28 days of curing, the specimens were reloaded for a second time, till failure in the third loading cycle. From the obtained stress-strain curves, the first-cracking-strength and regain in first-cracking-strength were compared once again.

Figure 4 represents the stress-strain curves of a specimen healed in wet/dry-cycles and three parts are visible. The first loading part is the preloading (strain from 0% until 1%), the second part is the first reloading (an additional strain of 1%) and the third part is the second reloading (until failure).

![Stress-strain curve](image)

Figure 4: Typical stress-strain curve with the different cracking and healing stages, together with the indication of first-cracking-strengths $\sigma_{fc}$ and the slopes of the curve at every stage.

During the healing periods, microscopic observations were performed at regular time intervals by means of a stereo microscope (Leica S8 APO with DFC 295 camera). The visual closure hereby served as a qualitative measurement for the autogenous healing capacity.
3 RESULTS

Due to the addition of microfibers, multiple cracking was observed, giving all samples a ductile strain-hardening behaviour. The crack width is hereby a very important parameter. If large cracks are formed, the building blocks will be consumed after some time and the autogenous healing will no longer be optimal. In this research, the crack widths were limited to 30-50 μm, as was also the case in [5]. Due to the addition of SAP particles, this multiple cracking behaviour was enhanced. The macropores formed by the SAPs act as crack initiators, increasing the ductile behaviour. Also, the crack width tended to decrease slightly, but the difference was not statistical significant. Due to partial reopening of the cracks at first reloading, the crack width increased slightly. Again, the differences were not significantly different. This was confirmed by microscopic observations and analysis of the crack widths.

By examining the crack width before and after curing, the percentage of crack closure could be quantified. Figure 5a shows the visual crack closure in function of the initial crack width after the first healing cycle. Results show that cracks up to 30 μm heal completely and up to 150 μm heal partly when specimens are subjected to wet/dry cycles. Also Yang [5] and Li et al. [6] had similar results, but their limit of total crack healing was 50 μm instead of 30 μm. They also showed that, when stored in ambient air (without any liquid water available), samples cannot heal. It is clear that specimens healed under wet/dry cycles exhibit the best healing as a fair amount of water is available for autogenous healing. If superabsorbent polymers are added as well, the amount of healing is slightly higher. This is due to the fact that SAPs are able to seal a crack from intruding fluids, reducing the flow and thus establishing better circumstances for autogenous healing. Secondly, water is also available during the dry periods of the wet/dry cycle, thus increasing the possibility of autogenous crack healing. At a relative humidity of more than 90%, the healing is far less. However, specimens with superabsorbent polymers show partial healing. As SAPs are able to extract moisture from the environment, they will swell to a small extent, and then they will provide the water for further hydration of unhydrated binder particles in the crack. At a relative humidity of 60%, only the mixtures with SAPs show partial healing.

![Crack closure as a function of initial crack width](image)

**Figure 5:** Crack closure [-] after the first healing stage as a function of initial crack width (a), and a comparison between the first and second healing stage (b).
After the first healing period, most of the building blocks for self-healing, i.e. unhydrated cement particles and Ca\(^{2+}\) ions are consumed, reducing the possibility for autogenous healing. Specimens with SAPs in the second wet/dry cycle for example show an inferior visual closure of the crack compared to the same specimens in the first healing cycle (Fig. 5b).

Cracks may even be closed with deposited crystals after the two healing cycles. The strength of the new material was investigated by analysing the results from the loading experiments. The first-cracking-strength of all studied mixtures is shown in Fig. 6a. The first-cracking-strength for the mixtures without SAPs is higher than for the mixtures with SAP A. Due to the macropores in the mixtures with SAP-particles, the active cross-section is reduced, resulting in a lower first-cracking-strength. The macropores formed after emptying the water-filled SAP inclusions may promote multiple cracking behaviour as they serve as crack initiators. The strength is not reduced significantly when using the larger SAP B particle.

![Graph](image_url)

(a) First-cracking-strength $\sigma_{fc}$ at 28 days with standard deviation (a), and regain in first-cracking-strength after the first and second healing period (b) for all studied mixtures.

Samples with SAPs show a higher regain in first-cracking-strength than the SAP-free samples in all studied healing conditions (Fig. 6b). The regained first-cracking-strength for the samples healed in wet/dry-cycles is higher than for those healed in an environment with a RV > 90% which, in turn, is higher than for those healed in an environment with a RV = 60%. Healing in wet/dry-cycles provides the necessary water for the hydration of cement particles and the puzzolanic reaction of fly ash. This results in a regain in first-cracking-strength. The regain is higher for mixtures with SAPs than for mixtures without SAPs. In mixtures with SAPs, more water is available for the continued hydration of cement, puzzolanic activity and precipitation of calcium carbonate due to the absorption capacity of the SAP-particles. Increasing the amount of SAP from 0.5 m\% to 1 m\% also increases the regain in strength.

Ca\(^{2+}\) ions are consumed at the crack faces after the first healing period. This is visible in the results on visual crack closure and the regain in mechanical properties. The visual crack closure is about 20% lower when the specimens are reloaded for a second time. During the first reloading, only a limited number of new cracks were formed. So mostly the previous healed cracks reopen and there is a limited possibility for a renewed autogenous healing of the
crack. Most unhydrated cement particles are now hydrated and the Ca$^{2+}$ ions are mostly consumed to form calcium carbonate crystals. In the second healing stage, Ca$^{2+}$ ions present in the interior of the matrix need to diffuse towards the crack face. So, the crystallization becomes diffusion-controlled instead of surface-controlled as free Ca$^{2+}$ ions in the matrix need to travel towards the crack faces. This limits the speed of possible crystallization and thus autogenous healing and regain in mechanical properties.

SAP particles not only tend to increase the healing capacity at the first healing stage (from 46% to 75% in wet/dry cycles), but also at the second healing stage. The regain is still 66% at second reloading. Without the superabsorbent polymers, this value was only 28%.

The overall healing and closure of a crack may lead to less ingress of potentially harmful substances, thus increasing the durability and service life of civil structures.

4 CONCLUSIONS

SAP particles promote self-healing by providing water upon crack formation and this results in more visual crack closure and more regain in mechanical properties. The main mechanisms of self-healing are further hydration of unhydrated particles and the precipitation of CaCO$_3$ on the crack faces. To a certain degree the autogenous healing capability of cementitious materials is maintained during subsequent loading cycles. Cracks heal close during a second healing cycle and there is a regain in first-cracking-strength of specimens stored in wet/dry cycles. Even in an environment with a RV > 90%, there is a non-negligible healing capacity noticeable. Even though the active cross-section is reduced due to the macro pores resulting in a smaller first-cracking-strength, this effect is not significant when using larger SAP particles. The smart material with SAP B is thus an excellent material to use in future building applications.

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