Autogenous healing of cementitious materials promoted by superabsorbent polymers studied by means of X-ray computed microtomography

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Autogenous healing of cracks may offer a solution for brittle cementitious materials. Further cement hydration and calcium carbonate crystallization will hereby heal the cracks if sufficient building blocks and water are present. The building blocks are available through the well-designed mixture with a low water-to-binder ratio and water is available through the inclusion of superabsorbent polymers. These polymers are able to extract moisture and fluids from the environment and to provide it to the cementitious matrix for autogenous healing. This healing will lead to the regain in mechanical properties, as already found in previous research. As the crack seems to be completely visually closed at the surface, one may ask whether this healing is also 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 after autogenous healing. It was found that the autogenous healing in a cementitious material is dependent on the crack depth. Only the first part of the crack is closed by crystal formation in case of wet/dry cycles. In combination with superabsorbent polymers, the extent of healing was more substantial, even in the interior of the crack. There was even partial healing in the interior of the crack when stored at a relative humidity of 60% or more than 90%, but only in mixtures containing superabsorbent polymers. The smart cementitious material with superabsorbent polymers thus is an excellent material to use in future building applications as the healing extent is improved.
1. INTRODUCTION

Concrete cracks give an unsafe feeling and are aesthetically unwanted. Manual repair of these cracks is not only time-consuming, it is also very expensive. It would thus be beneficial if the material could heal on its own. This feature is available in cementitious materials with synthetic microfibres and superabsorbent polymers (SAPs) as additives. The microfibres restrict the crack width and the superabsorbent polymers provide the water. The extent of healing inside a specimen is, however, of great importance for the overall regain in mechanical properties. Therefore, high resolution X-ray microtomography (µCT) was used to visualize the healing. The technique already proved to be useful to visualize the healing in strain-hardening cementitious materials [1].

2. MATERIALS

The mortar mixtures contained CEM I 52.5 N, Class F fly ash (FA/CEM = 1), fine silica sand M34 from Sibelco (M34/B = 0.35), water (W/B = 0.30), polycarboxylate superplasticizer Glenium 51 (Spl/B = 0.0097), 2 volume-% of Polyvinyl-alcohol (PVA) fibres from Kuraray, and 1 m% of SAP expressed as mass-% relative to the cement weight. Additional water (51 l) was used to compensate for the loss in workability. The composition of the mixtures used, is shown in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>CEM</th>
<th>FA</th>
<th>M34</th>
<th>W</th>
<th>Spl</th>
<th>PVA</th>
<th>SAP</th>
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</thead>
<tbody>
<tr>
<td>REF</td>
<td>608</td>
<td>608</td>
<td>426</td>
<td>365</td>
<td>11.8</td>
<td>26</td>
<td>-</td>
</tr>
<tr>
<td>SAP</td>
<td>572</td>
<td>572</td>
<td>400</td>
<td>343</td>
<td>11.1</td>
<td>26</td>
<td>5.72</td>
</tr>
</tbody>
</table>

The type of SAP from BASF was a cross-linked potassium salt polyacrylate (476.6 ± 52.9 µm). The absorption capacity (Table 2) was determined by means of a filtration test and the moisture uptake by dynamic vapor sorption tests. The cement filtrate was obtained by mixing 10 g CEM I 52.5 N in 100 ml de-mineralized water for 6 h and subsequent filtration. All SAPs were vacuum dried with silica gel in a desiccator with a relative humidity (RH) of 3% prior to testing.

<table>
<thead>
<tr>
<th>SAP</th>
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<tbody>
<tr>
<td>De-mineralized water (pH = 6.5)</td>
<td>283 ± 2</td>
</tr>
<tr>
<td>Cement filtrate (pH = 12.8)</td>
<td>58 ± 2</td>
</tr>
<tr>
<td>at 60/90/98% RH</td>
<td>0.28/0.84/3.94</td>
</tr>
</tbody>
</table>

3. METHODS

Cracks were created by means of a Brazilian splitting test in small cylindrical specimens with a diameter of 6 mm and a height of 10 mm. After cracking, the samples were scanned at an age of 28 days by means of µCT and subsequently stored at 20 ± 2°C by applying wet/dry cycles (alternatively 1 h stored in water and 23 h at 60% RH), or by placing them in a climate chamber with a RH > 90% or 60%. After the healing period, the specimens were scanned again to study the formed healing products.
4. RESULTS

After performing microtomography before and after healing, both data sets could be subtracted. The result was the amount of formed healing products. By means of post-processing software, the amount of healing products could be calculated as a function of the total height of the specimen. This was done by visualizing the healed products along the vertical axis of the cylindrical specimen with a step size of 6 µm (which is the voxel size). These results are shown in Figure 1.

Figure 1: Amount of healing products over the total height of the specimen with REF RH>90% (grey), SAP RH=60% (yellow), SAP RH>90% (green), REF in wet/dry cycles (black) and SAP in wet/dry cycles (blue).

Reference samples without SAPs and without the presence of liquid water showed almost no healing. The moisture in the healing conditions was not enough to stimulate autogenous healing. When stored in wet/dry cycles, the amount of healing was higher. About 1-2% of the total cylindrical surface area contained healing products. More healing products were found at the top and bottom of the specimen. This is due to the presence of carbon dioxide near the surface, stimulating the formation of white calcium carbonate crystals.

If superabsorbent polymers were used, the healing increased substantively (Figure 2). After wet/dry cycles, the healing was more than double the amount if no SAPs were used. Due to the retaining of calcium-rich pore fluid during dry periods, more water is steadily provided towards the cementitious matrix for autogenous healing. In this way, the self-healing was stimulated. Even at 60 or 90% relative humidity, the amount of healing was noteworthy. This is because the SAPs are able to extract moisture from the environment and to provide it towards the cementitious matrix. This partly stimulated autogenous healing. The healing was about half of the one of specimens stored in wet/dry cycles but without SAP particles.

Elemental Dispersive X-ray analysis showed that the formed material was mainly composed of calcium carbonate (CaCO$_3$) (partly Ca(OH)$_2$ and calcium silicate hydrates (C-S-H)). This led to a regain in the mechanical properties as found in [2].
5. CONCLUSIONS

µCT is an extremely useful non-destructive technique to study the extent and amount of autogenous healing of a strain-hardening cementitious material. The combination of microfibres and superabsorbent polymers enhances the autogenous healing capacity. The material is able to show self-healing, even in standard laboratory conditions. SAPs are able to extract moisture from the environment and provide the moisture to the matrix for self-healing. They are promising materials to be used for self-healing.

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REFERENCES