Application of sodium silicate solution as self-healing agent in cementitious materials

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ABSTRACT: The application of sodium silicate solution as self-healing agent was investigated in this paper. The sodium silicate solution was stored in capsules that were embedded in the engineering cementitious composites (ECC). Three-point bending tests were carried out to pre-crack the ECC specimens at the age of 14 days. The healing agent was released into the cracks to promote self-healing. The self-healing phenomenon was observed by environmental scanning electron microscopy (ESEM). The X-ray microanalysis (EDS) was also applied to determine the chemical elements of the healing products. From the EDS results, the main chemical elements of the healing products are Si, O, Ca and Na. Based on the analysis of the Ca/Si and Na/Si ratio, it can be concluded that the healing products formed in the cracks are the composites of CSH and sodium silicate. Thus the main mechanism of self-healing by sodium silicate solution is the reaction of calcium cations with the dissolved sodium silicate and the crystallization of the sodium silicate. The pre-cracked specimens after self-healing were bent again to evaluate the strength recovery efficiency. The results demonstrate that the concentration of the sodium silicate solution is the main influence factor which determines the self-healing efficiency.

1 INTRODUCTION

Self-healing of cementitious materials is a well-known phenomenon. It was directly observed in cracked water pipes and also found in some old structures (Turner (1937), Nijland et al. (2007)). These observations suggest that the cementitious materials are able to heal the cracks under certain circumstance and thus prolong the service life of concrete structures. Therefore, self-healing of cementitious materials has attracted much attention in the last decade and many researchers explore how to promote self-healing of concrete structures efficiently. Dry (1996) used adhesive liquid core fibers to realize the repair of cracks in concrete. Nevertheless, it is more appropriate to call this repair method “self-sealing” rather than “self-healing”. Jonkers (2010) was exploring the self-healing of concrete with the help of bacteria. Alternatively, sodium silicate solution was applied to promote self-healing in concrete (webpage, 2010). However, no detailed results have been published by now. The mechanism and efficiency of self-healing by sodium silicate solution are not clear yet.

In this paper, the mechanism of self-healing by sodium silicate solution was discussed and the efficiency of this healing agent was evaluated. In order to do so, sodium silicate solution capsules were made and embedded into engineering cementitious composites (ECC²). Given the well controlled crack width of ECC, this composite was chosen as the research objective materials, which was originally invented by Li (1993) and modified by Zhou et al (2010).

²ECC is a class of ultra ductile fiber reinforced cementitious composites originally invented at University of Michigan. This material is characterized by high ductility in the range of 3-7%, tight crack width of around 60 µm and relatively low fiber content of 2% or less by volume (Zhou, 2011).
Three-point bending tests were carried out to pre-crack the ECC specimens at the age of 14 days. When the specimens cracked, the sodium silicate solution was released into the cracks to induce the self-healing. The self-healing phenomenon in the cracks was observed by environmental scanning electron microscopy (ESEM). The chemical elements of the healing products formed in the cracks were determined by X-ray microanalysis (EDS). According to the chemical elements of the healing products, the mechanism of self-healing by sodium silicate solution was analyzed. Finally, the healing efficiency was quantified by measuring the recovery of mechanical properties of the specimens after healing for 28 days, including the flexural strength, stiffness and deflection capacity. Deflection capacity herein is defined as the deflection that corresponds to maximal bending stress.

2 EXPERIMENTAL PROGRAMS

The experimental program, including three different schemes, is shown in Figure 1. The mix proportion of the ECC and the details of specimens for different tests were shown in Table 1 and Table 2, respectively.

![Figure 1. Experimental program for studying self-healing of ECC](image)

Table 1. Mix composition of ECC

<table>
<thead>
<tr>
<th>CEMI 42.5 N</th>
<th>Limestone powder</th>
<th>BFS</th>
<th>Water/powder ratio</th>
<th>Super plasticizer</th>
<th>PVA fiber (by volume, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>2</td>
<td>1.4</td>
<td>0.26</td>
<td>0.02</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 2. Details of specimens for different experimental programs

<table>
<thead>
<tr>
<th>Series No.</th>
<th>Volume fraction of capsule (%)</th>
<th>Sodium silicate concentration (g/100g)</th>
<th>Experimental programs</th>
<th>Total age (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>--</td>
<td>Scheme A</td>
<td>14</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>Empty capsule</td>
<td>Scheme A</td>
<td>14</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>Empty capsule</td>
<td>Scheme B</td>
<td>42</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>20</td>
<td>Scheme B, C</td>
<td>42</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>10</td>
<td>Scheme B</td>
<td>42</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>0 (Water)</td>
<td>Scheme B</td>
<td>42</td>
</tr>
</tbody>
</table>

For the mixing of ECC, the procedures were carried out following the reference (Zhou et al (2010)). The fresh ECC was casted into prisms with the size of 160 mm × 40 mm × 40 mm. During casting, the capsules with the diameter of about 5 mm were embedded in the fresh ECC.
specimens by hand. The volume fraction of the capsules was 5%. In order to manufacture the capsules, the sodium silicate solution was stored in sponge and sealed by wax. As shown in Figure 1, after casting all the specimens were first cured under sealed conditions at temperature of 20°C for 14 days. Afterwards, the specimens divided into two groups were bent by three-point bending machine. The support span of the bending test is 110 mm. For the first group, the specimens were bent until failure, indicated as Scheme A. For the second group, the specimens were bent to 1.0 mm to induce cracks as described in Scheme B and C. The cracked specimens in Scheme B and C were cured again for another 28 days in order to realize the self-healing. Finally, the flexural strength, stiffness and deflection capacity of the specimens after self-healing were tested by three-point bending. The specimens in Scheme C were observed by ESEM and tested by EDS. The details of the experiments are presented in the following sections.

2.1 Three-point bending test

The three-point bending tests, as shown in Figure 2, were carried out to induce cracks and to test the recovery mechanical properties after self-healing. The loading speed of the three-point bending was 0.01 mm/s. To induce cracks, the specimens were bent to 1.0 mm of the deflection. As shown in Figure 3, after pre-cracking, the solution stored in the capsules was released and transported into the matrixes along the cracks. The pre-cracked specimens were sealed by tape to prevent the water evaporation in the solution. When tested after healing, the specimens were bent until final failure.

![Figure 2. The setup of three-point bending](image2)

![Figure 3. Pre-cracked specimens](image3)

![Figure 4. The microscope photos of the samples](image4)
2.2  **ESEM observation and X-ray microanalysis**

The phenomenon of self-healing was observed by ESEM. The chemical properties of the healing products formed inside the cracks were investigated by EDS. There were two samples prepared for this test, as shown in Figure 4. In Sample A, one of a crack’s inside surfaces was exposed as the ESEM observing surface, while in Sample B a crack’s inside surfaces were perpendicular to the observing surface.

![Image of samples](image)

**Figure 5. The ESEM images of the samples**

3  **EXPERIMENTAL RESULTS AND DISCUSSION**

3.1  **ESEM observation and EDS test**

The ESEM images of self-healing behaviors in the cracks are shown in Figure 5. It is obvious that some solid phases were formed in the cracks. Some microcracks formed in the healing products during the vacuuming. The healing products in Pos1, as shown in the Figure 5(b), were tested by EDS technique. The corresponding results are presented in Figure 6. In this research, the healing products in 8 different positions were tested.

From the EDS analysis, the main chemical elements of the healing products are Si, O, Ca and Na. What should be mentioned is that there is no Ca in the original healing agent – sodium silicate solution. In comparison, the Ca/Si module ratio of the healing products formed in the cracks ranges from 0.26 to 0.76. Moreover, the Na/Si module ratio linearly decreases with the increase of Ca/Si module ratio, which is presented in Figure 7. Since soluble silicates react almost instantaneously with multivalent metal cations to form the corresponding insoluble metal silicate (Sheppard, (1986)), the chemical element Ca in the healing products reveals that the calcium cations from the ECC matrixes react with the sodium silicate solution and thus the CSH is formed in the cracks. However, there are not sufficient calcium cations to replace all the sodium cations in the solution. The still available sodium silicate crystallizes when the water of the solution evaporates or transports into the ECC matrixes. This is the reason why the Na/Si module ratio in the healing products increases with the decrease of the Ca/Si module ratio. Therefore, it can be concluded that the healing products in the cracks are the composites of CSH and sodium silicate. In terms of morphology, as presented in Figure 8, there are more microcracks formed in the healing products with low Ca/Si than that with high Ca/Si.

According to the discussion above, the main mechanism of the self-healing promoted by sodium silicate solution is the reaction of calcium cations with the dissolved sodium silicate and the crystallization of the still available sodium silicate.
Figure 6. The chemical elements of the healing products tested by EDS in Pos1

Figure 7. Comparison between Ca/Si and Na/Si

Figure 8. Morphology of the healing products with low Ca/Si ratio and high Ca/Si ratio

3.2 Impact of capsules on the mechanical properties

Figure 9 shows the mechanical behavior of the specimens with and without capsules. Both the flexural strength and the deflection capacity (the deflection that corresponds to the maximal bending stress) of the specimens of Series 2 (with capsules) show an apparent reduction compared with those in Series 1 (without capsules). It is obvious that the reduction can be attributed to the existence of the capsules. Correspondingly, the flexural strength reduces by about 27%, while the deflection capacity decreases by around 40%. Moreover, the deflection in the first crack also reduces by about 50%. Therefore, the negative effect of capsules on the mechanical properties should be taken into account when employing capsules to promote self-healing of concrete.

3.3 Recovery of mechanical properties

After self-healing of the cracks for 28 days the specimens were bent again to evaluate the recovery efficiency of the mechanical properties. The mechanical behavior of the specimens after self-healing is presented in Figure 10. The details of each series specimens are shown in Table 2. The mechanical properties of Series 2 are taken as the reference and the normalized values of other series are also presented in Figure 11.
Figure 9. Mechanical behaviors of specimens with and without capsules

Figure 10. Mechanical behaviors after self-healing

Figure 11. Comparison of recovery mechanical properties for Series 2 – Series 6

From Figure 10 and Figure 11, it can be learned that the self-healing takes place in the cracks revealed by the improvement of the mechanical properties in the pre-cracked specimens, compared to those of the specimens without self-healing agent. As described in Table 2, the specimens of Series 2 contain 5% (by volume) empty capsules. As there is no self-healing agent in the capsules, the mechanical properties of the specimens of Series 2 are not improved apparently, which are shown in Figure 10 and Figure 11. In contrast, the mechanical properties show a significant improvement when the sodium silicate solution is employed as the self-healing agent in the capsules. The deflection capacity of the specimens after self-healing reaches 1.3 times as that of the reference (Series 2) despite of a preloaded deflection of 1.0 mm when the concentration of the sodium silicate solution is 20g/100g. Both the recovery of flexural strength and stiffness are similar to the deflection capacity. It is obvious that the recovery efficiency reduces with decreasing solution concentration. The flexural strength and stiffness of Series 5, whose solution concentration is 10g/100g, are about 88% that of Series 4. Similarly, the deflection capacity of Series 5 is about 82% that of Series 4. When water is used as self-healing promoter, the recovery efficiency of the mechanical properties drops down distinctly, see Series 6 in Figure 10 and Figure 11. This can be attributed to the amount and cohesive...
property of the healing products. From the discussion above, the healing products are expected
to be the composites of CSH and sodium silicate. The amount and cohesive property of the
healing products rise as the concentration of the sodium silicate solution increases. When the
concentration of sodium silicate is 0 (water), the amount of healing products formed in the
cracks is very limited. However, the fraction of crystallized sodium silicate in the healing
products rises with increasing the concentration of sodium silicate solution. And the high
fraction of crystallized sodium silicate is able to increase the possibility of propagation of new
microcracks in the healing products. These new formed cracks show negative effects on the
durability and the recovery of mechanical properties. Further research should be carried out to
optimize the concentration of the sodium silicate solution.

4 CONCLUSIONS

The self-healing by sodium silicate solution was explored in this paper. The sodium silicate
solution was stored in capsules that were embedded in the ECC. Three-point bending tests were
carried out to pre-crack the ECC specimens at the age of 14 days. When the specimens cracked,
the sodium silicate solution was released to promote the self-healing. The self-healing
phenomenon in the cracks was observed by ESEM. EDS tests were carried out to determine the
main chemical elements of the healing products. The main chemical elements of the healing
products are Si, O, Ca and Na. The Na/Si module ratio of the healing products decreases
linearly with the increase of Ca/Si module ratio. Based on the analysis of the Ca/Si and Na/Si
ratio, it can be concluded that the healing products formed in the cracks are the composites of
CSH and sodium silicate. Thus the main mechanism of the self-healing promoted by sodium
silicate solution is the reaction of calcium cations with the dissolved sodium silicate and the
crystallization of the sodium silicate. After self-healing of the cracks the specimens were also
bent in a three-point bending machine to evaluate the recovery efficiency. The mechanical
properties show a significant improvement when the sodium silicate solution is employed as the
self-healing agent. The recovery efficiency rises with increasing the concentration of sodium
silicate solution. The results demonstrate that the concentration of the sodium silicate solution is
the main influencing factor which determines the self-healing efficiency.

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