INFLUENCE OF SELF-COMPACTING CONCRETE COMPOSITION ON SULFURIC ACID ATTACK

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Abstract

Sulfuric acid attack on concrete has been reported for over a century. Many scientific papers deal with the issue of concrete damage due to sulfate and sulfuric attack. The introduction of self-compacting concrete introduces new questions related to the behaviour of powder-rich mixtures in a sulfate environment.

This paper describes a simple testing method to investigate the influence of the concrete composition on the sulfuric acid attack. Concrete samples have been submerged in a sulfate solution, with a pH varying between 1.7 and 2.0. The mass variation has been recorded during 26 weeks, and the compressive strength of the submerged samples has been compared with reference samples at an age of 6, 13 and 26 weeks. Results indicate that SCC with limestone filler shows a significantly higher resistance against sulphuric acid attack, compared with SCC with fly ash and quartz filler and compared with traditional concrete. The type of superplasticizer does not have a significant influence.

1. INTRODUCTION

The composition of self-compacting concrete (SCC) is quite different from the composition of traditional vibrated concrete. In many cases, a large amount of fine fillers (like limestone filler, fly ash, ...) is added, in combination with a new generation of superplasticizers (polycarboxylates) [1]. The influence of the high filler content in SCC seems to be very fundamental for the understanding of the behaviour of the material. Hydration processes can be influenced [2], resulting in a modified pore structure of the cementitious material [3]. As a consequence, transport mechanisms and durability behaviour can be different in comparison with traditional vibrated concrete [3,4]. In the RILEM state-of-the art
report on durability of SCC [5], the durability behaviour of SCC has been reported in more detail, with ample reference to the existing literature. In this paper, the sulfuric acid attack of SCC will be focussed.

Boel et al. [3,6] applied chemical tests to evaluate the resistance of SCC subjected for six weeks to a 1.5 g/l sulfuric acid \((\text{H}_2\text{SO}_4)\) with \(\text{pH} = 1\). The SCC is a powder type SCC, considering two different limestone powders and fly ash. The influence of the cement content was also studied. In sulfuric solution, the use of fly ash instead of limestone powder resulted in an increase of the rate of deterioration. It was observed that the rate of deterioration increased by reducing the dosage of cement for fixed dosage of water and powder, increasing W/C ratio (increase water content or decrease cement content).

Al-Tamimi and Sonebi [7] investigated the resistance of SCC and conventional concrete subjected to 1% \(\text{H}_2\text{SO}_4\) solution. SCC containing 47% of carboniferous limestone powder and conventional concrete of W/B ratios 0.36 and 0.46 were immersed in sulfuric solution maintained at 20°C for periods up to 18 weeks. SCC showed less deterioration than the conventional concrete. It is to be mentioned that in limestone filler based SCC the thaumasite form of sulfate attack can also occur [5]. However, this is out of the scope of this paper.

By means of accelerated laboratory experiments, the sulfuric acid attack of different SCC mixes containing different types of fillers, has been further investigated. The results are reported in this paper.

2. MATERIALS AND METHODS

2.1 SCC mixes

In this research project, 8 SCC mixes and 1 traditional concrete mix are compared. The composition of the mixes can be found in table 1. SCC 20 is the reference mix. In SCC 21, 22 and 23, the limestone filler of SCC 20 has been replaced by an equal mass of limestone filler of a different supplier, quartz filler and fly ash respectively. SCC 24 is composed with the same materials as SCC 20, but with a different superplasticizer (SP). SCC 25 contains CEM III/A 42.5 N LA (= blast furnace-cement) instead of CEM I 52.5 R HES (= ordinary Portland cement). SCC 26 and 27 have been made with a higher W/C-ratio, equal to 0.55, by replacing a part of the cement by limestone filler in case of SCC 26 or by adding more water in case of SCC 27. The amount of SP has been adapted for each mix in order to obtain a sufficient self-compartmentability.
Table 1: Composition of the mixes

<table>
<thead>
<tr>
<th>TC20</th>
<th>SCC20</th>
<th>SCC21</th>
<th>SCC22</th>
<th>SCC23</th>
<th>SCC24</th>
<th>SCC25</th>
<th>SCC26</th>
<th>SCC27</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravel 4/14 (kg/m³)</td>
<td>1225</td>
<td>698</td>
<td>698</td>
<td>698</td>
<td>698</td>
<td>698</td>
<td>698</td>
<td>698</td>
</tr>
<tr>
<td>Sand 0/5 (kg/m³)</td>
<td>640</td>
<td>853</td>
<td>853</td>
<td>853</td>
<td>853</td>
<td>853</td>
<td>853</td>
<td>853</td>
</tr>
<tr>
<td>CEM I 52.5 R HES (kg/m³)</td>
<td>360</td>
<td>360</td>
<td>360</td>
<td>360</td>
<td>360</td>
<td>-</td>
<td>300</td>
<td>360</td>
</tr>
<tr>
<td>CEM III/A 42.5 N LA (kg/m³)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>360</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Limestone filler 1 (kg/m³)</td>
<td>-</td>
<td>240</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>240</td>
<td>240</td>
<td>300</td>
</tr>
<tr>
<td>Limestone filler 2 (kg/m³)</td>
<td>-</td>
<td>-</td>
<td>240</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Quartz filler (kg/m³)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>240</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fly ash (kg/m³)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>240</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Water (kg/m³)</td>
<td>165</td>
<td>165</td>
<td>165</td>
<td>165</td>
<td>165</td>
<td>165</td>
<td>165</td>
<td>198</td>
</tr>
<tr>
<td>SP 1 (kg/m³)</td>
<td>-</td>
<td>4.50</td>
<td>5.00</td>
<td>5.00</td>
<td>6.75</td>
<td>-</td>
<td>3.50</td>
<td>3.75</td>
</tr>
<tr>
<td>SP 2 (kg/m³)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>W/C (-)</td>
<td>0.46</td>
<td>0.46</td>
<td>0.46</td>
<td>0.46</td>
<td>0.46</td>
<td>0.46</td>
<td>0.55</td>
<td>0.55</td>
</tr>
<tr>
<td>C/P (-)</td>
<td>1</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>W/P (-)</td>
<td>0.46</td>
<td>0.28</td>
<td>0.28</td>
<td>0.28</td>
<td>0.28</td>
<td>0.28</td>
<td>0.28</td>
<td>0.33</td>
</tr>
</tbody>
</table>

50 l of each concrete mix have been prepared in a planetary mixer, first by mixing all solid materials during 15 seconds. After the addition of the water and mixing for 1 minute, the mixer has been stopped in order to add the SP, followed by two more minutes of mixing. In order to verify the self-compactability, the values of the slump flow, V-funnel flow time, L-box test and air content have been determined. Previous investigations on the same mixes have revealed that none of them shows segregation.

2.2 Test method

From hardened concrete specimens, 18 cores with a diameter 80mm and a height of 80mm have been drilled for each concrete mix. At the age of 28 days, 9 of these cores have been submerged in a H₂SO₄-solution. The other 9 cores have been submerged in water. The temperature of the sulfuric acid solution and the water have been kept constant at 20°C during the entire testing period. The sulfuric acid solution contained initially 1.5 g H₂SO₄ per liter of water. As a result, the pH-value measured was around 1.7. During the testing period, the pH of the solution has been measured every week and H₂SO₄ has been added in order to keep the pH between 1.7 and 2.

During the first six weeks, the mass variation of the specimens submerged in the sulfuric acid has been measured each week. After 6 weeks, the mass has been measured each two weeks.

At the age of 10, 17 and 30 weeks, corresponding to a submersion time of 6, 13 and 26 weeks, 3 specimens have been removed from the sulfuric acid solution and also 3 specimens have been taken out of the water. The loading surfaces of the specimens have been flattened and capped by means of mortar and the compressive strength of the six specimens has been determined two weeks later. In this way, the compressive strength of the exposed specimens can be compared to the unaffected material, which has been kept under water.

Note that the H₂SO₄-solution has not been mixed mechanically, which might result in some concentration gradient near the specimens. The attack is the result of diffusion of the sulfuric acid only, and not by convection. The pH-value of the solution has been measured after mixing, giving average values.
3. MASS VARIATION

The results of the mass variation, expressed as the average of the three specimens, submerged during 26 weeks, can be found in figures 1, 2 and 3. In each figure, the values of a specific group are compared to the reference mix: SCC 20. The reference time has been chosen to be 1 week of submersion time, in order to exclude the mass variation due to the initial absorption of water by the specimens.

As can be seen in figure 1, the mass variation with submersion time is not significantly different for SCC 21 (different limestone filler) and SCC 24 (different SP), compared to SCC 20. The traditional concrete (TC 20) shows a slight higher loss in mass near the end of the testing period. Note that these mass variations are rather small, compared to other results in literature [3], which is most probably due to the purely diffusive form of penetration by the sulfuric acid.

Figure 1: Mass variation of TC 20, SCC 20, SCC 21 and SCC 24, showing no significant differences.

Figure 2 shows the results of SCC 22 (quartz filler) and SCC 23 (fly ash) compared to SCC 20. Again, the mass variations are not large, but it can be seen that the concretes without limestone filler show a lower resistance to the sulfuric acid attack, which is due to the buffering capacity of the limestone filler.

Figure 3 shows the results of SCC 25 (CEM III/A), SCC 26 (W/C = 0.55, C/P = 0.5) and SCC 27 (W/C = 0.55, C/P = 0.6), compared to the reference mix. Mixes 25 to 27 are suspected to have a higher porosity compared to the reference, although no direct measurement has been performed. From this figure, it can be seen that SCC 25, SCC 26 and SCC 27, have started a second “attack-phase”. The attack is supposed to occur as follows: first, the sulfuric acid is absorbed in the concrete and reacts with the limestone filler, indicated
by an increase in mass. After a certain time, the acid increases the porosity of the outer shell of the concrete, which can possibly loose the connection with the inner part of the specimen. This has not been investigated in these experiments, but it has been observed in case of other specimens by means of tomography [8], as reproduced in figures 4 and 5. A sample, exposed to sulfuric acid, has been scanned after 22h (Figure 4), and after 21 days (Figure 5). After 22h only the outer zone (of 0.15 mm thick) is visibly attacked and pushed off. Within the rest of the sample no effect was noticeable. After 21 days, the damaged outer zone had a thickness of 0.45 mm, but it seemed like it consisted out of two layers with an air layer in between (with a maximum thickness of 0.20 mm).

![Mass variation graph](image)

Figure 2: The mass variation of SCC 22 and SCC 23, compared to SCC 20, indicating a lower resistance to sulfuric acid attack.

Due to this increase in porosity, the outer shell of the - at that time - unaffected part of the concrete starts to absorb sulfuric acid, creating a new shell with increasing porosity. As a result, the attack process is assumed to deteriorate the concrete in different shells, each time showing an increase and a decrease in mass, at least in case of concrete with limestone filler. Reflecting the results in figure 3, it is assumed that the acid attack in SCC 20 has not yet reached a second phase, while for the other concretes in figure 3, a second attack phase can be distinguished. This has only been observed in case of SCC 25, SCC 26 and SCC 27, probably due to the different cement type and higher W/C-ratio.

When comparing the results of SCC 25, SCC 26 and SCC 27 (fig.3) with the results of SCC 22 and SCC 23 (fig. 1), it is clear that concrete with limestone filler shows a better resistance to sulfuric acid attack, even with a higher W/C-ratio or a different cement type. As will be shown in the next section, also from the compressive strength analysis, the same conclusion applies.
Figure 3: The mass variation of SCC 25, SCC 26 and SCC 27, compared to SCC 20 indicates a second phase of the sulfuric acid attack.

Figure 4: Scan after 21h of exposure to sulphuric acid (from [8])

Figure 5: Scan after 21d of exposure to sulphuric acid (from [8])
4. REDUCTION OF COMPRRESSIVE STRENGTH

Figure 6 shows the reduction in compressive strength of the specimens. For each concrete mix, the ratio of the compressive strength of the specimens submerged in the H₂SO₄-solution to the compressive strength of the specimens submerged in the water is given at the submersion times of 6 (black diamonds), 13 (grey triangles) and 26 weeks (hollow black rectangles). The compressive strength, both in sulfuric acid and water, has been determined as the average of three results. Analysis has indicated that in most cases the decrease in compressive strength is significant.

The results can be divided in three different groups. The first group (boxes number 1) contains SCC 20, SCC 21 and SCC 24, which show a quite high strength ratio (80-85%). The second group (boxes number 2) shows a much lower strength ratio (65-70%). This group contains SCC 22 and 23, which shows also different behaviour for the mass variation, and TC 20. The third and last group contains SCC 25, SCC 26 and SCC 27. For these concrete mixtures, the strength ratio is high, but it can be seen that the difference between the ratios at 13 and at 26 weeks of submersion is quite high. This can possibly be explained by the second attack phase as mentioned previously. For the other concretes (except for TC 20), the attack is apparently in some kind of (temporary ?) equilibrium. Further investigation will indicate whether this equilibrium disappears with longer submersion times and whether a second attack phase also occurs.
From these results, it cannot be concluded what the final sulfuric acid resistance of each concrete is. If the theory of the attack in different phases is valid, special attention should be paid when analysing results which appear to be in a kind of equilibrium. This equilibrium might be temporary and the sulfuric acid attack might be underestimated in this case.

5. CONCLUSIONS

The sulfuric acid attack of 9 different concrete compositions, of which 8 were self-compacting, has been investigated by submerging specimens in a H₂SO₄-solution with a pH-value of around 1.7. The mass variation of the specimens has been recorded during 26 weeks. At submersion times of 6, 13 and 26 weeks, three specimens have been removed and their compressive strength has been determined, simultaneously with the compressive strength of three unaffected specimens which have been kept under water.

The results of the mass variation show that the limestone filler is acting as a kind of buffer for the sulfuric acid. Concrete without limestone filler shows a lower mass at the end of the testing period. For the SCC with CEM III/A and SCC with a higher W/C-ratio, a second attack phase can be distinguished within the measuring period. From tomographic analysis, reported in literature, it is suspected that, at least for concrete with limestone filler, the sulfuric acid attacks first the outer shell of the concrete. When the porosity of this shell is sufficiently high, a second shell is attacked.

The compressive strength shows that SCC without limestone filler shows a much lower final strength than SCC with limestone filler. The results of the SCC with CEM III/A and SCC with a higher W/C-ratio confirm the attack in different shells, showing a large difference between the results at 13 and at 26 weeks. As a result, the attack can appear to be in a kind of equilibrium, but it should be considered that this equilibrium can be temporary, and that the sulfuric acid can continue attacking another shell.

SCC made with limestone filler shows a significantly higher resistance to sulfuric acid attack compared to SCC with quartz filler and fly ash, even in case the SCC with limestone filler has a higher W/C-ratio or a different kind of cement.

No significant differences have been found between SCC with the two different superplasticizers used.

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REFERENCES


