ANALYSIS OF DIFFERENT CONTENTS OF BLAST-FURNACE SLAG EFFECT ON CARBONATION PROPERTIES OF HARDENED BINDER PASTE USING MICRO-XCT TECHNIQUE

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Abstract
Micro-X-ray computed tomography (micro-XCT) has now become widely available for the nondestructive evaluation of cementitious materials. In this study we use micro-XCT to in-situ investigate the microstructure evolution of hardened binder paste containing different contents (0%, 30%, 50% and 70%) of blast-furnace slag at different carbonation time (0, 3, 7 and 14 days), respectively. The carbonation front progress, gray values histograms and crack distribution are analyzed by XCT VG Studio MAX 2.1 software. At last, the optimum substitution content of BFS is determined from the ability of the resistance carbonation.

1. INTRODUCTION
Low-carbon development of the cement and concrete industries can be achieved by complete utilization of cementitious and pozzolanic by-products, such as fly ash (FA), blast-furnace slag (BFS) and silica fume (SF) produced by thermal power plants and metallurgical industries. The blast-furnace slag (BFS) is used to mix concrete due to limited silica fume resources in many countries. In addition, concrete added with BFS performs better early strength than that with FA so that concrete incorporated with BFS is advantageous for engineering application [1]. But, mixing the excessive amount of BFS materials can significantly increase the carbonation rate because of the consumption of calcium hydroxide. Therefore, it is very important to research the microstructure evolution of carbonation reactions of cementitious materials added with different content of BFS materials. Using the phenolphthalein indicator solution to monitor the carbonation depth has been well documented. However, the penetrating gas can have reacted at greater carbonation depths, causing a decrease in the pH-value beyond the carbonation depth indicated by the phenolphthalein spray test. So, the phenolphthalein measurement does not show the changes which may occur in partially carbonated concrete [2]. Meanwhile, the classic methods for
characterization of carbonation depth-profiles, such as thermogravimetric analysis, 
gammadensitometry and infrared spectroscopy, can only give information about carbonation 
depth, however, neither three-dimensional carbonation front shape nor cracks spatial 
distribution.

Micro-X-ray computed tomography (micro-XCT) has now become widely available for the 
nondestructive evaluation of cementitious materials. In the field of cement and concrete 
research, micro-XCT has been applied by various researchers in calcium leaching [3, 4], 
fracture [5], sulfate attack [6], cement hydration [7], and pore tortuosity measuring [8] and so 
on. Therefore, micro-XCT also can be applied to investigate the microstructure evolution of 
hardened binder paste with BFS in accelerated carbonation process. In this paper, the 
microstructure evolution of hardened binder paste containing different contents (0%, 30%, 
50% and 70%) of blast-furnace slag are in-situ investigated using micro-XCT at different 
carbonation time (0, 3, 7 and 14 days), respectively.

2. EXPERIMENTAL

Some cylindrical samples (about diameter 4.61 cm and length 7.88 cm) of hardened binder 
paste with BFS were prepared for the experiment. Portland cement (PC, 52.5, fineness: 
350m²/kg) and BFS (S95, fineness: 450m²/kg) were used for this study, whose chemical and 
mineral composition are given in Table 1 and Table 2, respectively.

Table 1 Chemical and mineral composition of the PC 52.5 used (all values are in mass %)

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>MnO</th>
<th>SO₃</th>
<th>Na₂O</th>
<th>Insol</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>62.60</td>
<td>21.35</td>
<td>4.67</td>
<td>3.31</td>
<td>3.08</td>
<td>0.54</td>
<td>0.27</td>
<td>0.18</td>
<td>2.25</td>
<td>0.21</td>
<td>0.59</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>C₃S</td>
<td>C₂S</td>
<td>C₄AF</td>
<td>C₃A</td>
<td>Gypsum</td>
<td>Others</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>55.5</td>
<td>19.1</td>
<td>10.1</td>
<td>6.5</td>
<td>5.0</td>
<td>3.8</td>
<td></td>
<td></td>
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</tbody>
</table>

Insol.: insoluble residue. LOI: loss on ignition.

Table 2 Chemical composition of the BFS used (all values are in mass %)

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>K₂O</th>
<th>SO₃</th>
<th>Na₂O</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>25-40%</td>
<td>~30%</td>
<td>10-15%</td>
<td>1-2%</td>
<td>&lt;6%</td>
<td>0.4-1.5%</td>
<td>&lt;6%</td>
<td>0.05-0.5%</td>
<td>0.2-1%</td>
<td></td>
</tr>
</tbody>
</table>

The binder was prepared at a water-binder-ratio 0.53. The substitution fractions of PC with 
the BFS are 0%, 30%, 50% and 70%, respectively. The mixtures were injected into 
cylindrical moulds (about φ=4.61 cm and h =7.88 cm) and rotated for 24 h to avoid any 
sedimentation. The mould were removed after 24 h, and the specimens were wrapped in two 
sheets of adhesive aluminium foil to ensure no drying and carbonation. The specimens were 
stored in a saturated Ca(OH)₂ solution and a temperature of 20±3°C for 3 months. After 
curing, the specimens were oven-dried at 50°C for 48 h and then sealed on top and bottom 
surfaces except for side surface by hot paraffin. The specimens were transferred to a chamber 
to accelerate the carbonation process. The exposure condition was maintained at a CO₂ 
concentration ≈20±3%, RH ≈70±5%, and T ≈20±5°C. During this period, in-situ micro-
XCT tests were carried out to evaluate the microstructure evolution at carbonation ages 0 day (after drying), 3 days, 7 days and 14 days, respectively.

The micro-XCT system (Y.CT Precision System, YXLON, Germany) was employed for tomography in the present study. A power setting of 195 kV and 0.41 mA was used for this experiment. The specimens were set in a holder mounted on a precision rotation table, and then the table position was adjusted to fit the image within the filed view. During scanning process, a conical X-ray beam was emitted as the specimen rotating through 360 degree. The X-ray CT raw data were then collected by 1080 projection images that were recorded by a CCD camera with an array of 1024×1024 pixels. Therefore, a 3D voxel size was 0.086 mm × 0.086 mm ×0.086 mm. The acquisition time for one projection was about 1 second. The total time acquisition of the data including the reconstruction of the images was completed in about 1 hour. A set of contiguous slices or cross sectional images in x-y plane was obtained wherein each slice was an array of voxels. Stacked up in z-direction, these slices formed the volumetric image [9].

3. RESULTS AND DISCUSSIONS

3.1 The evolution of gray values distribution

Standard micro-XCT images comprise gray value maps with gray values proportional to the linear attenuation coefficient at each material point. In Figure 1, the statistical gray values are counted for hardened binder paste before carbonation with different contents of BFS materials: 0%, 30%, 50% and 70%, respectively. The gray values are correlated to the density of the specimen components. There are two different peaks. The higher gray value peaks are hardened binder paste with 0% and 30% BFS, and the lower gray value peaks are hardened binder paste with 50% and 70% BFS. So, BFS materials can decrease the density of hydrated binder paste.

![Figure 1: The difference of gray values distribuition due to the contents of BFS](image)

In Figure 2, the evolution of gray values is counted for different carbonation time: 0 day, 3 days, 7 days and 14 days, respectively. The gray values are correlated to the density of the specimen components. As shown in Figure 2, the gray values distribution become from single peak (0 day) into two peaks (3, 7 and 14 days) after carbonation reaction. This is because the density of the carbonated product, calcium carbonate, is more than that of uncarbonated components. The peak with lower gray values is mainly uncarbonated components, and the other higher gray value peak appeared after carbonation reaction is carbonated products. As
carbonation time goes on, the decrease in uncarbonated peaks over time following the increase in the peaks of the carbonated products can be clearly distinguished. In addition, when the carbonation time becomes longer, the gray values of uncarbonated and carbonated parts become lower and the peaks move to the left, particularly at carbonation time of 14 days. This is largely because many cracks appear during the carbonation shrinkage process, and cracks decrease the density of the samples.

As shown in Figure 2, the carbonation rate of hardened binder paste with BFS is greater than that of no BFS, and this is because of the consumption of calcium hydroxide for the hydration of BFS. In Figure 2(b and c), the hardened binder pastes with 30% BFS and 50% BFS are not completely carbonated at 14 days. In Figure 2(d), the hardened binder paste with 70% BFS have been completely carbonated at 3 days. So, the optimum substitution content of BFS is 50%.

Figure 2: The evolution of gray values distribution at different carbonation time

3.2 The evolution of carbonation front shape and crack distribution

In Figure 3 (top view images) and Figure 4 (side view images), the carbonation front progress, and crack distribution are analyzed by XCT VG Studio MAX 2.1 software for hardened binder paste with different contents of BFS materials: 0%, 30%, 50% and 70% at different carbonation time. The density of the carbonated products is more than that of that uncarbonated parts. So, the gray values of the carbonated products are more than those of the uncarbonated parts. As the image brightness is directly proportional to the density of the specimen components, the lighter voxels are associated to higher density phases (e.g. carbonated parts) whereas grayer voxels are associated to lower density phases (e.g. uncarbonated parts). As shown in Figure 3 and Figure 4, the decrease in the uncarbonated
parts and the increase in the carbonated products over time can be clearly distinguished. The carbonation rate of hardened binder paste with BFS is greater than that of no BFS. The hardened binder pastes with 30% BFS and 50% BFS are not completely carbonated at 14 days. In Figure 2(d), the hardened binder paste with 70% BFS have been completely carbonated at 3 days. So, the optimum substitution content of BFS is 50%. After the carbonation reactions, many cracks appear due to the carbonation shrinkage process, and these cracks significantly accelerate the diffusivity of carbon dioxide. Therefore, the carbonation reaction near the crack tip is faster than that for the non-crack parts, as shown in Figure 3 and Figure 4.

Figure 3: Top view images of different carbonation ages

0% BFS

30% BFS

50% BFS

70% BFS

Figure 3: Top view images of different carbonation ages
11. CONCLUSIONS

Based on the experimental study presented in this paper, the micro-XCT technique is a powerful method to in-situ monitor the microstructure evolution of cementitious materials in the carbonation process. The carbonation front progress, gray values histograms and crack distribution are analyzed by XCT VG Studio MAX 2.1 software.

Figure 4: Side view images of different carbonation ages
BFS materials can decrease the density of hydrated binder paste. As carbonation time goes on, the decrease in uncarbonated peaks over time following the increase in the peaks of the carbonated products can be clearly distinguished. The carbonation rate of hardened binder paste with BFS is greater than that of no BFS. The hardened binder pastes with 30% BFS and 50% BFS are not completely carbonated at 14 days. The hardened binder paste with 70% BFS have been completely carbonated at 3 days. So, the optimum substitution content of BFS is 50%.

Many cracks generate along the carbonation direction due to carbonation shrinkage. At the same time, the carbonation rate near the crack tip is faster than that for the non-crack parts, because cracks significantly accelerate the carbon dioxide diffusion rate and shorten the diffusion distance.

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REFERENCES