Application of X-ray CT to the Study of Microstructure and Diffusivity in Cementitious Materials

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Introduction

At the beginning of its development, the X-ray CT technique originally was developed for medical analysis [1]. However, along with the advances in technology, the ability of X-ray CT continues to increase. Therefore, the use of X-ray CT is no longer intended for medical application but has expanded to other fields such as civil engineering especially for material science. Related to construction materials, there are many experimental methods that can be used to study the microstructure of cementitious materials such as scanning electron microscope (SEM) [2-4], backscattered electron (BSE) [5-7], mercury intrusion porosimetry (MIP) [8-10] and permeability test. However, each of those experimental methods generally only provides few aspects related to the microstructure of cementitious materials. On the other hand, there are many aspects which can be obtained from the microstructure of cementitious materials just through the use of X-ray CT technique.

This present study describes the versatility of the application of X-ray CT technique to study the microstructure and diffusivity of cementitious materials. In this research, there are two types of X-ray CT systems used to acquire the 3D image of the internal structure of cementitious materials i.e. synchrotron X-ray CT at SPring-8, Japan and micro-focus X-ray CT at Hokkaido University, Japan. Through the application of X-ray CT technique this research could provide better understanding of the microstructure change in cementitious materials. In addition, with the proposed X-ray CT technique coupled with in-situ tracer diffusion test, the transport mechanism of diffusion inside crack and through the uncracked matrix would be further understood.

Materials and Method

Low alkali cement paste specimen with a composition of 40% OPC, 20% silica fume and 40% fly ash and water to binder ratio of 0.5 (hereinafter HFSC-CP-50) was prepared with increased curing periods from 2 days to 146 days and after leaching test for 13 weeks for synchrotron X-ray CT with resolution of 0.5 µm/voxel at SPring-8, Japan. As a comparison, normal cement paste specimen (hereinafter OPC-CP-50) was also prepared in similar manner. Details of specimen preparation for X-ray CT scan are described elsewhere [11-13].

High strength concrete of a water cement ratio of 0.3 was prepared to investigate the change of pore structure due to high temperature exposure followed by different re-curing method. Re-curing either in water or in air was carried out for one and four weeks. In the study of deteriorated cementitious materials due to mechanical loading, synchrotron X-ray CT was combined with micro-tensile instrument and the observation during the application of load conducted in-situ inside synchrotron X-ray CT chamber.

Micro-focus X-ray CT was employed to observe cracked mortar specimens due to mechanical loading. The cracks in beam specimens of OPC mortar (hereinafter OPC-MR) and fly ash mortar (hereinafter FA-MR) of the size of 10 x 20 x 60 mm and cylinder specimens of the size of 20 mm in diameter and 40 mm in height were induced by flexural test and splitting tensile test, respectively. Subsequently, the 3D crack geometry was obtained from microtomographic images. The transport mechanism in cracked mortar specimen was clarified by employing micro-focus X-ray CT coupled with in-situ tracer diffusion test. Cesium carbonate solution (Cs₂CO₃) was considered feasible as the source of a tracer transport in crack space. Furthermore, the cesium tracer concentration both in crack space and uncracked matrix was calculated on the basis of profile of CT number. Then, the diffusion coefficient was determined by best-fitted curve of Fick’s second law.

The image analysis to extract voids in the microtomography images was explained with the method of a threshold on the basis of their grey level histogram. Furthermore, after void segmentation, a basic 3D-image analysis program called SLICE [14], was used to obtain the largest percolating void and connectivity through cluster multiple labeling technique. As for pore structure analysis, Thickness plugin in BoneJ [15,16] and Random Walk Simulation [17] were performed in 3D pore structure to examine the pore size distribution and its diffusion tortuosity, respectively. Meanwhile, for extracting the 3D crack from microtomography images of cracked specimen, Skeletonize process was explained with regard to the measurement of tortuous crack length. It was also explained that the Thickness plugin was also applied to the 3D crack analysis in order to determine crack width distribution as well as its constrictivity factor.

Results and Discussion

Pore Structure Evolution with Increasing Curing Periods

Using synchrotron X-ray CT the change in the porosity in OPC-CP-50 and HFSC-CP-50 specimens with increasing curing periods were examined. The pore structure parameters such ash total porosity, connectivity, and pore size distribution were obtained through the analysis of 3D
The total porosity for OPC-CP-50 specimen was 14.4%. From this result, it can be inferred that leaching significantly increases the total porosity of the normal cement paste specimen as compared with cement paste specimen with low alkali binder.

In addition, as shown in Figure 2(b) the diffusion tortuosity of OPC-CP-50 specimen before and after leaching test was estimated to be 284 and 7, respectively. Meanwhile, it was 63 and 31 for HFSC-CP-50 specimen before and after leaching test, respectively. Dissolution of hydration product in OPC-CP-50 specimen reduced dramatically the diffusion tortuosity to a single digit as more isolated pore become connected with percolated porosity. On the other hand, although there was a reduction in the diffusion tortuosity for percolated porosity of HFSC-CP-50 specimen, however, it was not dramatically when compared with that of OPC-CP-50 specimen.

Before leaching test, it is considered that transport process of any species in the HFSC-CP-50 specimen through its percolated porosity has less obstruction as compared with that of OPC-CP-50 specimen. However, as the diffusion tortuosity decrease dramatically in the OPC-CP-50 specimen after leaching, the transport process of any species in OPC-CP-50 through its percolated porosity is far more facile than that of HFSC-CP-50 specimen.
**High Temperature Exposure and Re-curing**

Following the cluster multiple labeling, slice images of the connected pore space were extracted for both water re-cured and air re-cured specimen. The resultant images are shown in Figure 3(a). The post-heating images clearly show that cracks formed in several ways: around aggregates which were completely inside the specimen; cracks which bridged between different aggregates; and cracks which bridged between aggregates and large air voids. In the air re-cured specimen, cracks formed in a similar manner as in the water re-cured specimen: distinct crack surfaces can be seen in aggregate-mortar interface, along with some crack bridging. Therefore, the volume of total and percolated porosity of heated specimen increased due to the presence of these cracks.

Figures 3(b) and (c) show the pore structure parameters derived from microtomographic images after segmentation and cluster multiple labeling processes. As shown in Figure 3(b), in the water re-cured specimen the total porosity after heating was 9.4%. Meanwhile, for the air re-cured specimen (Figure 3(c)) it was slightly higher to the value of 9.9%. At 7 days of water curing, the total porosity of water re-cured specimen reduced to 5.9%. Unlike water re-curing, air re-curing did not lead to large reduction in total pore volume, with a decrease of only 0.5%. Further re-curing both in water and air up to 28 days only contributed to a minor reduction in the total pore volume.

**Microstructure Study under Tensile Force**

In this specific study, the change in the microstructure before and after tensile load of 4.27 N was difficult to be observed from microtomographic images. It is considered that the maximum load could not be reached in the experiment due to loss of grip on the clamps of specimen. In order to prove this phenomenon, we observed the change in the position and diameter of the void target due to the application of load. In fact, voids have a tendency to change in its shape when the load is applied in cementitious materials. As the result, the coordinate of void target in load applied condition changed largely in Z direction (load direction). Meanwhile, it was little changed in both X and Y direction. However, the change of the position of void target was not accompanied by the change of its diameter. There was no change in the diameter of void target in X, Y and Z coordinate. This result indicates that the microstructure of fly ash mortar specimen did not respond the tensile load due to loss of grip on the clamps of specimen. The amount of load applied before losing grip unable to generate considerable strain that can be detected with spatial resolution of 0.5 μm/voxel. In this way, the stress level occurred on the load bearing phases cannot be determined.

Although there was no definite result of this experiment, however, by improving the quality both sample preparation and loading instrument, the behavior of microstructure under external load could be observed through the application of synchrotron X-ray CT combined with other mechanical tests.

**Observation and Quantification of Crack Geometry**

Micro-focus X-ray CT was used to examine the crack in the mortar specimens. The cracks in beam specimens of the size of 10 x 20 x 60 mm and cylinder specimens of the size of 20 mm in diameter and 40 mm in height were induced by flexural test and splitting tensile test, respectively. Subsequently, the 3D crack geometry was obtained from microtomographic images. Figure 4(a) and (b) shows 3D crack network of splitting tensile cracked and flexural cracked mortar, respectively. Through the analysis of 3D crack geometry, the crack geometry parameters such as

<table>
<thead>
<tr>
<th></th>
<th>h = 2 mm</th>
<th>h = 6 mm</th>
<th>h = 10 mm</th>
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</thead>
<tbody>
<tr>
<td>Water re-curing</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>Air re-curing</td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Figure 3. Images of percolated porosity space in water and air re-cured specimen.
tortuosity and constrictivity were obtained as shown in Table 1. The tortuosity of splitting tensile crack in the mortar specimen with the maximum aggregate size of 1.7 mm and compressive strength ranged from 21 to 29 MPa was found to be around 1.25 to 1.26. Meanwhile, it ranged from 1.13 to 1.14 for the flexural crack in the mortar specimen with maximum aggregate size of 1.7 mm and compressive strength ranging from 31 to 46 MPa. This result implies that crack tortuosity was independent to the crack opening width and whether fly ash was added or not. It is considered that the type of cracks play important role on the tortuosity of crack as well as mechanical properties of the specimen.

The mechanical properties of specimen play important role on the tortuosity of crack. Under the same maximum aggregate size but with lower compressive strength, the crack tortuosity of splitting tensile crack specimen was higher than that of flexural crack specimen with higher compressive strength.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>W/B</th>
<th>S/B</th>
<th>OPC/(FA+OPC)</th>
<th>Crack opening width (μm)</th>
<th>Tortuosity (τ)</th>
<th>Constrictivity (δ)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Splitting tensile crack</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- OPC-MR-60-51</td>
<td>0.6</td>
<td>2</td>
<td>0</td>
<td>51</td>
<td>1.25</td>
<td>0.54</td>
</tr>
<tr>
<td>- OPC-MR-60-152</td>
<td>0.6</td>
<td>2</td>
<td>0</td>
<td>152</td>
<td>1.25</td>
<td>0.59</td>
</tr>
<tr>
<td>- FA-MR-60-127</td>
<td>0.6</td>
<td>2</td>
<td>0.3</td>
<td>127</td>
<td>1.26</td>
<td>0.80</td>
</tr>
<tr>
<td><strong>Flexural crack</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- OPC-MR-50</td>
<td>0.5</td>
<td>2.5</td>
<td>0</td>
<td>20-40</td>
<td>1.14</td>
<td>0.67</td>
</tr>
<tr>
<td>- FA-MR-50</td>
<td>0.5</td>
<td>2.5</td>
<td>0.3</td>
<td>45-55</td>
<td>1.13</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Note: W/B is the water to binder ratio by mass, S/B is the sand to binder ratio by mass, and for FA specimen fly ash was replaced for OPC by 30% by mass. Residual crack opening width of splitting tensile crack and flexural crack were measured by clip gauge and microscope, respectively.
The presence of voids plays an important role on the constrictivity of the crack. The addition of fly ash could reduce the effect of constrictivity in the crack as presence of fly ash decrease the number of voids in the mortar.

Table 2. Diffusion coefficients of oven-dried flexural cracked specimen

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Residual crack opening width (μm)</th>
<th>Diffusion coefficient along the crack (m²/s)</th>
<th>Diffusion coefficient through the uncracked matrix (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>- OPC-MR-50</td>
<td>20-40</td>
<td>$1.70 \times 10^{-9}$</td>
<td>$9.12 \times 10^{-11}$</td>
</tr>
<tr>
<td>- FA-MR-50</td>
<td>45-55</td>
<td>$9.03 \times 10^{-10}$</td>
<td>$3.47 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

On the other hand, the presence of voids and type of cracks plays an important role on the constrictivity of the crack. The addition of fly ash could reduce the effect of constrictivity in the crack as presence of fly ash decrease the number of voids in the mortar.

Quantification of Transport Properties in Cracked Cementitious Materials

Cesium tracer diffusion tests were conducted in the different type of cracked mortar specimens and the diffusivity was evaluated by using micro-focus X-ray CT on the basis of the change of the CT number. The crack in the beam specimen with size of 10 x 20 x 60 mm was induced by flexural test and the crack in the cylinder specimens with size of 20 mm in diameter and 40 mm in height was induced by splitting tensile test. As for flexural crack specimens, the specimens were oven dried before cesium tracer diffusion test. Meanwhile, for splitting tensile crack specimens, the specimens were immersed in the water for 24 hours before cesium tracer diffusion test and the observation was made in-situ inside X-ray CT machine.

Table 2 show the diffusion coefficient of oven-dried flexural cracked specimens. The diffusion coefficient of cesium tracer along the crack in the oven-dried flexural crack specimen with crack opening width less than 50 μm was almost reached the diffusion coefficient of cesium in the free water ($2.06 \times 10^{-6}$ m²/s [18,19]). Considering the initial condition of flexural crack specimens was oven-dried, thus, that mobility of cesium tracer along the crack may involve more than one transport mechanisms but not only diffusion. The apparent diffusion coefficient of cesium tracer in the uncracked matrix of FA specimen was smaller than that of OPC specimen. The drying process before diffusion test may enhance the pozzolanic reaction resulting in the increased resistance to diffusivity.

As for splitting tensile cracked specimen, the observation of cross sectional image of splitting tensile crack specimen in the cesium expose condition shows that the tracer only fills the crack occupied by water. Thus, the immersion process for 24 hours before cesium tracer diffusion test did not produce fully saturated crack, and leaving behind air pockets. In the next exposure time, the results showed that there was no addition of crack space filled by tracer. In this way, the diffusion of tracer only followed the path that formed on the short period of exposure time.

Table 3 shows the diffusion coefficient of partially saturated of splitting tensile cracked specimens. The diffusion coefficients along the crack for partially saturated OPC and FA specimens with roughly equivalent crack opening width are greater than the diffusion coefficient of cesium in free water in the first one hour. However, for the succeeding exposure time the diffusion coefficient decreased drastically up to the level where the diffusion coefficient is lower than the diffusion in the free water.

Furthermore, the average value of the apparent diffusion coefficient variation of the uncracked matrix for OPC-MR-60-152, FA-MR-60-127 and OPC-MR-60-51 are $6.46 \times 10^{-12}$, $2.88 \times 10^{-12}$, $5.18 \times 10^{-13}$ m²/s, respectively. The apparent diffusion coefficients of cesium ion obtained in this study are considered reasonable and lay within reported ranges by previous research [20,21].

For the specimen of OPC-06, the diffusion coefficient was increased with the increasing crack width opening. In this regard, the specimen with larger crack width opening has a higher diffusion rate indicated by diffusion coefficient and hence higher concentration of solute occurred in the crack. Furthermore, higher concentration of solute in the crack increased the penetration of solute towards the uncracked matrix. However, this mechanism is also affected by the level of diffusivity resistance of the uncracked matrix. These results suggest that solute content in the crack space actually governs the supply of the diffusive cesium at the surface area perpendicular to the diffusion in the uncracked body.

Similar to the results obtained from previous study, the addition of fly ash with longer curing period lead to a reduction of the diffusion coefficient in its uncracked body as

Table 3. Diffusion coefficients along the crack of partially saturated splitting tensile cracked specimens

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Initial to 1 hr</th>
<th>Diffusion Coefficient (m²/s)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>1 hrs to 3 hrs</td>
</tr>
<tr>
<td>- OPC-MR-60-51</td>
<td>&quot;*&quot;</td>
<td>&quot;*&quot;</td>
</tr>
<tr>
<td>- OPC-MR-60-152</td>
<td>$4.4 \times 10^{18}$</td>
<td>$8.2 \times 10^{-10}$</td>
</tr>
<tr>
<td>- FA-MR-60-127</td>
<td>$3.0 \times 10^{18}$</td>
<td>$8.0 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

* Not calculated because there is no change in CT Number up to 9 (nine) hours exposure time
compared with that of OPC specimen, although those diffusion coefficients along the crack were almost the same as given in Table 3. Fly ash concrete can normally exhibit increased resistance to diffusivity due to its dense microstructure caused by pozzolanic reaction. Kumar et al [20] found the reduction of the effective diffusion coefficients of cesium ion in cement pastes blended with blast-furnace slag and silica fume. Likewise, it can be said that this observed effect of reduced cesium diffusion can be explained by the fly ash addition to the specimen.

In addition, this study points out that the diffusion coefficient in the crack is 100 times higher than that of the uncracked matrix. On the other hand, the JSCE Standard Specification for Concrete Structures specifically mentions that the diffusion coefficient of chloride ion in cracked concrete with crack opening width larger than 100 µm is 1000 times than that of in the uncracked matrix. The result obtained from this study is slightly lower than that of the JSCE. However, it must be underlined that the JSCE takes into consideration the diffusivity in the cracked concrete could not separate the diffusivity in the crack and uncracked matrix in the cracked concrete.

**Conclusion**

In this research the versatility of the application of X-ray CT has been presented while several new findings were also provided. It is highly expected that by using X-ray CT, the microstructure in cementitious materials will be more explored in the near future. X-ray CT technique can also be combined with other testing methods. Using X-ray CT technique coupled with in-situ tracer diffusion test would allow further understanding of the transport mechanism of diffusion in cracked cementitious materials.

**References**


