THREE-DIMENSIONAL IMAGING OF CEMENT-BASED MATERIALS WITH X-RAY TOMOGRAPHIC MICROSCOPY: VISUALIZATION AND QUANTIFICATION

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Abstract

X-ray computed microtomography is now becoming a popular non-destructive method to study the microstructure of materials. As this technique operates on the same basic principle of medical computed tomography (CT) scanners, it provides the three-dimensional (3D) reconstruction of images from finite radiological images; but with much higher spatial resolution. For example, microfocus X-ray CT systems are now being designed to study the internal microstructure of specimen at spatial resolution of order of several microns. Furthermore, since the development of synchrotron as an X-ray source, advanced X-ray CT system is continually improving to approach spatial resolutions to submicron level. Such high-resolution technique is referred in this paper as X-ray tomographic microscopy (XTM) to highlight the distinction of this 3D imaging technique from the relatively well-established method of 2D microscopic imaging obtained from optical or electron microscope.

This paper, therefore, demonstrates the use of XTM technique to investigate the microstructure of cement-based materials. The potentials for high resolution microtomographic images to understand the 3D microstructure of cement-based materials in relation to the durability performance of these materials are given. For instance, the application of synchrotron microtomography to examine the pore connectivity and tortuosity of the 3D pore space in hardened cement paste is presented. In addition, application of microfocus X-ray CT to characterize the air void system of air-entrained mortar is also described in this paper.

Keywords: microstructure, X-ray tomographic microscopy, porosity, tortuosity, air void

1. INTRODUCTION

It is widely recognized that the investigation of the microstructure of cement-based materials plays an important role in studying the durability of these materials. For example, optical and electron microscopy are known to be one of the established research tools to examine the microstructure of cement and concrete. However, it has been acknowledged that
the destructive or invasive way of specimen preparation prior to analysis may produce problematic artifacts. Moreover, the limitations of observing a two-dimensional section of a three-dimensional structure from these techniques must also be taken into consideration. In this regard, X-ray tomographic microscopy is a viable noninvasive and nondestructive technique for three dimensional (3D) microstructure investigations of cement-based materials.

X-ray tomographic microscopy (XTM) is essentially synonymous to X-ray computed microtomography in which high spatial resolutions of 3D images are achieved. However, the term XTM is used in this paper to delineate the method as a form of X-ray microscopy that uses tomographic reconstruction techniques to build three-dimensional images of microstructures [1]. In fact, the application of X-ray computed microtomography is an established and rapidly evolving technology in biomedical, geological, and materials research. This technique has also received considerable attention in cement and concrete research (e.g., see [2-6]). Herein, we report on some of the results of our on-going studies as regard to the X-ray tomographic microscopy of cement-based materials. In this paper, we describe both the qualitative and quantitative information that can be extracted from the microtomographic images obtained from two different computed tomography (CT) systems: the synchrotron-based microtomography and the microfocus X-ray CT.

2. BACKGROUND

Computed tomography (CT) is a technique for obtaining volumetric measurements of the X-ray attenuation coefficient, creating images that map the variation of the X-ray attenuation coefficient within objects. This scanning technique (CT scan) has been originally and still most frequently used in medical diagnostic radiology. In general, an X-ray beam is sent to the specimen and the transmitted beam is recorded on a detector. According to Beer-Lambert’s law, the ratio of the number of transmitted to incident X-ray photons is related to the integral of the linear attenuation coefficient (LAC) of the material along the path that the photons follow through the specimen. The resulting image (or radiographs) is a superimposed information or projection of a volume in a 2D plane. To get the 3D information, radiographic projections of the specimen are taken at many angles or projection views. In medical CT, this is commonly done by turning the X-ray source and the detector around the object (which in this case is a human patient). While in most industrial CT scanners, which is particularly applied to inanimate objects, the specimen is the one being rotated while the X-ray source and detector are fixed in position. Once these projections are available, a reconstruction algorithm can be used to produce the contiguous two dimensional images which provide a discrete approximation of the distribution of X-ray attenuation coefficient within the volume of the imaged specimen. This two dimensional image is commonly referred to as slice because it corresponds to the cross-section of what would be seen if the specimen were sliced along the scan plane. Each slice is a matrix of voxels (volume element or 3D pixel) in which each voxel is associated with a gray scale value that is related to the measured linear attenuation coefficient (see Fig. 1).

As the linear attenuation coefficient (LAC) is a sensitive measure of atomic composition and density, CT technique could therefore provide nondestructive 3D visualization and characterization of internal structure without the time-consuming and difficult sectioning of specimen as being done in other X-ray microscopy techniques. As long as the spatial resolution could be made small with respect to the microstructural feature of interest, the
volumetric image obtained from these measurements could provide valuable 3D structural information. Generally, to achieve the high resolution requirement for XTM, there are two X-ray sources that can be used. The first one uses the monochromatic parallel beam from synchrotron radiation and the second one uses the polychromatic divergent beam produced by a microfocus X-ray tube (see Fig. 2). It is, however, beyond the scope of this paper to provide the detailed description of their principles and operations. Instead, we provide here just a brief description of the two different X-ray CT systems we used in our study.

Fig. 1: An illustration of pixel, voxel and slice. Each voxel is associated with an attenuation coefficient as shown by the color shade.

3. THE X-RAY CT SYSTEMS

Figure 2 describes the schematic diagram of the X-ray CT systems that were used in the microstructure investigation of cement-based materials.

3.1 Synchrotron microtomography

SPring-8 (Super Photon ring-8 GeV) which is the largest third generation synchrotron radiation facility located at Hyogo, Japan has beam-lines (e.g., BL20XU/BL47XU) that support a very high resolution X-ray CT system. The system consists of an X-ray light source from the beam-line, double crystal monochromator, high precision rotation stage, and high resolution X-ray image detector [7]. For example, the available X-ray energy from BL20XU

Figure. 2: The two X-ray CT systems used in this study.
can be tuned within the range of 8-38 keV. Using a high precision rotation stage, the image was taken at different views through 180 degrees rotation. The transmitted images are then detected by X-ray imaged detector which consists of thin scintillator, optic system and CCD camera. Tomographic reconstruction is done using a public domain computer program in use at SPring-8, which employs the convolution back projection algorithm to generate the slice images.

3.2 Microfocus X-ray CT

At Hokkaido University, Japan, there is an available microfocus CT system (TOSCANER-3000µhd, Toshiba IT & Control Systems Corporation, Japan) maintained by the Laboratory of Terrestrial Field Engineering. The CT system mainly consists of a microfocus X-ray source, a specimen manipulator, an image intensifier (II) detector coupled to a CCD camera, and an image processing unit. The X-ray source has a 4 µm focal point with an X-ray tube voltage that ranges from 20-225 kV. The source-to-specimen distance and source-to-detector distance can be varied to obtain the desired geometric magnification. The micromanipulator precisely positions the specimen table in the X-ray beams and rotates it under computer control through 360 degrees for projection data acquisition. The table position and motions and camera options are under the control of the host computer. The host computer receives the projection images and performs the data processing, and the image reconstruction using a built-in reconstruction program for cone beam geometry.

4. APPLICATION TO CEMENT-BASED MATERIALS

4.1 Theoretical LAC of different phases in cement-based materials

To gain insights into what one might expect when cement-based materials are scanned, the theoretical linear attenuation coefficients of selected components over the range of available X-ray spectrum were determined (see Table 1). First, mass attenuation coefficients (MAC) of the elements of interest (e.g., C, H, O, Si, Al, Fe, S, etc.) at various X-ray energy levels were obtained from the NIST database [8]. For compounds and mixtures with known chemical compositions, the MAC values, as well as, the mean atomic number ($Z$) can be obtained by simple additivity rule, i.e., combining values for the elements according to their proportions by weight. The mass attenuation coefficients were then multiplied by mass density to compute the theoretical LAC. These theoretical values can provide a priori information as regard to the relative brightness or voxel intensity associated with each component. In general, given the range of grayscale level, the brightness intensity of the voxels in microtomographic images is directly proportional to the associated LAC. Accordingly, air void and pore space would be imaged as dark voxels relative to the cement paste matrix while the anhydrous cement would be imaged as brighter relative to the hydrated cement products.

From Table 1, it can also be inferred that the higher beam energy is less sensitive to attenuation contrast resulting to poor differentiation between some features of interest in cement-based materials. Although lower beam energy generally provides better contrast, the X-ray needs to be sufficiently energetic to penetrate the sample with adequate photon counting statistics. But if it is too powerful, it may result to poor contrast between the various phases. Nevertheless, the range of available X-ray energy in the CT system we used is sufficient enough to provide good contrast between the pore space or air voids and the solid matrix.
Table 1: The theoretical LAC of phases in cement paste at various X-ray energy levels

<table>
<thead>
<tr>
<th>Phase, Notation(^a)</th>
<th>Z</th>
<th>density ((g/cm^3))</th>
<th>LAC ((1/cm)) at various X-ray energy ((E, \text{keV}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Alite, C(_3)S (\alpha)</td>
<td>15.1</td>
<td>3.21</td>
<td>177.98</td>
</tr>
<tr>
<td>Belite, C(_2)S (\beta)</td>
<td>14.6</td>
<td>3.28</td>
<td>167.96</td>
</tr>
<tr>
<td>Aluminate, C(_1)A (A)</td>
<td>14.3</td>
<td>3.03</td>
<td>148.23</td>
</tr>
<tr>
<td>Ferrite, C(_4)AF (F)</td>
<td>16.7</td>
<td>3.73</td>
<td>279.37</td>
</tr>
<tr>
<td>Free lime, C (\alpha)</td>
<td>16.6</td>
<td>3.32</td>
<td>227.28</td>
</tr>
<tr>
<td>Quartz, S (\phi)</td>
<td>10.8</td>
<td>2.65</td>
<td>50.38</td>
</tr>
<tr>
<td>Anhydrite, C(_2)S (\alpha)</td>
<td>13.4</td>
<td>2.98</td>
<td>125.46</td>
</tr>
<tr>
<td>Gypsum, C(_2)SH (_2) (\alpha)</td>
<td>12.1</td>
<td>2.32</td>
<td>79.82</td>
</tr>
<tr>
<td>Periclase, M (\beta)</td>
<td>10.4</td>
<td>3.58</td>
<td>53.90</td>
</tr>
<tr>
<td>Portlandite, CH (\delta)</td>
<td>14.3</td>
<td>2.24</td>
<td>118.96</td>
</tr>
<tr>
<td>Calcium silicate hydrate, (\text{C}_1\text{SH}_4) (\text{CSH}_4)</td>
<td>12.1</td>
<td>2.12</td>
<td>75.05</td>
</tr>
<tr>
<td>Calcium silicate hydrate, (\text{C}<em>{1.7}\text{SH}</em>{1.3}) (\text{CSH}_{1.3})</td>
<td>13.1</td>
<td>2.60</td>
<td>108.53</td>
</tr>
<tr>
<td>Ettringite, (\text{C}_6\text{A}<em>2\text{S}<em>3\text{H}</em>{12}) (\text{CAH}</em>{12})</td>
<td>10.8</td>
<td>1.70</td>
<td>45.35</td>
</tr>
<tr>
<td>Monosulfate, (\text{C}_6\text{A}<em>2\text{S}<em>3\text{H}</em>{12}) (\text{CAH}</em>{12})</td>
<td>11.7</td>
<td>1.99</td>
<td>64.26</td>
</tr>
<tr>
<td>Water, (\text{H}_2\text{O}) (\text{H})</td>
<td>7.2</td>
<td>1.00</td>
<td>5.33</td>
</tr>
<tr>
<td>Air (dry) (\beta)</td>
<td>7.4</td>
<td>0.001</td>
<td>0.0062</td>
</tr>
</tbody>
</table>

note: (a) C=CaO; S=SiO\(_2\); A=Al\(_2\)O\(_3\); F=Fe\(_2\)O\(_3\); S=SO\(_2\); H=H\(_2\)O; M=MgO

4.2 Pore structure characterization of hardened cement paste with synchrotron microtomography

The 3D micro-geometry of pore structure in hardened cement paste plays a fundamental role in governing transport processes that influence the durability-based performance of these materials. For example, aggressive species (e.g., chlorides, sulfates, etc.) from the environment could penetrate the concrete structures through the tortuous and connected pore space of the hardened cement matrix. With synchrotron microtomography, we were able to examine the pore space in three dimensions at submicron resolution. For this study, 15 keV of X-ray energy was used and 1500 projection images were taken. After reconstruction (1300 contiguous slices) and image normalization, each slice (8-bit grayscale image) is an array of 2000 x 2000 voxels with a voxel dimension of 0.5 x 0.5 x 0.5 \(\mu\)m\(^3\). From the reconstructed volumetric images of hardened cement pastes, 3D image analysis and random walk simulation were employed to measure porosity and tortuosity, respectively. Details of the concept and the procedure are described elsewhere (see [9-10] and the references therein).

For the purpose of illustration, the representative results from the specimen of OPC50-2d (water to cement ratio of 0.50 and curing time of 2 days) are shown in Fig. 3.
ordinary portland cement (OPC) contains, by mass basis, 67.80% of CaO, 21.30% of SiO₂, 3.80% of Al₂O₃, 2.41% of Fe₂O₃, and 2.20% of SO₃. In addition, the fineness of OPC in terms of Blaine specific surface area is 3200cm²/g.

From the original data set, a volume of interest (VOI = 450³ voxels = 0.011 mm³) was extracted to avoid the edge effects, as well as, to reduce the computational time of processing the images (see Fig. 3a). Then, by applying a segmentation routine, the binary image in Fig. 3b was produced which distinguished the pore space (white) from the solid matrix (black). From this segmented porosity, the largest percolating pore cluster was identified from connectivity analysis with the cluster multiple labeling technique (see Fig. 3c). In contrast to that of the dead-end and isolated pore clusters (gray), it is assumed that this largest percolating pore cluster (white) would most likely contribute to the macroscopic transport property of the cement paste. Hence, the so-called effective porosity is associated with the largest percolating pore cluster in the segmented porosity. Moreover, 3D random walk simulation was performed in the said pore cluster to estimate the diffusion tortuosity as shown in Fig. 3d. This tortuosity is related to the restricted diffusion of walkers in the 3D pore space as described by their mean square displacement through time. Thus, this kind of information could be useful to understand the 3D micro-geometry of paste’s pore structure in relation to the transport properties of concrete.

4.3 Air void characterization of air-entrained mortar with synchrotron microtomography and microfocus CT

It is widely accepted that the entrained air voids play a beneficial role for the freeze-thaw durability of concrete. Determination of the air void diameter distribution and air-void system parameters such as the spacing factor and air content is generally performed using an optical microscope and procedures such as the linear traverse or modified count method as outlined in ASTM C457. These parameters, particularly the spacing factor, have been shown to provide valuable information in relation to the performance of concrete against freeze-thaw damage. However, the limitation of characterizing the 3D air void system from a 2D image using one-dimensional linear traverse method or non-dimensional point count method must be borne in mind [6]. In this study, we applied synchrotron microtomography and microfocus CT for the 3D imaging of the air void system in an air-entrained fly ash mortar. This mortar (FA-A) has a sand to cement ratio of 3.8, a water to binder ratio of 0.50, with fly ash 30%
replacement, and a measured initial air content of 6.6%. The experimental parameters for the XTM of the mortar specimen are summarized in Table 2.

Table 2: Experimental parameters for the X-ray imaging of air-entrained mortar

<table>
<thead>
<tr>
<th>Experimental parameters</th>
<th>X-ray CT system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specimen size of mortar (FA-A)</td>
<td>about 1.5 mm in diameter and 1 mm in length</td>
</tr>
<tr>
<td>X-ray source</td>
<td>Synchrotron</td>
</tr>
<tr>
<td>X-ray energy</td>
<td>20 keV &lt; 90 keV (90 kV, 0.089 mA)</td>
</tr>
<tr>
<td>Number of projections (radiographs)</td>
<td>3000</td>
</tr>
</tbody>
</table>

Fig. 5 shows a representative slice obtained from the synchrotron microtomography and microfocus CT. In Fig. 5a, one can see distinct features of the microstructure that can be inferred as the air voids and pore space (very dark), hydrated cement products (dark to light gray), sand particles (gray patch), and unreacted cements or high-density minerals (white and bright specks). On the other hand, the images (e.g., see Fig. 5b) from the microfocus X-ray CT provided poor definition of the features between the sand particles and cement paste; and also exhibited significant edge artifacts due to beam hardening. This could primarily be attributed to the difference between the characteristics of the X-ray source of microfocus CT and synchrotron microtomography. The synchrotron-based X-ray is a tunable monochromatic parallel beam and very intense resulting to a better spatial resolution and contrast sensitivity, as well as, to accurate mapping of linear attenuation coefficient and elimination of beam hardening artifacts. On the other hand, microfocus X-ray has some limitations in terms of its source intensity and use of polychromatic cone beam. Aside from the obvious lower spatial resolution (or lower signal-to-noise ratio) of the microfocus CT as compared with that of synchrotron microtomography, the poor contrast between the sand and cement paste could be caused by inadequate photon counting statistics, as well as, the signal-to-noise problem associated with using X-ray energies that are not optimized to the specimen size [1]. In
addition, the beam hardening, which is a common artifact from using polychromatic X-ray spectrum, may cause difficulty in differentiating precisely the microstructural variations in the microtomographic images.

Nevertheless, the good contrast between air voids and the solid matrix in the microfocus CT image could still allow us to extract quantitative information from a considerable size of the region of interest (see Fig. 5b: ROI = 500 x 500 voxels) for air void analysis. For the purpose of illustration, some of the results of the air void characterization using the volumetric image (VOI = 500 x 500 x 200 voxels \( \approx 171.1 \text{ mm}^3 \)) obtained from the microfocus CT are presented here. The freely available ImageJ [11] and SLICE software [12] were used for 3D visualization including the image processing, understanding and analysis.

Prior to the extraction of air void from the solid matrix through segmentation routine, contrast enhancing, denoising, sharpening, and smoothing of the images in the VOI were employed. Then, a supervised thresholding for region-based segmentation was applied to obtain a set of binary image wherein white and black voxels represent the air void and solid matrix, respectively (see Fig. 6). One could estimate the local entrained air content by dividing the total number of white voxels (air void) to the total voxels of VOI. In this case, the air content is estimated to be 6.2 %. However, from this image, one can also see some overlapping of air voids which could distort the results of the image analysis of air voids. Thus, we applied a watershed algorithm [13] to separate the overlapping air voids as much as possible prior to connectivity analysis. The term “watershed” comes from the analogy wherein the grayscale image is treated as a topographic surface, i.e., the pixel intensity corresponds to the height of the point in the map. Accordingly, the resulting watershed lines mark the boundaries of “catchment basins” in the image. Such method of watershed-based splitting of overlapping air voids is illustrated in two dimensions in Fig. 7.

To identify and measure each individual air void, connectivity analysis through cluster multiple labeling technique [12,14] was also applied with the exclusion of those voids that are connected to the edges or face boundaries of the VOI. From this analysis, the resulting local entrained air content and air voids number density (number of air voids per unit volume) are 5.3 % and 82 per cubic mm (13949 voids / 171.1 mm\(^3\)), respectively. The air void diameter was approximated from the equivalent diameter, which is the diameter of the sphere having a volume equivalent to that of the said void. Fig. 8 shows the isolated air void system in 3D and the corresponding air void equivalent diameter distribution. Note that it is also possible to obtain the Powers spacing factor by estimating the specific surface of voids (\( \Lambda \)) from the 3D image. In this case, the specific surface which is the ratio of the total surface area of voids to the total volumes of voids was computed to be 63.7 mm\(^{-1}\). Assuming a paste to air content ratio (\( \rho/A \)) of 6.98 based on the given mix proportion of FA-A mortar, the spacing factor (\( \bar{L} \))

![Figure 7: An outline of steps for splitting of overlapping voids using watersheds.](image-url)
was estimated to be 0.085 mm. Hence, this air-entrained mortar which is expected to perform adequately against the freeze-thaw damage has shown a satisfactory spacing factor. In practice, the Powers spacing factor, as an indicator of frost durability of air-entrained concrete, is usually prescribed in the range of 0.20-0.25 mm.

![Figure 8: 3D volume rendering of air voids and quantification of air void diameter distribution.](image)

5. CONCLUDING REMARKS

As the X-ray CT system continues to improve in spatial resolutions and overcome the limitations in specimen size, X-ray tomographic microscopy (XTM) would be a powerful noninvasive and nondestructive tool to obtain the 3D microstructure of cement-based materials. In this study, XTM was carried out by means of a microfocus X-ray CT and also by a synchrotron-based X-ray CT system. At present, the spatial resolution for microfocus CT is in the order of few tens of microns and can be used for specimen of centimeter size. On the other hand, the synchrotron-based CT provides higher spatial resolution at submicron scale but is limited to specimen of millimeter size. It should also be noted that the synchrotron radiation facilities is not readily accessible and may be limited to only few days of experiment. On the one hand, one could access more easily the commercial tabletop microfocus CT scanners wherein the resolution may be sufficient for one’s study. However, one should also take into consideration the artifacts from the polychromatic cone beam which can be avoided with the use of monochromatic synchrotron source. Thus, the choice of the CT system including the specimen size and resolution would be based on the research objective. We hope that the examples provided here would serve as an impetus for further utilization of this technique to understand the durability of cement-based materials from the point of view of 3D microstructure.

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