Quantitative characterization of three-dimensional pore structure in hardened cement paste using X-ray microtomography combined with centrifuge driven metal alloy intrusion

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Abstract

In this paper, a centrifuge device is proposed to facilitate the intrusion of a low-melting point metal alloy into the pore space of hardened cement paste. X-ray microtomography is combined with metal centrifugation porosimetry (MCP) to quantitatively investigate 3D pore structure. The low-melting-point metal alloy is melted and introduced into pore space in pastes with water cement ratio of 0.5 and 1.0 at a temperature of 65 °C. 3D pore structure is quantitatively analyzed by X-ray microtomography after the molten metal alloy has been consolidated. A new threshold value segmentation method for pore space was proposed using conversion coefficient on region of interest (ROI). Porosity and pore size distribution are tested by MCP and compared with the results based on mercury intrusion porosimetry (MIP). The results show that the contrast between pore space and solid phase in the X-ray microtomography device image is improved. The total porosity obtained by MCP was found to be consistent with the results obtained by MIP.

Keywords: X-ray microtomography; Porous material; 3D pore structure; Quantitative characterization; Cement

1. Introduction

Cement-based materials are considered as one of the most vital materials, as they play an important role in infrastructure development [1]. These materials consist of liquid, solid and gas phases whose properties are strongly correlated with the performance of modern concrete [2–3]. Porosity in cement-based materials is directly

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associated with the mechanical performance as well as transport properties \cite{4}. Hence, quantitative characterization of pore structure of cement-based materials is important to assess the performance of concrete \cite{5}.

Several commonly used techniques are available for characterization of pore structure in cement-based materials, including small-angle X-ray scattering, Brunauer-Emmett-Teller adsorption and mercury intrusion porosimetry (MIP) \cite{6}. Among them, MIP technique is the most widely employed technique in research due to its advantages such as large dynamic range of pore size characterization (from a few nanometers to a few hundred micrometers), high performance and short testing durations. However, this method has limited applications due to the ink bottle effect \cite{7} and it assumes cylindrical pore geometry \cite{8}. Due to these assumptions, the estimation of pore parameters such as porosity, pore connectivity and surface-to-volume ratio by the MIP method are inaccurate. Moreover, the detailed topology of 3D pore structure has not be obtained until now, which is crucial to the performance in cement-based materials. Although, scanning electron microscopy (SEM) has been conventionally applied to analyze pore structure as it offers a high resolution, the low contrast between pore space and solid phase limits the information of pore structure to 2D only.

As a well-established technology, X-ray computed tomography (X-ray CT) can achieve the visualization of 3D pore structure \cite{9}. However, current results mostly focused on pore structure of concrete with larger pore size, such as foamed concrete \cite{10,11} and cracked concrete \cite{12} due to high contrast between pore space and solid phase. The limited application of X-CT in common or high performance concrete are mainly due to the fact that the threshold value between pore space and solid phase in CT slice figure is not obvious arising from relatively low attenuation. Therefore the classification of threshold value is subjective \cite{13}. In order to reduce subjectivity, contrast agents have been applied in porosity characterization of porous material, such as Wood’s metal \cite{14-18}, polymethylmethacrylate (PPMA) \cite{19} and mercury \cite{20}. Pore structure \cite{14-16} was analyzed only on 2D using Wood’s metal combined with high pressure. Wood’s metal was also used in clay rock \cite{17} to obtain 3D structure of materials combined with focused ion beam (FIB). PPMA \cite{19} and mercury \cite{20} were applied to research pore structure in crystalline rock with ordinary CT imaging. In addition, the resolution of ordinary X-ray CT and micro X-ray CT used are not enough for micro pore scale research \cite{21}. Hence there is need for techniques that have a high contrast and a high precision to image 3D pore structures in cement-based
In this study, a novel contrast enhanced X-ray microtomography technique has been employed for the first time to quantitatively characterize 3D pore structure in cement pastes. A new threshold value segmentation method for pore space was proposed based on ROI combined with volume compensation factor. The metal alloy is centrifuged into pore spaces to enhance their contrast in X-ray microtomography images.

2. Materials and methods

2.1 Materials and instrumentation

2.1.1 Preparations of specimen

The cement used in this study is a Chinese standard Graded P•Ⅱ 52.5 type Portland cement with a density of 3150 kg/m³ and specific surface area of 369.60 m²/kg. Its chemical composition is listed in Table 1. It has an initial and final setting time of 132 min and 187 min, respectively. Its compression and flexural strength for a 28 day curing duration under standard conditions are 59.60 MPa and 9.20 MPa, respectively.

Table 1
Chemical composition of cement

<table>
<thead>
<tr>
<th>Cement</th>
<th>Chemical composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO₂</td>
</tr>
<tr>
<td>Content</td>
<td>21.35</td>
</tr>
</tbody>
</table>

Cement pastes were prepared with water cement ratio (w/c) of 0.5 and 1.0. Cavity formation was facilitated in the prepared specimens to hold the molten metal using the proposed device, as shown in Fig. 1(a). Firstly, the fresh cement paste was poured into the tube and then pressed down the bar-pipe plug to produce the cavity. Then, the samples were put into a rotating device to constantly and slowly rotate up and down during the whole setting and hardening time of the fresh cement paste. After the setting and hardening of the paste, the bar-pipe plug was dialed out carefully and replaced with the pipe cap, curing paste at 20±1°C/95% RH for 28 d and 14 d (Table. 2). Finally, the specimens were soaked in ethyl alcohol for 3 d to terminate hydration and dried at a temperature of 65°C in the air oven until mass constancy to exclude gas in pores of the hardened cement paste.
Fig. 1 Schematics of the proposed centrifugal device design. (a) Cavity formation device, (b) Thermal-insulation centrifuge tube and (c) Centrifuge machine

Table 2

<table>
<thead>
<tr>
<th>Sample name</th>
<th>w/c</th>
<th>Age (days)</th>
<th>Centrifuge Speed (RPM)</th>
<th>Intrusion Pressure (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.5</td>
<td>28</td>
<td>4000</td>
<td>12.02</td>
</tr>
<tr>
<td>A</td>
<td>0.5</td>
<td>28</td>
<td>4000</td>
<td>12.02</td>
</tr>
<tr>
<td>B</td>
<td>0.5</td>
<td>14</td>
<td>4000</td>
<td>12.02</td>
</tr>
<tr>
<td>C</td>
<td>1.0</td>
<td>14</td>
<td>4000</td>
<td>12.02</td>
</tr>
</tbody>
</table>

2.1.2 Proposed centrifuge device design

The experimental set-up used to intrude the metal into the sample consisted of an in-house developed thermal-insulation centrifuge tube (Fig. 1(b)) and a centrifuge machine (maximum speed: 4000 r/min) (Fig. 1(c)). Firstly, the molten metal alloy was injected into the cavity of sample. Then, the sample was tightly and hermetically coated with extruded polystyrene (heat conductivity coefficient 0.030 W/ (m·K)) to maintain the experiment time (65°C). Finally, the sample was placed in a centrifuge tube to be subjected to the centrifugal process at 4000 r/min for 30 min. Subsequently,
the specimen was cooled below 47°C, after which a cylinder with diameter of 1.0 mm was drilled for X-ray microtomography (Fig. 2). Three samples (A, B, C) were prepared under the conditions and one untreated sample was prepared under the same formation and curing conditions for control group, as listed in Table 2.

**2.1.3 Metal alloy properties**

The metal alloy used in this experiment has a chemical composition of 43.7%Bi, 20.6%Pb, 8.6%Sn, 5.8%Cd, 20.1%In and other trace elements (tested by X Ray Fluorescence), which is similar to Bismuth alloy [22] as shown in table 3. The metal alloy has a melting point of 47°C and a specific gravity of 9.4 g/cm³. Compared with Wood’s metal [23], the metal alloy has lower Lead, lower Cadmium and extra Indium. Although the volume change of the metal alloy on crystallization was not experimentally determined, an estimate of 0.0057 mm/mm expansion for a 500 h post-casting duration was considered for a similar metal [24]. The metal alloy-cement paste contact angle changed with temperature between 110°~130°(tested by high temperature vacuum contact Angle tester), which is close to the mercury-paste contact angle (117°~140°) [25], as shown in the Fig. 3. In order to facilitate energy-saving and avoiding decomposition of ettringite in hydration products, a temperature of 65°C was chosen for the experiment. The surface tension of the metal alloy was \( \sigma = 0.508 \text{N/m} \) at a temperature of 65°C.
Fig. 3 (a) Diagram of contact angle, (b) Contact angle between the metal alloy and the cement paste as a function of temperature

Table 3

<table>
<thead>
<tr>
<th>Chemical composition of cement</th>
<th>Composition by weight</th>
<th>Melting point</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>The metal alloy</td>
<td>43.7% Bi, 20.6% Pb, 8.6% Sn, 5.8% Cd, 20.1% In</td>
<td>47°C</td>
<td>9.40</td>
</tr>
<tr>
<td>Bismuth alloy[1]</td>
<td>44.7% Bi, 22.6% Pb, 11.3% Sn, 5.3% Cd, 16.1% In[2]</td>
<td>47-52°C[22]</td>
<td>9.16[22]</td>
</tr>
<tr>
<td>Wood’s metal[2]</td>
<td>50.0% Bi, 26.7% Pb, 13.3% Sn, 10.0% Cd[23]</td>
<td>70°C[23]</td>
<td>9.38[23]</td>
</tr>
</tbody>
</table>

2.1.4 Experimental parameters

In this study, the model of X-ray microtomography scanner was Y.CT Precision (Zeiss, Germany) and the type of detector was Y.XRD 1601. The intensity of the X-ray beam after sample penetration was measured by 1024 detectors. The voltage and current of X-ray tube was 40 kV and 75 µA. The rotation angle of sample platform was 360° and increment of rotated samples was 0.0010rad. A tray was placed on the sample platform and a support device was placed at the top of the tray. All samples were scanned at the same station using the X-ray microtomography over 5 hour scanning time, and images with a pixel size of 1 μm were reconstructed using VGStudio MAX software.

The metal alloy-paste contact angle was measured by high temperature vacuum contact Angle tester (Dataphysics, OCA25HTV). Solid metal alloy was heated into molten metal alloy in the temperature of 65°C and dripped to the surface of paste, then the contact angle was measured subsequently. The MIP tests were done on Autopore
IV9510 (Micromeritics) with a low pressure of 0.53 psia mercury filling pressure and maximum intrusion pressure of 60000.00 psia.

2.2 Centrifuge intrusion procedure

Due to capillary action and a favorable contact angle between the molten metal and paste, an external force can drive the molten metal into the pore space [25]. Other factors such as the density of the metal, the speed of the centrifuge device and the centrifugal radius are also relevant. For the proposed device, the intrusion pressure $P$ can be calculated as (Eq. 2.1),

$$P = \frac{1}{2} \omega^2 \rho (2RX + X^2)$$

(1)

Where, $\omega$ is the centrifuge speed, whose unit is rad/s, $\rho=9.4$ g/cm$^3$ is the density of the molten metal alloy, $R=48.0$ mm is the distance from the center of centrifuge to the surface of molten metal in the tube, $X=82.0$ mm is the depth of molten metal alloy to the upper surface of the cement sample.

The corresponding pore size is derived based on Washburn’s equation [21] as,

$$p = -\frac{4\sigma \cos \theta}{d}$$

(2)

Where, $\sigma=0.508$N/m, $\theta=110^\circ$~$130^\circ$ (here $\theta=120^\circ$ was chosen), when $P=12.02$MPa (Table 2), the result of $d$ is 0.085 μm, which means that the minimum capillary pore radius can be invaded by the molten metal alloy using the experimental set-up.

2.3 Segment pore methods

In this study, threshold value was significant to segment pores from the base material and to calculate porosities and the pore size distributions. Due to overlapping greyscale part of the metal alloy and treated samples, it’s essential to reasonably choose region of interest (ROI) where embrace the vast majority of the metal alloy but very little untreated sample greyscale. Pixel ratio on ROI was counted for treated samples, which named incipient porosity ($P_i$). And pixel ratio of the metal alloy on ROI was volume compensation factor, which named conversion coefficient ($\mu$). Then, actual porosity ($P_a$) can be calculated as,

$$P_a = \frac{P_i}{\mu}$$

(3)

Finally, the threshold value of sample was determined based on ROI. Porosity based on the threshold value was calculated again, which named $P_t$. The threshold
value could be constantly adjusted until \( P_t \) was very close to \( P_a \). Thereby, pore structure can be reconstructed based on ultima threshold value and pore size distributions can be calculated in one fixed direction.

3. Results and discussion

The different phases in the samples could be seen with improved contrast since the atomic number of elements in the cement pastes (Si, Ca, O, Al, etc.) was lower than the metal alloy constituents (43.7%Bi, 20.6%Pb, 8.6%Sn, 5.8%Cd, 20.1%In, etc.) in the pores. The high gray values (brightness) in the image indicated that the molten metal alloy was favorably intruded into the pore structure [20]. Appropriate image thresholding was performed to highlight the metal zone and to calculate the porosity and pore size distribution of the specimens.

3.1 SEM images

As shown in Fig. 4 a), the SEM images of sample A, B and C were compared with untreated sample. The areas of high brightness show the zone of pore structure occupied with the metal alloy. In order to determine pore space, firstly, straight line was chosen to across the SEM image of samples and intensity (gray value 0~255) was shown using ‘Line Profile’ of Image-Pro Plus software, as demonstrated in Fig. 4 b). Little or no intensities of untreated sample reached to gray value 255 in spite of 5 lines were chosen to parallelly across the SEM image. Differently, some intensities of sample A, B and C were reached to gray value 255 because the metal alloy. The reasons are that cement grains surface were completely covered with outproduct in cement hydration [27, 28], especially low density C-S-H [29], which lead to more density contrast between cement and the metal alloy. Hence, greyscale 255~255 was considered as ROI in the SEM images. \( P_t \) was counted for sample A, B and C as 11.41%, 17.73% and 25.32% based on ROI. Pixel ratio of the metal alloy on ROI was calculated as 96.15%, which was the conversion coefficient (\( \mu = 0.9615 \)). Therefore, \( P_a \) was calculated as 11.87%, 18.44% and 26.33%, respectively. As shown in Fig. c), the threshold values of 251~255, 248~255 and 245~255 were chosen to distinguish the metal alloy (pore space) and cement using segment pore methods when \( P_t \) is very close to \( P_a \), as demonstrated in Table 4.
Fig. 4. a) SEM image, b) Intensity to distance, c) The extracting pixels of pores space by Image-Pro Plus software (sample A, B and C based on the grayscale 251~255, 248~255 and 245~255, respectively)

Table 4

<table>
<thead>
<tr>
<th>Pore structure</th>
<th>Sample name</th>
<th>Actual porosity $P_a$ (%)</th>
<th>ROI</th>
<th>Conversion coefficient $\mu$</th>
<th>Threshold value</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D</td>
<td>A</td>
<td>11.87</td>
<td>255~255</td>
<td>0.9615</td>
<td>251~255</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>18.44</td>
<td>255~255</td>
<td>0.9615</td>
<td>248~255</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>26.33</td>
<td>248~255</td>
<td>0.9715</td>
<td>245~255</td>
</tr>
<tr>
<td>3D</td>
<td>A</td>
<td>22.74</td>
<td>185~255</td>
<td>0.9709</td>
<td>184~255</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>27.24</td>
<td>185~255</td>
<td>0.9709</td>
<td>183~255</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>50.53</td>
<td>180~255</td>
<td>0.9709</td>
<td>180~255</td>
</tr>
</tbody>
</table>
Porosity in 3D pore structure

As shown in Fig. 5a), gray level intensity was found to be the lowest in the untreated sample and increased for the samples A, B, C and the metal alloy. This is attributed to the fact that the gray level is closely related to the density and the composition of sample \cite{25}. The peak of the gray level in X-ray microtomography image of the metal alloy was mainly composed of heavy metal elements (43.7%Bi, 20.6%Pb, 8.6%Sn, 5.8%Cd, 20.1%In, etc.), which was higher than that of the untreated sample.

In 3D structure, greyscale 185–255 was chosen as ROI, which involved 0.08% untreated sample and 97.09% the metal alloy greyscale, respectively. It’s acceptable that $P_i$ was counted for sample A, B and C as 22.08%, 26.45% and 49.06% based on ROI. Pixels ratio of the metal alloy on ROI was calculated as 97.09%, which was the conversion coefficient ($\mu=0.9709$). $P_a$ of 3D structure in sample A, B and C were calculated for as 22.74%, 27.24% and 50.53%, which were consistent with values obtained using MIP (25.28 %, 29.61% and 53.34%), as demonstrated in Table 4 and Fig. 5 (b). Considering the results of MIP as references, the relative errors between the proposed method and MIP were 10.05%, 8.00% and 5.27% for the tested samples, which were found to be the highest in the sample A and decreased for sample B and C. The porosity based on MCP was slightly lower than that determined by MIP, due to pore wall breakage caused by high pressures when using MIP \cite{8}.

\[ \text{Fig. 5 Comparison of porosity between MCP and MIP} \]

Reconstruction of 3D pore structure

In order to distinguish pore space and solid phase, the intruded samples (A, B and C), untreated sample and the metal alloy were examined by X-ray microtomography.
system under the same conditions. The threshold values of 184–255, 183–255 and 180–255 were chosen to distinguish the metal alloy (pore space) and cement when $P_t$ was very close to $P_a$, as shown in Fig. 6.

Fig. 6 The image of untreated sample and treated samples (A, B and C based on the threshold of 184–255, 183–255 and 180–255)

3.4 Pore size distribution in 3D pore structure

The pore size distribution is an important parameter used to describe the probabilities of different apertures in modern concrete. Considering the isotropy in spatial distributions of porosity, sample A, B and C were visualized in direction X, as shown in Fig. 7 (a). The smallest pore size was 2 μm because of the accuracy of instrument, and the pore size distributions in the three directions were similar. The most probable aperture decreased for sample A, B and C, in that order. This can be attributed to the fact that lower w/c ratio can increase the density of the paste and therefore reduce the pore space available for the metal alloy intrusion, similar to the influence of a longer curing time [5].

Pore size calculated by MCP was compared with the results tested by MIP as shown in Fig. 7(b). It is evident that the most probable aperture calculated by MCP
was greater than determined by MIP. Firstly, this can be partially explained by the heterogeneity of the pore structure in the cement-based material. The calculated direction of pore size by MIP is based on the volume of mercury entered, which strongly correlated with the metal-paste contact angle \(^{25}\). In other words, different aperture can be observed when the same one pore was researched in different observed direction. As for MIP, geometric surface of minimum-value aperture in the same pore space is preferentially filled by mercury, which named section pore size demonstrated in the vertical plane of pores \(^{21, 25, 26}\). Differently, one fixed direction \(^{30}\) (direction X, Y or Z) of pore size investigated by MCP should be chosen for all pores before calculation, which strongly correlated with the selection of direction. Mostly, the pore size based on MCP is not minimum-value aperture in the same pore space, which named non-section pore size in the non-vertical plane of pores. From geometry considerations, the non-section dimension is larger than section dimension, which is analogous to the hypotenuse of a rectangular triangle being greater than the right-angle side. Secondly, the thresholding value based on images is the important factor to influence pore size distributions. Comparing with cement, the metal alloy is defined as pores space based on ROI combined with conversion coefficient. What's more, the minimum capillary pore radius that can be invaded by the molten metal alloy using the experimental set-up is 0.085 μm and the smallest pore that could be distinguished by X-ray tomography is size of 2 μm, which directly generate that the pore size distribution will certainly be different from that provided by MIP. Therefore, the diameter (MCP) is longer than or equal to the diameter (MIP). Spatial distribution of porosity in cement-based materials is characterized by heterogeneity \(^{30, 31}\).

![Fig. 7](image-url) (a) Pore size distribution in X directions for 3D pore structure of sample A, B and C, (b) Comparison between MCP and MIP in the Pore size distribution from direction X
3. Conclusions

X-ray microtomography combined with metal centrifugation porosimetry (MCP) using a novel metal alloy, was applied for the first time to quantitatively investigate 3D pore structure in hardened cement paste. The contrast between pore space and solid phase in X-ray microtomography imaging was improved due to the intrusion of the low-melting-point metal alloy. A new threshold value segmentation method for pore space was proposed based on ROI combined with conversion coefficient. The porosity determined by MCP was close to MIP for the samples examined in this study and the relative errors in the range of 5.27-10.05% were found in the values given by MCP and MIP. It was established that the proposed MCP method is a powerful and reliable technique for studying the 3D pore structures in cementitious materials, and it could be speculated that future experiments could carried out on the other materials.

Acknowledgments

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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