Pore structure of blended cement paste by means of pressurization–depressurization cycling mercury intrusion porosimetry

Yong Zhang¹*, Bei Wu¹, Jian Zhou², Guang Ye¹, Zhonghe Shui³
(¹) Microlab, Materials & Environment, Delft University of Technology, Delft, The Netherlands
(²) Sinoma Research Institute, Sinoma International Engineering Co., Ltd., Beijing, China
(³) State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan, China

Abstract: Concrete containing supplementary cementitious materials (SCMs) has different durability properties from that containing pure Portland cement. The durability of concrete is always associated with the properties of microstructure, especially pore structure. Pressurization–Depressurization Cycling Mercury Intrusion Porosimetry (PDC-MIP) was recently developed which can overcome the “ink bottle” effect and provide a more accurate estimation of the pore size distribution in cement-based materials. In this study, the PDC-MIP was applied to characterize the evolution of pore structure of cement pastes blended with fly ash and/or limestone powder. The results revealed that as hydration proceeds the volume of gel pores (<0.01 um) increased while the volume of capillary pores (>0.05 um) decreased. The addition of fly ash increases the volume of gel pores (<0.01 um).

Keywords: mercury porosimetry; pore size; supplementary cementitious materials

1 Introduction

The environmental impact of infrastructure projects is becoming increasingly important issue in engineering design. The CO₂-emission from cement production amounts to more than 8% of the global anthropogenic CO₂-emissions [1]. Great opportunities lie in the utilization of blended cements, in which clinker is partially replaced by supplementary cementitious materials (SCMs), such as blast furnace slag from the steel industry, fly ash (FA) from the coal electricity plants, and limestone powder (LP). The durability of concrete made of blended cements develops differently from that of concrete made of pure Portland cement.

The durability of concrete is always associated with the properties of microstructure, especially pore structure. The addition of SCMs affects the pore structure of cement-based materials because of the change of particle packing as well as the change of hydration process. A variety of pore size types are created with the hydration process, from several nano meters to micro meters. The main hydration products, calcium-silicate-hydrate (C-S-H), consist of molecular-scale interlayer pore spaces as well as nanometric gel pores between C-S-H particles [2]. The micrometric capillary pores are interstitial spaces between unhydrated grains, usually irregular in shape, and represent the space corresponding to the originally water filled space [3]. Pore size characterization is of great interest in correlation between microstructure and macro properties. Using regression method, the pore size was catalogued into different groups in various studies [4–6]. The shrinkage is mainly governed by the pore sizes < 0.01 nm. While the strength and permeability is dominated by the pore sizes 0.01-0.5 um.

Mercury intrusion porosimetry (MIP) has been widely used for measuring the pore structure of porous materials. With the assumption that pores in cementitious materials are cylindrical and entirely and equally accessible to mercury, the correlation between the applied pressure and the pore diameter can be described using the Washburn equation [7]:

\[ D = \frac{(-4\gamma \cos \theta)}{P} \]

* Corresponding author affiliation and e-mail address
where, $D$ is the equivalent pore diameter being entered, $P$ is the pressure required to overcome the opposition to entry, $\gamma$ is the surface tension of mercury, $\theta$ is the contact angle between mercury and pore wall. Generally, the measurable pore sizes range from several nanometres to 100 micrometres.

Numerous publications have described the pore structure features of hydrating/hydrated cement-based materials measured by MIP method [8-11]. The traditional MIP method has been proved to be inappropriate for the measurement of real pore size distribution in cement-based materials [11]. This is because the traditional MIP method measures pore size on the basis of the diameter of the accessible throat pores through which mercury penetrates to reach internal pores. This inherent limitation of MIP is called the “ink-bottle” effect [8]. Regardless of the maximum pressure attained, depressurization always results in a hysteresis of mercury extrusion [12]. As illustrated in Fig. 1, the large pore with a diameter $d_1$ can be filled with mercury only when the small pore with a diameter of $d_2$ has been intruded. The small pore and the large pore behind are defined as ink-bottle pores and throat pores, respectively, and $v_1$ and $v_2$ are ink-bottle pore volume and throat pore volume respectively.

![Figure 1 Schematic illustration of “ink-bottle” effect](image)

MIP with Pressurization–depressurization cycles was developed to get insight of “ink-bottle” effect [13]. Step-by-step pressurization–depressurization cycles (repeated 10 times) were applied to determine the volumes of connected pores. Recently, pressurization–depressurization cycling mercury intrusion porosimetry (PDC-MIP) is developed. Instead of a continuous pressurization from the minimum pressure to the maximum pressure followed by a continuous depressurization from the maximum pressure to the atmospheric pressure, the applied pressure is increased from the minimum to the maximum by repeating pressurization–depressurization cycles at each pressure step [14], whereby the ink-bottle pore volume corresponding to each throat pore size can be determined. In order to calculate the pore size distribution, it is assumed that the fractions of the ink-bottle pores are equal to that of the pores with the diameter larger than the corresponding throat pores. Based on volume fraction, each ink-bottle pore volume will be thereafter allocated to the larger pore sizes. This novel method employs the principles of pressurization–depressurization cycles but is capable of better understanding the pore size distributions.

The objective of this paper is to apply PDC-MIP method for characterizing the pore structure of cement paste blended with fly ash and/or limestone powder. The influence of SCMs and water to binder (w/b) ratio were experimentally investigated.

## 2 PDC-MIP

### 2.1 Test sequence

The PDC-MIP testing sequence has been described in details by Zhou et al. [13]. As shown in Fig. 2, the pressure applied starts from $P_{1,\text{in}}$ and increases up to $P_{2,\text{in}}$, and then decreases to $P_{2,\text{ex}}$ for the first pressurization-depressurization cycle. The ratio $P_{2,\text{in}}/P_{2,\text{ex}}$ is the ratio between the cosine values of intrusion contact angle and extrusion contact angle $\cos\theta_{\text{in}}/\cos\theta_{\text{ex}}$. In the $n$th cycle, pressure increases from $P_{n,\text{ex}}$ to $P_{n+1,\text{in}}$ and then decreases to $P_{n+1,\text{ex}}$. The corresponding cumulative intrusion volumes are $V_{n,\text{ex}}, V_{n+1,\text{in}}$ and $V_{n+1,\text{ex}}$ respectively. Eventually, the test is finalized when the maximum pressure is applied.

![Figure 2 Schematic of test sequence](image)
Following this test sequence, the increment volume of mercury intrusion increasing pressure from $P_{n,\text{in}}$ to $P_{n+1,\text{in}}$ can be divided into two parts: throat pore volume ($V_{n+1}^{\text{th}}$) and ink-bottled pore volume ($V_{n+1}^{\text{ink}}$). The calculation can be figured out as follows:

$$V_{n+1}^{\text{th}} = V_{n+1}^\text{in} - V_{n+1}^\text{ex}$$

$$V_{n+1}^{\text{ink}} = V_{n+1}^\text{in} - V_n^\text{in} - V_{n+1}^{\text{th}} = V_{n+1}^\text{ex} - V_n$$

### 2.2 Data analysis

The ink-bottled pore volume ($V_{n}^{\text{ink}}$) is allocated into the pore size bigger than $\phi_{\text{th}}$. According to the volume fraction of each throat pore size, the pore size distribution is calculated as follows:

- **Step one:** $V_{1,1} = V_1^{\text{th}} = V_{2,\text{in}} - V_{2,\text{ex}}$, assuming the largest pore does not have ink-bottle effect.
- **Step two:** $V_{1,2} = V_{1,1} + V_{2}^{\text{ink}}, V_{2,2} = V_{2}^{\text{th}}$
- **Step three:** $V_{1,3} = V_{1,2} + V_{3}^{\text{ink}}(\frac{V_{1,2}}{V_{1,2} + V_{2,2}}), V_{2,3} = V_{2,2} + V_{3}^{\text{ink}}(\frac{V_{2,2}}{V_{1,2} + V_{2,2}}), V_{3,3} = V_{3}^{\text{th}}$

- **Step n:** $V_{n,n} = V_{n, n-1} + V_{n}^{\text{ink}}(\frac{V_{1,n-1}}{V_{1,n-1} + V_{2,n-2} + \ldots + V_{n-1,n-1}})$

where $V_{i,n}$ indicates the volume of pores size $D_i$ calculated at step $n$.

Figure 2  Illustration of the PDC-MIP testing sequence with pressurization-depressurization cycles (left) and cumulative pore fraction in the comparison of different test methods (right)

Based on the above data analysis method, the cumulative pore fraction vs. pore diameter can be determined. It is shown in Fig. 2 that the total mercury intrusion measured by PDC-MIP is in good agreement with the other measurements. In particular, PDC-MIP yields a relatively coarser pore size compared with the results of the traditional MIP method.

### 3. Experiments

#### 3.1 Materials

Materials used in this work are Portland cement (CEM I 42.5N), FA, and (LP). The mix composition is shown in Table 1.

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>w/b</th>
<th>Portland cement</th>
<th>FA</th>
<th>LP</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1-PC-0.4</td>
<td>0.4</td>
<td>100%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M2-PC-0.5</td>
<td>0.5</td>
<td>100%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M3-PC-0.6</td>
<td>0.6</td>
<td>100%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M4-FA10-0.5</td>
<td>0.5</td>
<td>90%</td>
<td>10%</td>
<td></td>
</tr>
</tbody>
</table>
3.2 Sample preparation

Cement pastes with w/b ratios of 0.4, 0.5, and 0.6 were mixed with a HOBART mixer at low speed for 1 minute and at high speed for 2 minutes. Then the fresh paste was poured into plastic bottles and shaken on the vibration table to remove big air bubbles and then sealed with lids. In order to avoid bleeding, the samples were rotated for one day and then placed in a standard curing room with the condition of 20°C and 98% RH. After cured for 28 days, 105 days, and 182 days, the samples were split into small pieces. Liquid nitrogen was used to stop the further hydration of the cement paste [10]. Then these pieces were moved into a freeze-dryer with temperature of −24°C and under vacuum at 0.1 Pa. Until the water loss was below 0.01% per day, the samples were used for the PDC-MIP measurements.

3.3 PDC-MIP test

PDC-MIP measurements were performed with Micrometrics PoreSizer 9320. The test was conducted in two stages: continuous pressurization from 0.004 MPa to 0.15 MPa, then a hundred pressurization–depressurization cycles were repeated at increasing pressures from 0.15 MPa to 210 MPa. Volume measurements were corrected by a blank run for differential mercury compression and for specimen compression. Since this volume is not of interest, the pores with the equivalent pore diameter larger than 10 um were not considered in this study.

4. Results and discussions

4.1 Porosity

The total volume of intruded mercury allows for a measure of the porosity accessible to mercury at maximum applied pressure. It has been proved a valuable index for comparing pore structure between different mixtures.

Fig. 3 shows the experimental results of the open porosities by PDC-MIP. Each data of porosity was the average of three measurements, with a good accuracy. Porosity varied with the different samples in a wide range, decreasing with the curing age. The addition of fly ash increased the porosity throughout the curing ages, and the higher replacement level leaded to the higher porosity. In fly ash-blended cement paste, the porosity decreased greatly from the first month to three month. While after this period, the porosity evolved quite limited up to half year, which indicates that a dormant period subsequently occurs during which little fly ash has reacted. This conclusion agrees well with the results from Luke and Glasser [15]. The addition of limestone powder diluted the hydrating cement paste, leading to higher porosity.

![Figure 3 Open porosity obtained by PDC-MIP tests](image-url)
4.2 Pore size distribution

4.2.1 Pore size distribution of cement paste

A pore size distribution analysis was carried out in a range of pore diameter from 0.007 to 10 μm in this study. In order to get more insight into the pore size distribution of cementitious system, the measured results were divided into four size groups: gel pores (< 0.01 μm), small capillary pores (0.01-0.05 μm), medium capillary pores (0.05-0.5 μm), large capillary pores (> 0.5 μm), according to Young and Sidney Mindess [4]. Fig. 4 shows the results of the pore size distribution of six samples at the curing age of 182 days obtained by PDC-MIP method.

As shown in Fig. 4, the volume of gel pores is almost unchanged with the increasing w/b ratio. At the meantime, capillary pores, especially the medium capillary pores (0.05-0.5 μm), are increasing greatly as w/b ratio increases. This implies the dilution effect (increasing water-to-cement ratio) mainly works on medium capillary pores (0.05-0.5 μm). The addition of fly ash increases the volume of gel pores (< 0.01 μm). This observation is characteristic for materials containing SCMs owing to the smaller pore size resulting from the pozzolanic reaction. Increasing replacement level of fly ash from 10% to 30% leads to the formation of more large capillary pores (> 0.5 μm). Limestone powder is considered as an inert SCM, and its addition in fly-ash cement dilutes the hydrating cementitious system, resulting in the increase of the volume of small and medium capillary pores (0.01-0.5 μm). This also provides evidence that the dilution effect plays an important role in the formation of small and medium capillary pores (0.01-0.5 μm).

4.2.2 Evolution of pore sizes

The changes of pore size distribution resulting from continuous hydration are displayed in Fig. 5. All samples show pore size distribution towards a finer one, as time elapses. As the hydration proceeds, the volume of gel pores (<0.01 μm) increases, while the volume of capillary pores is considerably decreased. In particular, the gel pores of FA-blended cement paste is significantly increased with curing age from 28 days to 182 days, indicating the active pozzolanic reaction occurred in later ages. As a result, the calcium hydroxide Ca(OH)$_2$ is consumed by pozzolanic reaction, producing secondary C-S-H gel. The formation of secondary C-S-H gel refines the pore structure by transforming coarser pores into finer ones, and the volume of continuous capillary pores is, therefore, proportionally decreased. The less the Ca(OH)$_2$ content in the hydrated binder matrix is, the less the volume of continuous pores is [16]. Interestingly to note that with the continuous hydration, the small capillary pores in Portland cement paste decreased while in
FA-blended paste increased. This might be ascribed to the different mechanisms in hydration process.

Figure 5 Volume evolution of pores in different size ranges for the different pastes mixtures aged from 28 days to 182 days.

4.3 Evolution of throat pore and ink-bottle pore

Throat pores influence the pressure and breakthrough during intrusion, which play dominated role in ink-bottle problem. The throat pores and ink-bottle effect is changing with hydration ages. Fig. 6 reveals the evolution of throat pore size distribution and corresponding ink-bottled pore size distribution in pure Portland cement paste (w/c=0.5) at the age from 28 days to 182 days.

As shown from ink-bottle pore size distribution in Fig. 6, the more throat pores exist, the more ink-bottled pores forms. The mercury entrapment (ink-bottle effect) is more pronounced with the throat to smaller pore size, and the maximum amount of mercury entrapment occurred when the threshold pore diameter is intruded. While afterwards the ink-bottle effect is becoming less apparent and less mercury is entrapped.

From the graph of ink-bottled pore volume vs. pore diameter, the ink-bottle effect turns to be less apparent when threshold pore diameter has been intruded, which indicates the changes of connectivity of pore network and also implies different refinement mechanism of the smaller pores.

At the curing age up to half year, much less ink-bottled pores exist in the pore size range of 0.08-0.3 um, and most of the pore entrapment located in the size range smaller than 0.1 um. It is believed that the tortuosity is determined by the pore entrapment (ink-bottle pores), therefore the transport properties are possibly governed by the pore sizes smaller than 0.1 um.

Figure 6 Volume of each throat pores (left) and associated ink-bottled pore volume (right), 0.5-w/c-ratio Portland cement paste at the age of 28, 105, or 182 days
5 Conclusions

This study reveals that PDC-MIP is effective in the characterization of pore size features of cementitious system. Confidence in the validity and reproducibility of the experiment was established. It can not only solve the ink-bottle problem, but also provide fundamental information of the throat pore size distribution as well as the corresponding ink-bottle pore size distribution. This information provides better understanding of the pore structure of cement-based materials, and is valuable for the study of transport-related durability properties.

From the results presented earlier in this study, key findings are the following:

- The pore sizes of cement paste towards to a finer distribution with hydration process. The volume of gel pores (< 0.01 um) increases with curing age while the volume of medium capillary pores (0.05-0.5 um) and large capillary pores (>0.5 um) decrease with curing age. The dilution effect (increasing water-to-cement ratio) has influence mainly on the pore sizes range of 0.05-0.5 um.
- The addition of fly ash refines the pore size of cement paste by increasing the volume of gel pores and small capillary pores (0.01-0.05 um). The addition of limestone powder dilutes the cementitious system and results in volume increment of the pores (0.05-0.5 um).
- The more throat pores exist, the more ink-bottled pores form.

REFERENCES

Journal article:

Dissertation
Conference proceedings


Book

