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Pore shape analysis using centrifuge driven metal intrusion: Indication on porosimetry equations, hydration and packing

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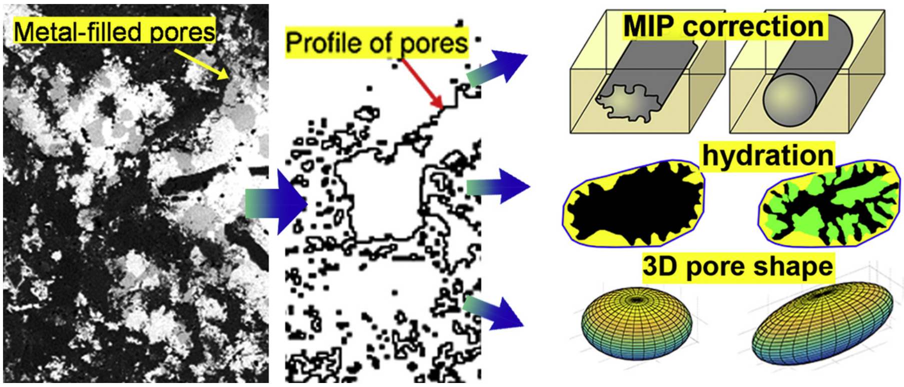
HIGHLIGHTS

- Centrifuge-driven low-melting metal intrusion, low energy electron BSE for sharp imaging of pores in cement.
- 2D profiles of pores extracted from the sharp BSE images to characterize pore shape.
- Pore shape affects MIP and the Washburn's equation was corrected based on circularity of pores.
- 2D profiles linked with hydration, packing and 3D pore shape via solidity and aspect ratio.

GRAPHICAL ABSTRACT



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ABSTRACT

Porosity is an intrinsic property of many cementitious materials. This study uses a new centrifugation-based low-melting-point metal intrusion technique to characterize and analyze the shape of pores in cementitious materials. Low energy electrons with ultra-long beam dwell time are used to obtain nano meter level resolution of the pore shape. Three descriptors, namely circularity, solidity, and aspect ratio, are proposed to represent the area-perimeter relationship, hydration and packing and 3D shape of the pores, respectively. Circularity is found to hold a consistent power correlation with pore size. Based on this correlation, the Washburn's equation is modified to correct the biased prediction of pore size using mercury intrusion porosimetry (MIP). Solidity, is found to decrease with increased pore size, denser packing of cement particles and more hydration products. Aspect ratio of the observed pores is found to average at about 2 representing an oblate ellipsoid shape of pore in 3D space.

1. Introduction

Pore structure characterization is essential for studying the properties and behavior of cementitious materials. The mechanical properties, such as Young's modulus, strength, and fracture toughness of cementitious material are strongly correlated with the pore size and structures Taylor [1]. For example, it was found that the increased porosity reduces the strength of concrete [2] and cements [3]. The nature of pores also plays a significant role on the freeze and thaw of concrete [4] and strength and thermal conductivity of low-density cementitious materials such as foam concrete [5–8]. Understanding of the pore structures is also critical to study the effect of nanoparticle additives [9] on the properties of

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cementitious materials since these nanoparticle can fill and refine the pore structures [10]. Pore characteristics and pore connectivity also affect the durability aspects of cementitious material. The alkaline-silica reaction showed dependency on the porosity of the cement and concrete [11]. The pore characteristic are also deterministic factors that affect chloride ion transportation [12] and water permeability of concrete [5]. Moreover, Porosity and pore pressure build-up is a crucial factor for spalling and residue strength of concrete under fire [13].

Three commonly used techniques are available to characterize these pore structures. The first technique is based on measuring the adsorption of gas molecules on solid surfaces and deriving the porosity using mathematical models such as BET theory [14,15]. The second utilizes the porosimetry method (MIP) [16], which uses a non-wetting liquid such as mercury to intrude into the pores and measure the amount of liquid intruded under different pressures [17,18]. The pore size distribution is derived based on force equilibrium between the surface tension of the liquid and the intrusion pressure [17–21]. The last technique is image analysis, based on pore images usually obtained via microscopy. The method is often used for collecting statistics regarding the pores [17,22–25]. Image analysis is also preferred for characterizing the true pore structure, due to direct visualization and measurement of the pores whereas the other two methods use mathematical models to obtain the pore information indirectly.

Past studies using image analysis have focused mainly on pore size characterization [17,22–24]; only a few have qualitatively investigated the shape of pores. Using images of epoxy impregnated pores, Wang and Diamond found that the pores had a high degree of convolution and were significantly elongated [26]. Willis et al. [24] studied the major axis and minor axis of each pore, but only to determine the pore size. Lloyd et al. studied the spatial distribution of pores in geopolymer polymer gels [27] and derived the pore size distribution from the pore images. Lange et al. used images of epoxy impregnated samples to calculate the pore size distribution and shape factor of pores [23]. Due to the limited contrast between epoxy and cement, the blurred image of the observed pores [23] imposed errors on the interpretation. Although past work based on image analysis has qualitatively addressed the critical limitation of porosimetry methods such as mercury intrusion porosimetry (MIP) [19], these existing studies have not addressed the essential link between the pore shape and nature of pores and the porosimetry measurement. One reason for the lack of attention in the literature to pore shape could be the requirement of very clear images of pore boundaries, referred to as pore profile in this paper. For example, a blurred image of a pore can still give fair estimation of the size (area) of the pore but can introduce large errors to the estimated profiles of pores.

In order to quantitatively analyze the shape (profile) of the pores based on images, the current imaging techniques need to be improved to obtain a clearer view of pore profile. In this study, the shape of pores in cement is characterized and analyzed using a new scheme proposed by the authors [28]: a centrifugation-based low-melting-point metal intrusion (CLMI) technique. This technique allows the intrusion of low-melting-point metals with standard laboratory centrifuges. Some researchers have used low-melting-point metal such as Wood's metal to replace epoxy as the intrusion material [20,29,30] to highlight pores. Wood's metal produces a much clearer view of the pores than epoxy because of the large difference between the atomic numbers [31] of the metal and cement [23,30]. The CLMI method is easier to implement routinely since it requires no customized high pressure chambers [24] or control units [27] as for traditional Wood's metal intrusion methods. Furthermore, the contrast and clarity of pore shapes under BSE are heavily affected by the energy of electrons, interaction volume, and signal contrast [32]. In this study, low energy electrons with ultra-long beam dwell time are used to enhance the resolution and contrast of images to obtain clear views of pore profiles.

Using this new technique, high resolution data of pore profiles can be obtained. Three new descriptors are defined to interpret pore structures, namely circularity, solidity, and aspect ratio of the pore. The pore shape analysis scheme demonstrated here not only provides more information about the nature of pores and the effect of hydration but also can be used to correct the mathematical model used in porosimetry (such as MIP). On the basis of quantitative analysis of pore shapes, Washburn's equation was modified to produce more accurate estimations for future MIP applications in cementitious materials. This paper also demonstrates how high resolution pore shape data from 2D observations can be correlated statistically with pore shape in 3D space. This 2D-3D correlation is essential for 3D realization of pore structures and for constructing cement hydration models. This study provides new ways to characterize the pore shapes to obtain more information about the nature of pores in porous material. The pore shape analysis method mentioned in this study will also benefit the research of porous ceramics and geomechanical materials.

2. Experimental program

2.1. Materials and instrumentation

Type GP Ordinary Portland Cement (OPC), conforming to the requirements of Australian Standard AS 3972 [33], was used. Two low-melting-point metals, whose properties are shown in Table 1, were purchased from Rotometals, Inc.

A Nova 450 SEM was used to perform BSE imaging of the sample. The proposed CLMI technique [28] was implemented using an Eppendorf Centrifuge 5702 with the swing bucket rotor. The assembly of the intrusion device is shown in Fig. 1. A set of aluminum containers was used to hold the sample and the melted metal in the swing bucket and plastic foam was used to reduce heat loss from the container. Centrifugal force was generated by the spinning rotor and the pressure increased with the depth of the melted metal as shown in Fig. 1.

2.2. Sample preparation and centrifuge intrusion process

Samples approximately 5 mm × 5 mm × 5 mm were taken from the cores of 20 mm OPC paste cubes with the w/c of 0.4 and 0.8. For the w/c = 0.4 and the w/c = 0.8 OPC, the samples were taken after being cured in saturated calcium hydroxide solution for 28 days and 7 days, respectively. Ethanol was used to stop hydration after sampling. The cement samples were reserved in vacuum for one week to remove liquids from the capillary pores.

Based on Fig. 1, the intrusion pressure P can be calculated as

$$P = \frac{1}{2}\rho\omega^2(2L_1H + H^2)/10^9 \tag{1}$$

where ρ is the density of the liquid metal, ω is the centrifuge speed with the unit of rad/s. L_1 = 48 mm, is the distance from the center of the centrifuge to the surface of liquid metal in the tube, H = 82 mm, is the depth of liquid metal to the upside of the cement sample.

Cement samples were placed in the container as shown in Fig. 1. The container was heated to 95 ± 2 °C and filled with liquid metal. Foam plastic was used to reduce heat loss from the container. The centrifuge ran for 10 min to allow cooling-down of the container so that the metal would harden under pressure. The depth of the metal H was controlled to 82 ± 2 mm for all the samples.

Ten samples were prepared using CLMI as shown in Table 2. C1 and C2 are calibration samples where Wood's metal was used to generate higher pressure (15.2 ± 0.34 MPa based on Eq. (1)) at 4400 rpm in order to obtain baseline information for the pores. The baseline information was used to develop relationships between pore shapes and the porosimetry equations. The non-toxic Fields' metal was used to prepare the 8 verification samples V1–V8 which were intruded at different speeds (pressure) of 200 rpm (0.03 ± 0.0005 MPa), 1100 rpm (0.77 ± 0.0173 MPa), 2200 rpm (3.10 ± 0.069MPa), and 4400 rpm (12.4 ± 0.28 MPa). These verification samples were used to verify the modified porosimetry equation developed in this work. The centrifuge time was 10 min, long enough to guarantee that the temperature of the metal dropped below its melting temperature.

2.3. BSE images and image analysis

Epoxy resin was used to mount the samples, that were then polished down to 0.1 μm grit. A thin layer of carbon was coated on the surface of each sample to prevent charging. BSE was used to image the samples at the magnification of 1000× using low energy electrons (5 keV). Five images were taken randomly at