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Influence of water-to-cement ratio and curing period on pore structure of cement mortar

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HIGHLIGHTS

- ▶ Porosity and hydration degree of mortar increased with increasing *w*/*c*.
- ▶ Total porosity of mortar decreased with increasing curing period.
- ▶ Existing models for pore size distribution of mortar were reviewed.
- ▶ A single lognormal distribution may not be adequate for pore size distribution.
- ▶ Compound lognormal distribution could be used to model pore size distribution.

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ABSTRACT

The effect of water-to-cement ratio (*w*/*c*) and age on the pore structure of cement mortar was determined through mercury intrusion porosimetry (MIP). The cement mortar specimens were prepared with *w*/*c* of 0.4, 0.5 and 0.6, and were tested at different curing ages (14, 28, 180 days). The degree of hydration of the cement in cement mortar was obtained by determining the non-evaporable water content. Test results have shown that, the degree of hydration increased with increasing curing time and water-to-cement ratio of the cement mortar for the ages of cement mortar varying between 14 and 180 days. An increase in the water-to-cement ratio increases the total porosity. In addition, the existing models of pore size distribution of cement-based materials has been reviewed and compared with test results in this investigation.

1. Introduction

The pore structure of cement-based materials is one of their most important characteristics and strongly influences both its mechanical behavior [1–3] and its transport properties [4–7]. The durability of cement-based materials depends on their permeability properties and it is affected by the pore structure.

Cement-based materials contain air voids, capillary pores and gel pores (the interlayer spaces in a calcium–silicate–hydrate gel), and the pores in concrete are randomly sized, arranged, and connected [8]. Because of the wide range of pore sizes [9], the microstructure of cement paste is very complex. Mercury intrusion porosimetry (MIP) is a commonly used method of determining pore size distribution in the range of pore sizes which significantly affect properties such as permeability. Image analysis techniques have been used with MIP to investigate the structures in porous materials and their relationship to materials' properties. In cement-based materials, there are large numbers of fine pores which cannot be observed by image analysis, and there are very large pores (voids) which cannot be correctly determined by mercury porosimetry [10,11]. Thus, overlap in the whole range may not be possible. On the other hand, the sizes of pore entrances that are determined by MIP may be reasonably considered as a dominating factor controlling the permeation of fluid [12–14]. MIP measurements can serve as comparative indices for the connectivity and capacity of the pore system in hydrated cements.

Different microstructure-based models for predicting the transport properties of cement based materials depending on their porosities and pore size distribution are summarized by Atahan et al. [15]. In these models, the mean pore diameter, water-to-cement ratio, degree of hydration or the maximum continuous pore diameter (i.e., critical pore diameter) are the main characteristics of the material which account for their permeability properties. Odler and Robler [16] have prepared cement pastes with different water-to-cement ratios which were hydrated at different temperatures for different times. They have shown that the main factor influencing the strength properties of the samples is their porosity. In their work, they also conducted MIP tests. Winslow and Liu [17] indicated that the cement paste in concrete and

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mortar has a pore size distribution different from that of a plain paste hydrated without aggregate. They showed that, in mortar and concrete, there was the additional formation of pores greater in size than the pore size of plain cement paste, and they thought that these larger pores are present only in the interfacial zone between the aggregate and cement paste.

This paper reports an experimental investigation into the changes in the pore structure of cement mortar brought about by changing the water-to-cement ratio (w/c) and hydration period. The changes in pore structure were quantified by using mercury intrusion porosimetry technique. In addition, the degree of hydration was determined. The existing models of pore size distribution of cement-based materials have been reviewed and compared with test results in this investigation.

2. Experimental program

2.1. Materials and specimen preparation

Ordinary Portland cement (ASTM Type I) without mineral additions was used as binder. In this work, three mixes of cement mortar with the w/c of 0.4, 0.5 and 0.6 were prepared. The fine aggregate was river sand consisting mainly of quartz, with 10% feldspar. The gradation test showed that the particle size of the sand was continuously distributed within the range of 0.4–2.5 mm with 80% of sand. The sand-to-cement (s/c) ratio is 2 for cement mortar. These mortars were cast in 100 mm cube molds. They were demolded after 1 day curing at 20 °C under 100% relative humidity (RH) conditions. The curing conditions were either in water at 20 °C or in an environmental chamber at 20 °C and 60% RH.

2.2. Mercury intrusion porosimetry (MIP)

Mercury intrusion porosimetry (MIP) is a widely used method for measuring the pore size distribution of cement-based materials. In MIP test, a sample is placed into a chamber, and surrounded by mercury, and then the pressure applied on the mercury is gradually increased. So, as the pressure increases, the mercury is forced into the pores of the sample. For filling a non-wetting fluid into a pore of the diameter d, a pressure P that is inversely proportional to the diameter of this pore must be applied [18–20]. This pressure is given by the Washburn equation as seen below [21]:

$$d = \frac{-4\gamma \cos\phi}{P} \tag{1}$$

where d is the apparent pore diameter, γ is the surface tension of the mercury, and ϕ is the contact angle between the mercury and the pore wall. The values for γ and ϕ were assumed to be 0.480 N/m and 140°, respectively.

The MIP tests were done on a Quantachrome Autoscan 33 porosimeter with a maximum intrusion pressure of 414 MPa was used. The weights of the samples were approximately 3 g. The cube specimens were removed from their curing environment at the age of the test. Mortar cores were cut and grinded smooth to produce 37-mm-diameter cylindrical specimens of 18 mm in thickness. At the age of 14, 28, 180 days, the specimens were crushed and placed in ethanol solution to stop hydration. The samples for the MIP test were then obtained by carefully breaking the core with a chisel. Small pieces of mortar, 3–6 mm, were taken from the middle of the core by a hand clipper. Before testing, the samples for the MIP test (which requires total removal of moisture) were dried in an oven at 105 °C until a constant mass was reached. The oven drying time was determined by repeated heating and cooling of several preliminary samples, and this was found to take about 3 h. To obtain the critical pore size of the specimens with different w/c and curing period, differential curves at the cumulative intruded pore volume vs pore diameter diagrams were also used.

In this investigation, the highest pressure used in these experiments was 212 MPa, according to a minimum pore diameter of 0.0069 μm. The higher the pressure is, the smaller the pores which can be intruded. However, one has to keep in mind that the increase in volume obtained at high pressure can be partly caused by bigger capillary pores which can only be reached by small pores [22–24]. As the pressure increases, the mercury is forced into the pore system on the surface of the sample. If the pore system is connected, a pressure may be reached at which mercury can penetrate the smallest pore necks of the system and penetrate the bulk sample volume. If the pore system is not connected, mercury may penetrate the sample volume by breaking through pore walls. As reported by various researchers [25–28], however, the MIP technique has some limitations. First, the Washburn equation was derived based on the assumption that the intruded pores are cylindrical. A second problem is known as the ink bottle effect, in which a larger pore is preceded in the intrusion path of the mercury by a smaller neck. This may produce pore-size distribution curves with somewhat exaggerated high volumes of smaller pores and small volumes of larger pores. Another nuisance lies in the fact that the sample must be dried prior to the intrusion. It has been indicated that some microstructural damage may occur during the drying process [29–33]. Despite these limitations, the MIP technique is still considered an invaluable tool and the appropriate method for comparing the pore structure and pore network characteristics of different types of cement-based materials [34,35]. Further details regarding the MIP techniques used and its limitations and applications can be found in Refs. [18,22].

2.3. Degree of hydration

The degree of hydration, α, is defined as the fraction of cement that has fully hydrated. For the present experiments, was determined experimentally by comparing the amount of non-evaporable water in a sample to the amount needed for complete hydration [36]. The degree of cement hydration of the cement mortar was determined in accordance with Zhang and Zhang [37]. The degree of hydration was estimated by the formula (2):

$$\alpha = w_n / W_{nu} \tag{2}$$

where W_{nu} is the non-evaporable water content at complete hydration which is taken to be 0.23 g/g of cement [38]. The specimen was ground into fine particles (passing 1.18-mm sieve) and then oven dried at 105 °C for 6 h. A sample of approximately 3 g was used and ignited at 1050 °C for 3 h. The non-evaporable water content $w_n C_{cem}$ per gram of cement was determined from Eq. (3).

$$w_n = (w_1 - w_2)/(w_1 - w_2)(w_2 \times C_{cem})(w_2 \times C_{cem}) \tag{3}$$

where w_1 is the oven-dried weight of the sample; w_2 is the weight after ignition; and is the percentage cement content in cement mortar. The degree of cement hydrated in the cement mortar was then calculated by Eq. (2).

3. Test results and discussion

3.1. Degree of hydration and porosity

The degree of cement hydration is shown in Fig. 1. As expected, the degree of cement hydration increased with time. At the same age, higher w/c ratios resulted in higher degrees of hydration. All specimens achieved approximately 60% hydration after 14 days. After nominal 180 days, hydration ranges from 68% for the 0.4 w/c to 81% for the w/c specimen.

The development of porosity in a series of cement mortars with different w/c is shown in Fig. 2. The porosity can be calculated knowing the density of the cement mortar, the mass of the sample and the intruded volume of mercury. From Fig. 2, it can be found that the porosity decreased with an increase in the period of hydration for all the water–cement ratios tested. The rate of decrease was higher at the early stages of hydration. Also, the porosity increased with increasing water-to-cement ratio. Numerous previous studies [39–42] have shown the phenomenon of increase in porosity with

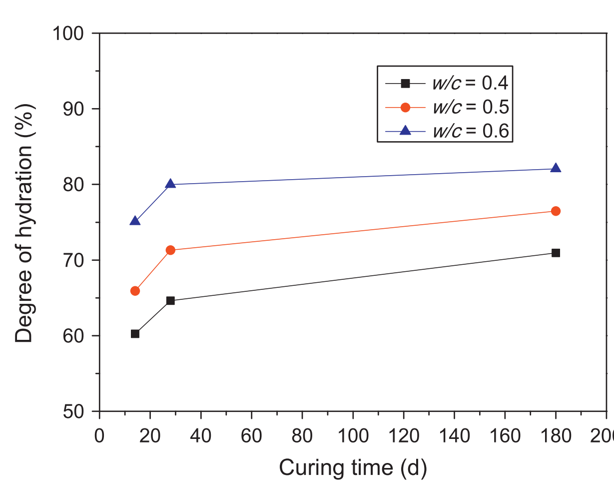

Fig. 1. Degree of hydration as a function of curing time.