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Pore structure characterization of early-age cement pastes blended with high-volume fly ash

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HIGHLIGHTS

- A pore structure characterization method of cement-based materials is presented.
- The effects of *w/b* and fly ash on early-age cement paste pore structure are analysed.
- A pore structure model is proposed for high-volume fly ash cement-based materials.

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ABSTRACT

High-volume fly ash is normally used as a partial replacement for cement to improve the workability, durability, and economic properties of concrete. The pore structure is an important factor affecting the performance of concrete. In this study, the influence of water-binder ratio (*w/b*) and fly ash content on the pore structure of early-age cement paste was determined using low-field nuclear magnetic resonance spectroscopy. Experimental results show that the most probable pore diameter increases with fly ash content and *w/b* and decreases with age. The porosity increases with *w/b* and decreases with age. A modified pore structure model, which is based on the existing models and the Weiball distribution, is proposed for high-volume fly ash cement-based materials.

1. Introduction

Concrete cracking is easy to generate and develop at an early age, and can seriously affect concrete durability [1]. Fly ash is a large coal-fired product, and it contains numerous leachable toxic trace elements. Fly ash adversely affects the ecological environment and human health when directly discharged into a landfill or an ocean [2,3]. Nevertheless, fly ash is a common pozzolanic material with numerous advantages. Fly ash, an additive of concrete, can improve the workability and the interface transition properties between the cement paste and the aggregate [4–6]. Moreover, this material can improve the mechanical properties and volume deformation of the concrete, effectively reducing the crack risk [7–10]. To save energy, reduce emissions, and improve the durability of concrete, the characteristics of high-volume fly ash concrete (HVFAC) have been studied widely [11–14].

Current research on the HVFAC focuses mainly on its macroscopic properties, such as strength, shrinkage, and durability [15–17]. Few studies on its microstructure have been conducted although many macroscopic properties of cement-based materials are closely related to the microstructure. The microstructure of cement-based materials is complicated, including macroscopic, microscopic, and other scales. The effects of different scales on the strength, deformation, permeability, and frost resistance of cement pastes vary. The compressive strength and elastic modulus depend mainly on the total pore volume (i.e., porosity), whereas the transmission properties, autogenous shrinkage, and creep are affected by micro-pores, including capillary and gel pores. To improve the properties of cement-based materials, various characteristics of HVFAC have been examined. The physical and chemical

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characteristics of fly ash have been analysed by scanning electron microscopy (SEM) [18]. Jiang et al. [19] found that fly ash is uniform spherical and can react with the hydrated cement product. Yu et al. [20] and Zeng et al. [21–22] studied the microstructural characteristics of cement-based materials with high-volume fly ash, but they did not present a pore structure model.

In terms of microstructure measurement technology, the pressurization-depressurization cycling mercury intrusion porosimetry, standard mercury intrusion porosimetry (MIP), nitrogen adsorption and desorption, and backscattered electron have been widely used [23–27]. However, these methods need pretreatment, that is, drying the sample before the test, which may damage the pore microstructure. In contrast, low-field nuclear magnetic resonance spectroscopy (LF-NMR) is a widely used method for porous media [28,29] that can obtain the water distribution in pore structures. Song et al. [30] summarized a few aspects of NMR research on porous media and determined that noninvasive methods of NMR detection in opaque samples were unparalleled. Yao et al. [31] compared MIP and LF-NMR in characterizing the pore size distribution of coal and found that the LF-NMR method was appropriate for characterizing coal fractures. Based on the LF-NMR measurement of the T_2 relaxation time of water molecules, Li et al. [32] proposed a comprehensive, facile, and effective method for the pore size distribution (PSD) investigation of porous microspheres. They concluded that the time saving and nondestructive properties made LF-NMR particularly convenient for achieving a comprehensive characterization of materials, especially for microstructures.

2. Materials and methods

2.1. Materials

In this study, PII 52.5 Portland cement with the Blaine specific surface area of 350 m^2/kg and density of 3180 kg/m^3 was used. Fly ash with a density, fineness, and water requirement ratio of 2160 kg/m^3, 20%, and 88%, respectively, was used in this study. Table 1 lists the chemical components of cement and fly ash, and Fig. 1 shows the SEM images of cement and fly ash particle morphology.

The *w/b* values in this study are 0.3 and 0.4. The fly ash contents by weight are 0, 30%, 50% and 70%. Table 2 shows the mixture proportions of fly ash cement pastes. In this table, SJ indicates that the cementitious material in the sample is cement only, and CF indicates that the cementitious material in the sample contains cement and fly ash. For example, 0.3CF30 represents a sample with a *w/b* value of 0.3 and a fly ash content of 30%.

Cement samples were mixed using a paddle mixer and the following procedure. Cement, water, and fly ash were weighed if necessary. After thoroughly mixing the cement with fly ash, water was added to the mixture in a blender. The mixture was initially mixed at 140 revolutions per minute (rpm) for 1 min. While pausing for 30 s, the cement paste adhering to the sides of the mixing bowl was scraped. The entire mixture was mixed for another 2.5 min at 285 rpm. After the test materials were mixed, the sample was loaded into a square mould with a side length of 2 cm. The samples were demoulded after being sealed at room temperature conditions (approximately 20 °C) for 24 h, and they were sealed for immediate curing to avoid drying the sample surface. Thereafter, the samples were maintained in a curing tank under standard curing condition (20 °C, 95% RH) to the prescribed ages of 3, 5, 7, 10, 14, 21, and 28 days.

2.2. Experimental methods

2.2.1. Mercury intrusion porosimetry

The principle of mercury intrusion is to calculate the volume of intrusion mercury by applying pressure to the porous medium. The pore is assumed to be a cylinder during the calculation. The PSD of the pore structure can be obtained by the Washburn [33] relation as follows:

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

where d is the equivalent pore diameter, nm; P is the applied pressure, MPa; γ is the surface tension of mercury, N/m; and θ is the contact angle between mercury and solids. The adopted mercury surface tension value and contact angle between the mercury and the solid surface were 0.485 N/m and 130°[21].

After the specified curing period, a sample with a size of nearly 2 mm was taken and crushed in its middle. The crushed sample was immersed in liquid nitrogen for rapid freezing for 5 min and then transferred to a freeze drier to avoid secondary damage during drying [20,34,35]. The drying period depends on *w/b* and the curing age of the sample.

2.2.2. Low-field nuclear magnetic resonance

The main factors affecting fluid relaxation in porous media are the relaxation of fluid on the surface of pore walls, molecular diffusion, and free fluid in pores. The pore water relaxation time is expressed as follows:

$$\frac{1}{T_2} = \frac{1}{T_{2s}} + \frac{1}{T_{2d}} + \frac{1}{T_{2b}} \tag{2}$$

where T_2 is the transverse relaxation time of the water molecule in the pore, ms; T_{2s} is the relaxation time of the water molecule on the pore surface, ms; T_{2d} is the relaxation time of molecular diffusion, ms; and T_{2b} is the relaxation time of the free water molecule in the pore, ms.

The technique used in this study is LF-NMR. Given that its echo time is very short, the influence of molecular diffusion relaxation, i.e., T_{2d}, can be neglected. Under normal circumstances, the relaxation of free water is much weaker than that of surface water. Therefore, the relaxation mechanism of the free water molecule in the pore, i.e., T_{2b}, is usually negligible. Under the condition of LF-NMR, the relaxation of pore water is primarily affected by the surface relaxation mechanism, i.e., T_{2s} [36]. The transversal relaxation time T_2 can be simplified to

$$\frac{1}{T_2} \approx \frac{1}{T_{2s}} = \rho_2 \frac{S}{V} \tag{3}$$

where S represents the pore area, nm^2; V represents the pore volume, nm^3; and ρ_2 is the surface relaxation rate, nm/ms.

Assuming that the pores are homogenous and cylindrical in shape, the relation between the pore diameter and T_2 can be derived as follows:

$$\frac{1}{T_{2s}} = \rho_2 \frac{S}{V} = \rho_2 \frac{4}{d} \tag{4}$$

$$d = 4\rho_2 T_{2s} = CT_{2s} \tag{5}$$

where d is the pore diameter, nm; and C is the conversion coefficient, nm/ms.

The conversion surface relaxation rate ρ_2 is used to describe the magnitude of relaxation of porous material and can be obtained by the gradual drying method. In general, ρ_2 is 12 nm/ms for cement-based materials [28]. Therefore, C is 48 nm/ms.

In this study, a PQ001 LF-NMR analyser was adopted in the pore structure experiment. The parameters of the equipment were set as follows.

The instrument magnetic field strength was set to 0.42 T, the magnet frequency was set to 18 MHz, and the magnet temperature was maintained at 32 °C ± 0.02 °C. After vacuum saturation in a room with the temperature controlled at 20 °C ± 1 °C by air conditioning, the specimen was crushed for placement in a cylindrical glass tube with a diameter of 25 mm and a length of 200 mm for the LF-NMR test. The frequency offset of radio-frequency signal (O1) and 90° pulse width (P1) were obtained using the sequence of free induction decay to calibrate the standard oil sample. Then, the transverse relaxation time (T_2) of specimens was obtained via the LF-NMR spectrometer using the Can–Purcell–Meiboom–Gill pulse sequence ($\pi/2$–τ–NECH π, half echo time τ is 180 s, NECH is 500). Table 3 shows the CPGM parameters of pure cement pastes for testing.

3. Results and discussion

3.1. Pore structure comparison between MIP and LF-NMR

Fig. 2 compares the cumulative pore volume of different cement pastes with *w/c* at 3, 7, 14, and 28 days from MIP and LF-NMR. First, the cumulative pore volumes of the two methods decrease with increasing pore diameter. They both decrease first slowly and then

Table 1
Chemical components of materials (%).

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	TiO_2	LOI
Cement	19.53	4.31	2.89	63.84	1.25	0.13	0.64	3.25	0.26	3.0
Fly ash	54.0	33.9	4.45	2.5	0.3	0.4	1.3	0.4	––	3.47