Continuous tracking of the relationship between resistivity and pore structure of cement pastes

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HIGHLIGHTS

- The quantitative relationship between electrical resistivity and pore structure is established.
- The effect of type of pores on electrical resistivity is explored.
- The evolution of resistivity is not only controlled by capillary pores but also C–S–H phases.

ARTICLE INFO

ABSTRACT

The electrical resistivity changes with time of cement pastes with water to cement ratio of 0.23, 0.35 and 0.53 were in situ continuously monitored by using a non-contact resistivity apparatus. To aid in understanding the evolution of effective resistivity, a hydration model CEMHYD3D was then utilized to simulate the early age formation of microstructure. Based on the effective media theory, the relationship between the change of relative resistivity and the evolution of total porosity, tortuosity factor and constrictivity is established. The results show that a lower water to cement ratio shows a smaller porosity and constrictivity as well as a higher tortuosity factor. Moreover, according to the experimental and simulated results, it is found that the evolution of resistivity is not only controlled by capillary pores but also C–S–H phases. Before arriving fully de-percolation time of capillary pores, the reduction of pores connectivity shows a higher influence on the paste resistivity than the decrease of capillary porosity. After that, the resistivity change of cement paste is mainly determined by the volume fraction of C–S–H.

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1. Introduction

Cement particles react with water and form a porous material with micropores of various sizes. Chloride ions ingress into concrete through pores and induces reinforcement corrosion, eventually causing the deterioration of concrete structure. Understanding the relationship between chloride diffusivity and pore structure is critical to predict the starting time of corrosion and the service life of cement-based materials. Concrete is known to be time-varying material. Pore structure continuously is developed and changed with hydration time that determines the final durability of the hardened concrete. Concrete porosity as well as other pore structure parameters such as size, distribution, shape and connectivity affects the transport behavior of harmful ions. Thus, a good knowledge of the pore structure evolution during the early age hydration process is of great importance to accurately evaluate the performance degradation of the cement-based materials.

Over the past several years, some methods were developed to characterize the pore structure, such as mercury intrusion porosimetry (MIP) [1], nitrogen sorption technique (BET) [2], backscattered electron (BSE)/image analysis [3–5]. However, since early age cement-based materials have not been hardened, MIP and BET require the drying and pretreatment of specimen and fail to measure the porosity and the pore size distribution. BSE technique can directly view and quantify two-dimensional (2D) information of pore structure, but could not obtain the connectivity in three-dimensional (3D) structure of concrete. Therefore, nondestructive methods should be applied to continuously monitor the early age evolution of pore structure.

To overcome the shortcomings of above experiments, a non-contact electrical resistivity apparatus invented has been used to monitor and interpret the hydration process of cement-based materials [6]. Although the effects of type of cementitious [7,8], water-to-cement ratio (*W/C*) [9], mineral admixtures [10], alkali content [11], and superplasticizer selection [12] on microstructure

formation process were systematically investigated, the relationship between resistivity evolution and pore structure has rarely been studied. In this study, utilizing the non-contacting electrical resistivity device, the early age changes in electrical resistivity were firstly monitored for cement pastes with different W/C. A digital-image-based model called CEMHYD3D was then selected as a computer model to simulate the evolution of microstructure. Finally, the relationship between relative resistivity and pore structure is established to evaluate the ions transport of cement pastes.

2. Materials and methods

2.1. Materials

A Chinese standard Graded 52.5 P I type Portland cement with the compressive strength and flexure strength of 60.5 MPa (8.77 ksi) and 8.7 MPa (1.26 ksi) at 28 days, similar to ASTM C150 type I cement, was used in this study. This cement was also tested by X-ray fluorescence spectrometer (JY/T 016-1996) and its chemical compositions and physical properties are listed in Table 1.

2.2. Electrical resistivity

The evolution of resistivity could be determined using a non-contacting electrical resistivity. The working principle and the measurement setup were described in the previous literature [6]. Compared to the conventional electrical measurement, the non-contacting electrical resistivity has two merits. (1) The transformer core was adopted to overcome the interfacial zone problem between the electrode and fresh paste. (2) Alternating current replaces direct current that can eliminate the polarization effect.

Three cement pastes with W/C of 0.23, 0.35 and 0.53 were mixed for 2 min in a planetary-type mixer at 45 rpm followed by 2 min at 90 rpm. The mixtures were cast into the ring-shaped mold of 1672 cm³ (102 in.³) in volume and compacted by hands to drive the air bubbles out. After sealing the sample by the attached lid, the apparatus was covered with a plexiglass cap to keep 100% relative humidity and 20 °C (68 °F) temperature during the test period. The measurement started to monitor the evolution of resistivity after casting. The data was automatically recorded by a computer program over 7 days and sampling interval was set to 1 min. Finally, the average height of specimen measured was input into the application program to calibrate the tested resistivity values.

2.3. Computer simulation of microstructure

Several models have been proposed to describe the evolution of cement microstructure during hydration process, as well as for predicting their transport properties and mechanical behaviors. These models can be usually divided into the discretization approach and the vector approach.

In the discretization approach, CEMHYD3D is one of the best-known and most widely-used models built by Bentz at the National Institute of Standards and Technology [13,14]. The vales of W/C in the simulated pastes were selected to match those in the real prepared pastes. The particle size distribution of cement was measured by laser diffraction techniques, as shown in Fig. 1. Additionally, the mineral compositions of cement were obtained by backscattered electrons (BSE) and X-rays, as provided in Table 2. According to the above experimental parameters, the unhydrated 3D microstructure is reconstructed by placing digitized spherical particles at random locations. A cellular automaton algorithm is then applied to a series of dissolution, discussion and reaction cycles. Finally, the microstructure information, including volume of hydrated products as well as hydration heat and degree, can be achieved at any hydrated time. The 3D images of a hydrated microstructure
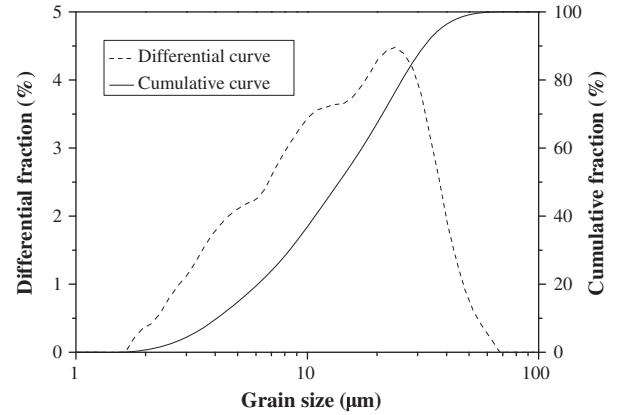

Fig. 1. Measured particle size distribution for cement.

using CEMHYD3D simulation at different cycles (time) of hydration are shown in Fig. 2. With development of hydration time, the volume fraction of mineral phases reduce, the hydrated products increase.

3. Results and discussion

3.1. Influence of pore structure parameters

The effective electrical resistivity (ρ_{eff}) of porous materials depends on the resistivity (ρ_0), relative volumes and geometric distribution of each phases. For cement paste, the relative resistivity can be expressed by the following relationship [15]:

$$F = \frac{\rho_{eff}}{\rho_0} = \frac{\tau^2}{\phi_{cap} \cdot \delta} \tag{1}$$

F called formation factor is defined as the relative resistivity. τ and δ represent the tortuosity factor and constrictivity of the pore network, respectively. ϕ_{cap} is the capillary porosity of cement paste. It is noted that C–S–H gel also has continuous pores as transportation path of ions. Therefore, the modified porosity-electrical resistivity formula is addressed as

$$F = \frac{\rho_{eff}}{\rho_0} = \frac{\tau^2}{\phi_p \cdot \delta} \tag{2}$$

$$\phi_P = \phi_{cap} + \phi_{gel} \tag{3}$$

where ϕ_P is the total porosity of cement pastes. ϕ_{gel} is the porosity of C–S–H gel pores. The total porosity of cement paste was widely measured by MIP [16,17], whereas MIP technique as a destructive technique fails to measure the early age porosity of paste. So, the CEMHYD3D can be used to investigate the porosity as a function of time. Although CEMHYD3D simulation can obtain the capillary porosity, the gel porosity is not directly acquired. As powers attributed a porosity of roughly 28% to C–S–H gel, the total porosity of cement paste is calculated based on simulated values of capillary porosity and C–S–H gel volume fraction.

For formation factor (or relative resistivity), the values of ρ_{eff} and ρ_0 should be determined. ρ_{eff} was investigated by non-contact

Table 1
Chemical compositions and physical properties of Portland cement.

Oxide	Composition (%)
CaO	62.6
SiO$_2$	21.35
Al$_2$O$_3$	4.67
Fe$_2$O$_3$	3.31
MgO	3.08
SO$_3$	2.25
K$_2$O	0.54
TiO$_2$	0.27
Na$_2$O	0.21
Loss on ignition	0.95
Density	3150 kg/m³ (196.5 lb/ft³)
Specific surface area	369.6 m²/kg (75.7 ft²/lb)

Table 2
Composition of mineral phases.

Mineral phases	Composition (%)
C$_3$S	52.36
C$_2$S	29.75
C$_3$A	4.77
C$_4$AF	13.12