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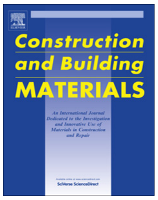

Impedance measurement to characterize the pore structure in Portland cement paste

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HIGHLIGHTS

- We developed an innovative non-contact impedance measurement.
- The relationship between the impedance response and cumulative pore volume is revealed.
- The methodology in this work is the pore fractal theory.
- Porosity and fraction of pore volume are obtained from impedance measurement and mercury, respectively.

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ABSTRACT

This paper proposes an alternative way to characterize the pore structure in cement pastes using an innovative non-contact impedance measurement. This methodology is based on the pore fractal theory: the fractal dimension for pore space is solved from two networks (fractal electrical network and pore structure network); the minimal pore diameter in the pore fractal theory is evaluated from electrical double layers model; the applicable scope of non-contact impedance measurement is addressed through frequency dispersion mechanism. Through the pore fractal theory and this impedance measurement, the relationship between the cumulative pore volume and impedance response of cement pastes is revealed.

1. Introduction

Pore structure of cement-based materials has great significance on their strength, permeability and durability [1]. In general, pores in cement pastes are classified according to their sizes into gel pores (below 10 nm), capillary pores (10 nm–10 μm), hollow-shell pores (10 μm–0.1 mm), and air voids (0.1 –1 mm) [2]. Pores in cement pastes, as passages of ions transportation, can be related to the impedance response of cement pastes [3]. Much effort has been devoted to correlating the impedance response with pore structure of cement-based materials [4–6]. However, the relationship between the cumulative volume of pores with size in a stated range and impedance response has not been studied in previous research yet. The cumulative pore volume is an important parameter to understand roles of pores with sizes in different ranges in hydration kinetic and transportation performance [2]. In this study, the pore fractal theory is proposed with an attempt to reveal this relationship via an innovative non-contact impedance measurement.

It has been found that cement-based materials are fractal porous media [7,8]. In this work, the fractal dimension for pore space of cement pastes can be derived from the combination of two networks (fractal electrical network and pore structure network). The concept of such combination was first proposed by Itagaki et al. [9,10].

Through the electrical double layers model, the minimal pore diameter to determine the probability density function of pore size distribution can be predicted. Electrical double layers at the solid–liquid interface include two layers: the compact layer and diffuse layer. The compact layer is made of solvated ions, adsorbed at the solid interface. The compact layer can be also separated into two planes: inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP). The diffuse layer is identified as the "buffer" zone between the compact layer and liquid bulk solution [11].

With the frequency dispersion mechanism [12,13], the applicable scope of pore size of non-contact impedance measurement having limited frequency domain can be addressed.

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2. Raw materials and sample preparation

In this study, Portland cement meeting the requirement of ASTM Type I was used to prepare cement pastes with water to cement ratios (w/c) 0.3, 0.4 and 0.5 by mass. Water used in the present study was de-ionized. The paste was mixed in a planetary-type mixer at 45 rpm for 2 min first and then at 90 rpm for 2 min. The cement pastes were cured in the environmental chamber with temperature 20 °C and humidity 60%.

3. Non-contact impedance measurement

3.1. Test system and test procedure

The working principle of non-contact impedance measurement in this study is shown in Fig. 1 [14]. The sine wave with frequency domain ranging from 1 kHz to 100 kHz is applied to the primary coil of the transformer via the signal generator. The ring-shaped specimen with volume 1.4 l can be identified as secondary coil of the transformer in Fig. 1. The voltage (about 0.1 V) applied onto the specimen can be calculated from transformer principle. The current going through the specimen is measured by leakage current meter. All of the impedance data will be saved continuously.

The precision of this system was calibrated with KCl solutions with different concentrations. Table 1 shows the standard resistivity of KCl solutions quoted from the handbook [15] and test results at frequency 1 kHz at 22 °C with this measurement. It is found that the maximal relative error of the system is 3.36%, which shows this system has a sufficient precision.

The sweep frequencies for one cycle were 1 kHz, 2 kHz, 4 kHz, 8 kHz, 16 kHz, 32 kHz, 64 kHz, 80 kHz and 100 kHz. The stimulus time of each frequency was about 5 s. The next cycle would run after 1 min. Data in three days from casting time was utilized to analyze the pore structure evolution.

Meanwhile, the exact total volume of the cement paste (V_s) can also be calculated from Eq. (1) in Fig. 2. Fig. 2 demonstrates the geometric form of the specimen with a trapezoidal section, in which r_1, r_2, r_3 and r_4 are the radii of the ring-shaped specimen and h is the specimen height.

$$V_s = \frac{2\pi h}{r_2 - r_1}\left(\frac{r_2^3}{3} + \frac{r_1^3}{6} - \frac{r_1 r_2^2}{2}\right) + \pi h\left(r_3^2 - r_2^2\right) + \frac{2\pi h}{r_4 - r_3}\left(\frac{r_3^3}{3} + \frac{r_4^3}{6} - \frac{r_4 r_3^2}{2}\right) \tag{1}$$

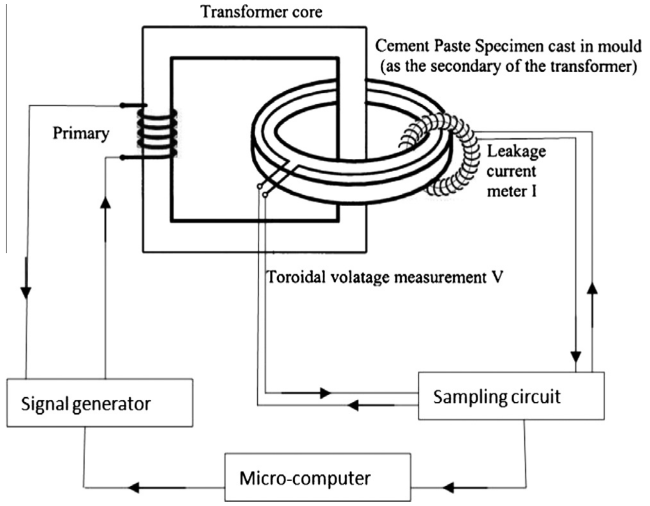

Fig. 1. Working principle of non-contact impedance measurement.

The radii and height of the specimen can be measured after the test is completed.

3.2. Pore fractal theory

3.2.1. Pore structure and fractal dimension

In fractal porous media, the number ($N(d)$) of pores whose diameters are larger than d and the probability density function of pore size distribution ($f(d)$) can be calculated as [16,17]:

$$N(d) = (d_{\max}/d)^{D_f} \tag{2}$$

$$f(d) = D_f \cdot d_{\min}^{D_f} \cdot d^{-D_f-1} \tag{3}$$

where d, $d_{\min}$, $d_{\max}$ are the given, minimal and maximal pore diameters in the media; D_f is fractal dimension for the pore space.

3.2.2. Fractal electrical network and pore structure network

The fractal dimension D_f in Eqs. (2) and (3) can be derived from fractal electrical network and pore structure network.

The macroscopic impedance response of cement-based materials under an external electrical stimulus results from the total contributions of electrical paths through which charge carrier travels in the pore solution. Therefore, it is necessary to investigate electrical property in a single electrical path within the pore solution. In principle, the electrical response of pore solution can be schematically illustrated in Fig. 3. Basically, there are three kinds of components in one electrical path: (1) R, means the resistance of pore solution; (2) L, stands for the inductance of the electrical path; (3) C, represents the interfacial capacitance between the solid and liquid phase. These three components (R, L and C) can simulate the electrical behavior of an electrical path well through series mode.

Based on fractal characteristic of pores and equivalent electrical components in an electrical path, the fractal electrical network can be drawn with the following assumption: all of pore clusters satisfy fractal requirements in all length scales (Nano, Micro and Macro), and are saturated with the conductive solution.

By analogy with the classical fractal electrical network [18], it is possible to establish a similar network to describe the electrical response of pore clusters in cement-based materials. It is basically a multistep network in which every RLC cell is linked together by different scaling factors (α β and γ) in each step, as shown in Fig. 4. Since it is easy to present the network with higher steps based on the prior network, Fig. 4 only lists fractal electrical network to Step 2 as an example.

Meanwhile, the topology of the fractal electrical network also has the corresponding pore structure network. Fig. 5 only lists pore structure network to Step 2 as well. The configuration of pore structure network proposed here is similar with the one developed by Itagaki et al. [9,10]. It should be emphasized that the individual cylinder of pore network in Fig. 5 represents pore clusters with some length scale, rather than an actual pore in the cement-based materials. The pore structure network is structured from the smallest cylinder and has two symmetrical branches in each step. From fractal electrical and pore structure networks, the relationship among scaling factors can be derived. The fractal dimension for pore space (D_f) can thus be determined. The resistance and inductance of the cylinder in the $(n-1)$th and nth step can be expressed as [19,20]:

$$R_{n-1} = 4\rho_0 l_{n-1}/(\pi d_{n-1}^2) \tag{4}$$

$$R_n = 4\rho_0 l_n/(\pi d_n^2) \tag{5}$$

$$R_n = \alpha R_{n-1} \tag{6}$$