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ESTIMATION OF POROSITY OF CEMENT COMPOSITES FROM ELECTRICAL PROPERTIES AND GENERAL EFFECTIVE MEDIA MODEL

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Abstract: *This paper studies electrical properties of ordinary Portland cement paste and mortar. Electrochemical impedance spectroscopy was used to evaluate the resistance of the solid phase and the connected capillary pores. Based on the knowledge of the resistances and the composition of the used composites, the porosity was evaluated by a general effective media model. Helium pycnometry and gravimetric method were used to calibrate the model parameters. The porosity of the material was then determined at different hydration times.*

Keywords: **Porosity, electrochemical impedance spectroscopy, general effective media model, cement paste, mortar.**

1. Introduction

The amount of capillary porosity influences many engineering properties of concrete and cement pastes such as elasticity, strength, permeability or electric conductivity. The strength of concretes usually increases with decreasing capillary porosity. The origin of porosity can be found on a micro-scale, where it is formed together with other hydration products and residual clinker. The mechanical parameters and volume fraction of these products can be used in multi-scale models to predict concrete macroscopic properties. The strength upscaling was performed e.g. within the continuum micromechanics framework, (Pichler, 2011). Thus, the correct volume of capillary porosity estimation is a necessary input for of multi-scale models.

Porosity can be obtained by many direct (e.g. X-ray nanotomography) or indirect (e.g. helium pycnometry) methods. Also, some researchers - McLachlan (1990); Neithalath (2006) - have used the resistance of cement-based materials (CBMs) for porosity evaluation. Electrochemical impedance spectroscopy (EIS) is a non-destructive method using alternating electric current (AC) that can be used to obtain electrical properties (resistance/capacitance/conductivity) of the material. The resistance can then be used for the porosity determination of a porous material by single or multi-phase analytical models, (Neithalath, 2006). The general effective media (GEM) model is a two-phase model considering the effect of the percolation threshold, the conductivity of the solid phase, and the conductivity of the capillary pores, (Sang, 2022). These parameters vary for different concrete mixture and requires calibration.

The objective of this paper is to evaluate porosity using the GEM model from measured electrical properties by EIS of ordinary cement paste mortar mixtures. Furthermore, calibrate GEM model parameters using indirect porosity measurement methods.

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2. Theoretical background

2.1. Electrochemical impedance spectroscopy

A principle of EIS lies in applying an electric current decomposed into a series of harmonic signals to the sample by a pair of electrodes. The electrodes can be attached to opposite surfaces or embedded in the material. The electric circuit is then used to evaluate the resistance and capacitance of the material.

At the micro-scale, CBMs consist of hydration products, unhydrated clinker, aggregate particles, and pores (empty or filled with pore solution). Therefore, CBMs cannot be considered as a single electrical resistor. Song (2000) et al. proposed an equivalent electric circuit model (Figure 1a.) consisting of three conductive paths in cementitious materials as shown in Figure 1b. The most important path is formed by capillary pores connected by pore necks, called continuous conductive path (CCP), that corresponds to resistance R_{CCP}. The discontinuous conductive path (DCP) is formed by capillary pores with an interuption formed by a thin layer of cement paste. A continuous bulk matrix forms the insulator conductive path (ICP).

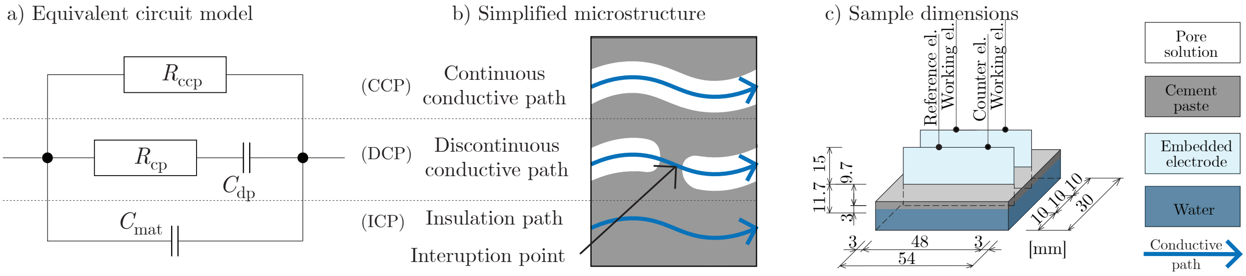

Fig. 1: a) equivalent electric circuit model, b) simplified microstructure of concrete with illustrated conductive paths, c) sample dimensions and electrode positions.

2.2. General effective media model

McLachlan (1990) et al. proposed an analytical model describing the relationship between electrical conductivity and porosity of a porous material. The general effective media (GEM) model is composed of two phases. The first phase is created by a solid matrix characterized by its low conductivity. The second phase is formed by pores characterized by high conductivity. In the case of CBMs, the samples need to be fully saturated with water, and the conductivity of the pore solution present in pores is measured. GEM model is described by equations, (Sang, 2022):

$$\phi_0 \cdot \frac{\zeta_0^{1/k} - \zeta^{1/k}}{\left(\dfrac{1-\phi_c}{\phi_c}\right) \cdot \zeta_0^{1/k} + \zeta^{1/k}} + (1-\phi_0) \cdot \frac{\zeta_1^{1/k} - \zeta^{1/k}}{\left(\dfrac{1-\phi_c}{\phi_c}\right) \cdot \zeta_1^{1/k} + \zeta^{1/k}} = 0, \tag{1}$$

$$\phi_0 = [(1-\phi_c) \cdot F^{-1/k} + \phi_c] \cdot \left(\frac{M^{1/k} - F^{1/k}}{M^{1/k} - 1}\right), \tag{2}$$

where ϕ_0 is capillary porosity, ϕ_c is the percolation threshold of capillary pores, ζ is total resistivity of CBMs, ζ_0 is resistivity of pore solution, ζ_1 is resistivity of solid phase, F is formation factor, and k is parameter related to the shape of pore structures. Parameter M is given by equation:

$$M = \frac{\zeta_1}{\zeta_0}. \tag{3}$$

Formation factor is a commonly used parameter in conductive models of CBMs and is written in the following equation:

$$F = \frac{\sigma_0}{\sigma} = \frac{\zeta}{\zeta_0}, \tag{4}$$

where σ represents total conductivity of CBMs, σ_0 represents the pore solution conductivity, (Sang, 2022). In case of CBMs, ϕ_c ranges from 0.15 to 0.2, (Bejaoui, 2007). The total resistivity of CBMs ζ equals the resistance of connected capillary pores measured by EIS. The resistivity of the pore solution ζ_0 is possible to estimate by the virtual method (freely available at NIST (2017)) with knowledge of the mineral composition of the cement from the estimated degree of hydration obtained from the Cemhyd3D model, (Bentz, 1997).

3. Experimental part

3.1. Sample preparation and experimental setup

Two types of mixtures with water to cement ratio of 0.4 from Portland cement CEM I 42.5R were prepared. First was ordinary cement paste (C), and second, was mortar (M) with siliceous aggregates (0-2 mm). The samples for EIS measurement were block shaped with dimensions of 54 $\times$ 30 $\times$ 11.7 mm (length, width, height) and with an embedded electrode from stainless steel as shown in Figure 1c. The covering layer of electrodes was set to 3 mm to avoid direct contact with water during measurement since the samples need to be immersed in water to prevent samples from drying. Cylindrical-shaped samples with a diameter of 27 mm and a height of 64 mm were prepared for porosity measurements by helium pycnometry and gravimetric method. Measurements by EIS, helium pycnometry and gravimetric method were performed at different hydration times (1, 3, 7, 14, 28, 54, and 84 days age).

EIS measurements were performed in the frequency range 12 MHz - 100 Hz, in 10 steps per decade and with an amplitude of 10 mV. The measurement device was connected to the electrodes embedded in the sample with a reference, a counter, and two working electrodes. The measured data were then interleaved with the fit based on the equivalent circuit model shown in Figure 1b. The resistances and capacity were evaluated.

Cylindrical shape samples were cut into 7 mm slices at each observation time. Subsequently, the gravimetric method measured the open porosity $\phi_{0,grav}$ and the bulk density of the samples. The matrix density of the dried samples was obtained by helium pycnometry. Then the total porosity $\phi_{0,pyc}$ of the studied material was calculated based on the bulk density measured by the gravimetric method and matrix density.

3.2. Results and discussion

The resistances R_{CCP} of C and M mixtures increases with increasing hydration time, as shown in Figure 2a. This phenomenon corresponds to the formation of new hydration products and an associated porosity decrease, as shown in Figure 3. The resistance of the M mixture has $\approx$ 2 times larger values compared to the C mixture as the aggregates reduce the number of conductive paths in the matrix. The same reason can be applied to the lower total porosity of the M mixture than the C mixture. The porosity obtained by the gravimetric method $\phi_{0,grav}$ has higher values than the porosity obtained by helium pycnometry $\phi_{0,pyc}$ since the size of the measurable pores is different by both methods.

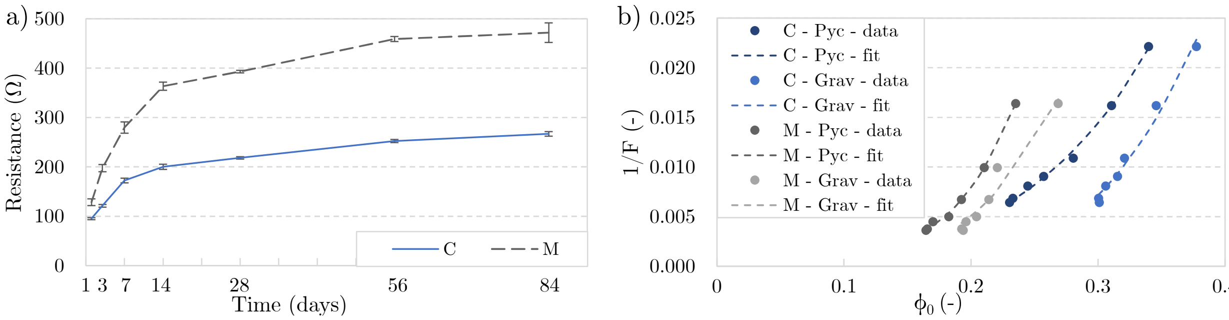

Fig. 2: a) Resistance of continuously connected pores of C and M mixtures, b) GEM model calibration.

The GEM model requires several measurements over time to calibrate the unknown parameters ζ_1 and k to evaluate the porosity from the EIS experimental data. Thus, experimental total porosity obtained from helium pycnometry and gravimetric method was used to calibrate the GEM model constants. The total porosity measured at all observation times was plotted versus the formation factor as shown in Figure 2b. Then the function was fitted according to Equation (2). The values of the parameter k and resistivity of solid phase ζ_1 were estimated to ensure the most appropriate fit. These values vary for each mixture and method used for calibration. Also, the most accurate fit was found for ϕ_c value of 0.2.

Based on the calibrated parameters, the GEM model calculated the porosity of both mixtures. The calculated values of $\phi_{0,GEM,grav}$, $\phi_{0,GEM,pyc}$ differs from experimentally obtained values. The influence of the method used for calibration is noticeable, as shown in Figure 3. However, the difference between total porosity and the calculated by the GEM model for the gravimetric method (18 %) is much higher compared

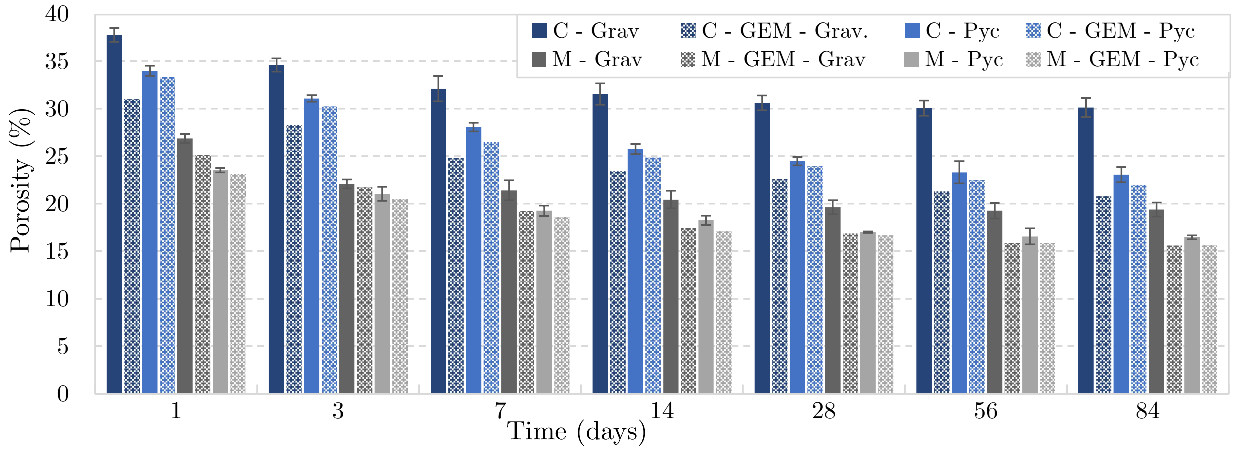

Fig. 3: Porosity measured by helium pycnometry, gravimetric method and calculated by GEM model.

to helium pycnometry (3 %). Also, the GEM model reflects the increasing values of resistances for mature (56, 84 days) mixtures by decreasing porosity, contrary to experimental techniques where the difference in porosity is almost negligible.

4. Conclusions

The EIS can reliably and non-destructively detect the changes in the microstructure of cementitious composites during continuous hydration by detection of increasing resistances. The EIS resistance was used as an input to the GEM model to calculate the porosity of the mixtures. However, the direct evaluation of the porosity is possible only after calibrating GEM model parameters such as k, ζ_1, and ϕ_c. Therefore, the porosity obtained from other experimental technique is necessary for parameter determination. Helium pycnometry, contrary to the gravimetric method, is suitable for model calibration as documented by the low difference between the model prediction and the experimental porosity.

Acknowledgments

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