Review

The review of pore structure evaluation in cementitious materials by electrical methods

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HIGHLIGHTS

- The evaluation of pore structure by electrical methods is reviewed.
- Some equivalent circuit models of AC methods are discussed.
- Merits and demerits of ACIS and non-contact methods are commented.

ARTICLE INFO

ABSTRACT

This paper reviews the evaluation of pore structure in cementitious materials by means of electrical impedance methods from the view point of direct and alternative current tests with or without electrodes. Some main equivalent circuit models in the literatures, which are employed to evaluate the pore structure from experimental results of alternating current impedance spectroscopy (ACIS), are discussed. The latest utilization of non-contact resistivity/impedance measurement for the hydration monitoring, pore structure and transportation investigation is presented in this review. The related merits and demerits of ACIS with electrodes and non-contact methods and their application scenarios are also discussed.

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1. Introduction

Cement is the most used artificial material in the world, and more than 2.5 tons of cement are consumed per person yearly. In general, cement-based materials are considered as porous composite materials that consist essentially of a binding medium within which are embedded particles or fragments of aggregate. The complex pore network in materials has great impact on their strength, permeability and durability, etc. [1,2]. Pores in cement-based materials vary in size and shape. They are classified into several types [3]: (1) pores in the hydrated cement paste, including gel pores, capillary pores, hollow-shell pores and possible air voids; (2) pores in the fine or coarse aggregates; (3) pores existing in the interfacial transition zone between aggregates and the cement paste matrix; (4) water bubble caused by bleeding or construction deficiencies; (5) internal discontinuous pores caused by humidity and/or temperature changes.

The formation mechanism and roles of air voids, hollow-shell pores, capillary pores, and gel pores are introduced in the following: (1) Air voids in hardened cement paste are referred to entrapped or entrained voids. The size of entrapped air voids introduced from inadvertent mixing or placing of cement-based materials is above 1 mm, whereas the entrained air voids produced from air-entraining chemical agent are always isolated and have the diameter between 10 µm and 1 mm [4]. (2) When unconsolidated hydrates form within the original cement grain boundaries at the early-age of hydration process, hollow-shell pores appear [5]. These pores with the "ink-bottle" throat usually develop around peripheries of cement grain to hinder the continued hydration. Hollow-shell pores remain saturated with pore fluid independent of self-desiccation effects [6]. (3) Capillary pores are known as the initially water-filled spaces interconnecting each other in the cement paste [7]. Capillary pores have highly irregular shape. Capillary pores are usually full of ionic solution that is in equilibrium within hydrated pastes. Capillary pores have a significant impact on transport processes [3]. (4) The calcium silicate hydrate (C-S-H) colloidal gel usually contains pores that are named as gel pores located inside the hydration products which accumulate between the liquid region and the unhydrated cement particles [8]. It is considered that gel pores have a very small size (approximately 0.5 nm), which is only an order of magnitude larger than that of water molecules [3].

The pore characteristics of porous medium often include: pore configuration, porosity, pore size distribution, etc. (1) Pore configuration: closed pores have great impact on bulk density, mechanical strength and thermal conductivity [9], but minor effect on permeability [10]. On the contrary, interconnecting pores provide passageways for liquids to move through materials and devote great efforts on the transportation performance [3]. (2) Porosity: the porosity of cement-based materials is associated with the initial water to cement ratio, the compaction mode, the hydration degree and the amount of mineral admixtures. However, as the pore size range is generally wide enough, it is extremely difficult to determine the porosity using one single technique [11]. (3) Pore size distribution: pore size distribution stands for the fraction of

the pore volume within a specified pore range. The pore size distribution is often represented by a separated histogram or a continuous function having one or more peaks depending on the nature of the pore system tested [3,11,12]. Pore structure parameters measured are influenced by many factors (characterization techniques themselves, inherent features of microstructure, curing conditions, hydration ages, and the specimen preparation) [3].

In this work, we review the evaluation of pore structure in cementitious materials by electrical methods. Some representative equivalent circuit models adopted to interpret the pore structure evolution from alternative current methods are presented and commented. The latest application of non-contact resistivity and impedance measurements to study the pore structures of cementitious materials are described emphatically.

2. Test methods for pore structure evaluation

A wide variety of methods have been utilized to determine the pore structure in cement-based materials. Some techniques (such as mercury intrusion porosimetry and gas adsorption) focus on open pores [13]; while others, i.e., small-angle scattering, can measure both open and closed pores [14]. Generally speaking, the techniques that study the pore volume and/or pore size distribution in porous medium can fall into direct and indirect methods [15]. In direct methods (optical microscopy and scanning electron microscopy), a physical image is generated to reveal the morphology of pores in two-dimensional mode, and converted to the three-dimensional space via certain stereology algorithm [16]. In indirect methods, an external stimulus is applied onto the materials and the corresponding feedback response of materials is recorded though a suitable sensor. Pore structure parameters are calculated through equivalent physical parameters instead such as electrical impedance, density or adsorptive capacity, etc [3]. These methods include mercury intrusion porosimetry, gas adsorption, pycnometry, thermoporometry, electrical impedance, nuclear magnetic resonance, small-angle X-ray and neutron scattering [15]. In each technique, more than one pore parameters can be investigated [3]. However, it should be also noted that sometimes most experimental techniques cannot measure the true value of pore parameters (porosity, surface area of pores and/or pore size distribution), perhaps due to the pretreatment of cement-based materials. Each method gives characteristic values based on some theoretical or empirical assumptions of the method used and on the intrinsic nature of the specimen tested. Therefore, values of pore structure parameters derived from different methods may not achieve a perfect agreement [3].

3. Electrical methods for pore structure evaluation

Plenty of works focused on the resistivity/conductivity response in cement-based materials [17–21]. The principle of electrical methods is briefly illustrated in the following. On the whole, the conduction of electric current through the pure cement paste can be visualized as two components [22]: one is the ionic conductivity through the free evaporable water, which depends upon ionic concentration, temperature, and type of ions in solution [23]; the other is the electronic conduction through the gel, gel-water and unreacted cement particles [24]. For cement-based materials, the conductivity of solid phases (aggregates, cement clinkers and hydrated products) and vapor phases is considered to be several orders of magnitude smaller than that of liquid ones [24]. As early as 1968, Monfore [25] considered that the conduction of cement-based materials was contributed by ions in the free water, and the principle ions were Ca^{2+}, Na^+, K^+, OH^-, and SO_4^{2-}. Since the amount of free water in a typical cement paste varied from about