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Empirical time-dependent tortuosity relations for hydrating mortar mixtures based on modified Archie's law

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HIGHLIGHTS

- Mortar mixes were tested for time-dependent formation factor (*FF*) & tortuosity (*m*).
- *FF* and *m* both increase with curing time, decrease in *w/cm*, and increase in SCM.
- *m* was correlated to parameters of pore size distribution.
- *m* follows pore system refinement and an increase in non-uniformity of pore sizes.

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ABSTRACT

Using sensor-based electrical data, empirical time-dependent tortuosity (τ) formulas as functions of pore size distribution (PSD) parameters were developed for 12 hydrating mortar mixtures. The inverse of the formation factor (*FF*) was used to obtain Archie's exponent (m), which is an indicator of tortuosity. PSD parameters were inferred from theoretical water vapor sorption isotherms. The results clarify the effects of curing time and mixture design on *FF* and tortuosity. Additionally, it is shown that m correlates with pore system refinement and increase in disparity of pore sizes, suggesting the usefulness of this parameter in describing pore system's intricacy.

1. Introduction

Concrete is the most versatile construction material across the globe, yet nondurable concrete structures frequently fall short of their intended service lives, in some cases by decades. Concrete durability distresses mainly involve ingress of water (and detrimental ions) throughout the pore network, which varies greatly over a wide size range: from 0.5 nm interlayer spaces to 10 µm large capillary pores [1]. In addition to pore size and volume fractions, transport properties of concrete are governed by pores shapes, spatial distribution, connectedness, and tortuosity [2].

Pore tortuosity (τ) is a complex material property, which indicates the pore system's geometric complexity and was defined in literature in a variety of ways. In a few studies, τ was defined as the inverse of connectivity [3,4]. In another source, geometrical tortuosity (τ_g) was defined as the ratio of the effective length (L_e), which is the shortest length between two random points in the pore space to the length of the straight line that connects the two points (L) [5].

$$\tau_g = \frac{L_e}{L} \qquad (1)$$

Diffusive tortuosity refers to the limiting value of the ratio between self-diffusion coefficient in a free space (D_0) to that in the confined geometry of a pore space (D) when the time approaches infinity [5]:

$$\tau_{diff} = \frac{D_0}{D};\ t \to \infty \qquad (2)$$

Besides the definitions above, empirical relations were developed to describe τ as a function of other pore system parameters. Nakarai et al. (2006) proposed a simple empirical relation to

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estimate τ as a function of total porosity (P_t) [6,7]. This model was adopted in several studies [8–10].

$$\tau = 1.5\tanh[8(P_t - 0.25)] + 2.5 \tag{3}$$

These relations are difficult to experimentally confirm. In a few studies, τ_{diff} was inferred from simulated diffusion processes using reconstructed three-dimensional images of the cement paste; however, this process is experimentally and computationally demanding [11–13].

Another method to deduce transport properties of porous materials is by electrical conductivity (resistivity) [e.g. [14–16]]. This method is advantageous because electrical data are easily obtainable, and the method is non-destructive to the pore system structure. The effective electrical conductivity of the bulk concrete (σ_{eff}) as a three-phase composite material is a function of the conductivity of the solids (aggregate and hardened cement paste), liquid (pore solution), and the gas phase (empty pores). In comparison to the pore solution, the solid and gas phases exhibit poor conductivities. Therefore, σ_{eff} is primarily driven by the pore solution conductivity (σ_0), and the geometric properties of the liquid-filled pores. The correlation between σ_{eff}/σ_0 and the volume fraction of liquid-filled pores (P_l) was described using the modified parallel law:

$$\frac{\sigma_{eff}}{\sigma_0} = P_l\beta \tag{4}$$

where, β indicates pores' connectivity. Reciprocal of σ_{eff}/σ_0 is known as the formation factor (*FF*), which was recently recommended as an indicator of concrete durability [17,18]. It is known that mixtures with higher values of *FF* are more durable as evident in their lower rapid chloride permeability, and propan-2-ol diffusivity [17,19]. Like the modified parallel law, Archie's law was developed based on tests of brine-saturated rocks [20]:

$$\frac{\sigma_{eff}}{\sigma_0} = CP_t^m \tag{5}$$

where, m is Archie's exponent known to relate with the pores' tortuosity (τ), C is a constant typically assumed as one. Since the degree of saturation (S) substantially influences electrical conductivity of semi-saturated porous materials, a modified form of Archie's law was developed to account for the effect of S:

$$\frac{\sigma_{eff}}{\sigma_0} = CP_t^m S^n \tag{6}$$

where, n is an empirical constant ranging from 3 to 5 for hardened cement paste and mortar [17]. Total porosity is used in Eq. (6) because S^n transforms *FF* for non-saturated concrete (left-hand side of Eq. (6)) into the respective *FF* for a fully saturated mixture [21]. In studies of rock formations and pervious concrete, m was defined as a constant ranging from 1.5 to 4 in value disregarding the development of m with time and dependence on mixture design [20,22–25]. The results of a study by Nokken and Hooton (2008) also suggested a range from 1.34 to 4.73 for m in hardened concrete, rather than a time-dependent relation to define the physical meaning of m [26]. Since the pore system is under continuous change during the cement hydration, using a constant value to define τ is simplistic and does not bear any physical implication. In a study by Xiao and Li (2008) time-dependent m [$m(t)$] was determined for each mixture from bulk resistivity [$\rho(t)$] curves [27]:

$$\ln[\rho(t)] = \ln[\rho_0(t)] - m(t)\ln P_t(t) \tag{7}$$

where, $\rho_0(t)$ is pore solution resistivity. The suggested values of m within the first 48 h of hydration ranged from 1.25 to 2.27 in Xiao and Li (2008)'s study [27]. This relation accounts for the time-dependency of m and can be further built upon to include the effect of mixture design parameters.

The present study is a step toward developing more realistic relationships to describe τ via Archie's exponent. In this study, time-dependent *FF* and m-values as indicators of τ were computed for 12 hydrating mortar mixtures using continuous sensor-based electrical conductivity data. Tortuosity was then defined as a function of different mixture design parameters and curing time for all mixtures. These relations can be used to better assess the durability properties of cementitious composites.

Further, a step-by-step procedure was followed using theoretical water vapor sorption isotherms (WVSIs) to establish pore size distribution (PSD) curves for four of the mixtures at various ages. The PSD curves were used to identify any correlations between τ and the various parameters that define the PSD curves. The latter analysis will help understand the physical influences of the pore system properties on tortuosity and transport properties of the system.

2. Experimental design

2.1. Overview

Fig. 1 schematically shows the steps taken to obtain τ based on m at various stages of hydration for all tested mixtures. The steps taken to identify correlations of τ with PSD at respective ages for a group of four mixtures (marked as MW) are also shown in Fig. 1. Sensor-based σ_{eff}, and experimentally determined P_t, in combination with the simulated σ_0 were used in the modified Archie's law (Eq. (6)). Further, the evaporable water content established in the laboratory at different stages of hydration were used to obtain the time-dependent S for each mixture, which is another parameter required in Eq. (6). Finally, the time-dependent Archie's exponents for the four MW mixtures were correlated with the respective time-dependent PSD curves, developed based on theoretical WVSIs.

2.2. Description of mixtures

Twelve mortar mixtures were used in the experimental matrix. The mixtures were prepared in the laboratory based on the proportioning presented in Table 1. The control mixture contained ordinary Type I/II Portland cement, river sand (fineness modulus 3.06 and bulk specific gravity 2.526), aggregate-to-binder ratio at 1.95, and the water-to-cementitious ratio (*w/cm*) was 0.45. Four sets of mixtures comparable to the control were prepared as described below:

- Mixtures with varied contents of Water (MW): all parameters same as the control, except for the water content which varied in *w/cm* from 0.35, to 0.40 and to 0.50.
- Mixtures with varied contents of fly ash (MF), all parameters same as the control, except cement was partially replaced with Class F fly ash in 20, 40 and 60 percent by mass.
- Mixtures with varied contents of ground granulated blast furnace slag (GGBFS) (MS), all parameters same as the control, except cement was partially replaced with GGBFS in 20 and 40 percent by mass.
- Mixtures with varied contents of Silica Fume (MSF), all parameters same as the control, except cement was partially replaced with silica fume in 5, 10 and 15 percent by mass.

The chemical composition and properties of the implemented cement and supplementary cementitious materials (SCM) are provided in Table 2. Portland cement was from Ash Grove Cement Company, fly ash from Sundance power plant, GGBFS from JFE Mineral Company in Kurashiki City, Japan, and silica fume from Norchem Inc. Fly ash and GGBFS were tested in Lafarge, North