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A fractal approach to determine thermal conductivity in cement pastes

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HIGHLIGHTS

- Thermal conductivity of cement pastes is studied.
- A fractal model for thermal conductivity is developed.
- A fractal simulation for thermal conductivity is established.

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ABSTRACT

This paper presents a preliminary work to evaluate the thermal conductivity performance in pure and blended cement pastes with fly ash, slag and silica fume. The thermal conductivity of cement pastes cured in saturated and dry status with different hydration ages are also measured and predicted by quick thermal conductivity meter (QTM) and innovative non-contact impedance measurement (NCIM) based on a newly proposed fractal model. Besides, a corresponding simulation of fractal-like network is developed to evaluate the influences of pore structure parameters, intrinsic thermal conductivity coefficients of solid and water or gas phase on thermal conductivity performance of cement pastes.

1. Introduction

Cement-based materials are the most used artificial materials in the world, and more than 2.5 tons of cement-based materials are consumed per person yearly [1]. One of the challenges in the design of mass cement-based materials is to avoid the generation of cracks, which is caused by the heterogeneous distribution of temperature and stress [2]. Thermal gradients in cement-based materials can induce the internal stress which leads to cracking on a microscopic or macroscopic scale [3]. Therefore, understanding the thermal property at early-age of cement-based materials is essential to study the behavior of cracks development. Various component models have been utilized to evaluate the thermal conductivity of cement-based materials, including the classical Maxwell–Euken equation [4], the series equation [5] and Hashin–Shtrikman bounds [6,7]. In general, most of these model parameters were determined by fitting the model to a set of experimental measurements and these models were then used to predict thermal conductivity under other conditions [4–7]. Therefore, a comprehensive model of thermal conductivity in cement-based materials is not well-established until now.

On the other side, fly ash, slag and silica fume are widely used in cement-based materials since they can reduce the cost of materials, conserve energy and alleviate the environmental pressure to a great degree. However, few of literatures studied the influence of fly ash, slag and silica fume in cement-based materials on the thermal conductivity [5,8,9].

Besides, cement-based materials have proved to be typical fractal objects in certain length scales [10–13]. Winslow found that the surface of hydrated cement pastes presented typical fractal characteristic based on X-ray scattering technique [10]. Lange et al. provided a unique insight into the nature of fractal pore

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structure of cement pastes observed from massive backscattered electron images [11]. Livingston interpreted the nucleation and growth for the hydration of main raw cement clinker using a fractal model [12]. Arandigoyen and Alvarez investigated microstructure development of cement-based materials taking porosity, pore size distribution and surface fractal dimension into account [13]. In the meantime, recent studies [14,15] show plentiful of relations enabling the effective evaluation of physical quantities, such as permeability of fluids or heat transportation in porous building materials, to the representation of fractal geometry based on two-dimensional Sierpinski carpet or three-dimensional Menger sponge [16,17]. Therefore, it is possible to develop a rational fractal model to evaluate the heat conduction performance based on pore transportation mechanism in cement-based materials.

In this study, the thermal conductivity of pure and blended cement pastes with fly ash, slag and silica fume are measured by quick thermal conductivity meter (QTM) and predicted by a fractal model combining with the non-contact impedance measurement (NCIM). This model involves two fractal dimensions, intrinsic thermal conductivity coefficients of solid and water or gas phase, some geometric parameters of cement pastes, minimal and maximal pore diameters. Besides, a simulation based on the fractal-like network is further proposed to study the influence of pore structure parameters, intrinsic thermal conductivity coefficients of solid and water or gas phase on thermal conductivity performance of cement pastes.

2. Materials and experiments

2.1. Materials and preparation procedure

In this work, pure cement pastes with different water/cement ratios and blended cement pastes with different dosages of fly ash, slag or silica fume were prepared for thermal conductivity measurement by the quick thermal conductivity meter (QTM) and non-contact impedance measurement (NCIM). Ordinary Portland cement meeting the requirement of ASTM Type I and de-air water were used. Cement pastes with water to cement ratios (w/c) of 0.3, 0.4 and 0.5 by mass were prepared and marked as P3, P4 and P5. Cement pastes with notations of F10, F20, F30 and F40 were also prepared; F10, F20, F30 and F40 stood for pastes with the water to binder ratio (w/b) of 0.4, in which 10%, 20%, 30% and 40% of cement were replaced by fly ash by mass. Similar, notations of S10, S30, S50 and S70 represented that 10%, 30%, 50% and 70% of cement were replaced by slag and w/b ratio was 0.4. Also, 5% and 10% of cement in pastes of SF5 and SF10 with w/b ratio 0.4 were replaced by silica fume, respectively. These pastes were mixed in a planetary-type mixer at 45 rpm for 2 min first and then at 90 rpm for 2 min. The detailed mix proportion of cement pastes is also shown in Table 1. The chemical compositions of the cement, fly ash, slag and silica fume are given in Table 2. The morphology of cement, fly ash, slag and silica fume is shown in Fig. 1.

2.2. Quick thermal conductivity meter

In this study, the quick thermal conductivity meter (QTM) device manufactured by Kyoto electronics was used. Its measurement range is from 0.023 to 12 W m^{-1} K^{-1} with a relative error ±3%. The basic working mechanism of this device is similar with that of traditional two-linear-parallel-probe method. It can measure the thermal conductivity of cement pastes within 60 s using probes which consist of a single heater wire and thermocouple. When constant electric power is applied to the heater, the temperature of the wire increases with time following an exponential progression. Thermal conductivity of cement pastes (k_{QTM}) can be determined by QTM as:

$$k_{QTM} = q\ln(t_2/t_1)/[4\pi(T_2 - T_1)] \quad (1)$$

where q is generated heat per unit length of cement paste; t_1 and t_2 are measured time length; T_1 and T_2 are temperature at t_1 and t_2.

Cubic specimens with dimensions of 100 × 100 × 100 mm with mix proportions described in Section 2.1 were prepared. The dimensions of pastes in this work are satisfied with the recommended range of sample size in QTM test. Three samples were made for each mix proportions. The thermal conductivity of cement pastes at hydration age of 1, 2 and 3 days was measured from three faces of each sample to gain an average value of thermal conductivity. In order to investigate the influence of curing conditions on the thermal conductivity, two identical batch fresh cement pastes for each mix proportion were cured under different curing conditions, viz., "saturated" and "dry" status. For the case of "saturated" status, cement pastes were cured in the environmental chamber with temperature (20 °C) and relative humidity (100%) till to the specific hydration age; whereas for the case of "dry" status, cement pastes were under air dry curing under temperature (20 °C) and relative humidity (20%) followed 1 month oven dry at 60 °C before the QTM test.

Table 1
Mix proportion of cement pastes.

Pure cement paste	Water to cement ratio	
P3	0.3	
P4	0.4	
P5	0.5	
Cement paste blended with fly ash	Water to binder ratio	Cement to fly ash ratio
F10	0.4	9/1
F20	0.4	8/2
F30	0.4	7/3
F40	0.4	6/4
Cement paste blended with slag	Water to binder ratio	Cement to slag ratio
S10	0.4	9/1
S30	0.4	7/3
S50	0.4	5/5
S70	0.4	3/7
Cement paste blended with silica fume	Water to binder ratio	Cement to silica fume ratio
SF5	0.4	95/5
SF10	0.4	9/1

2.3. Non-contact impedance measurement

The non-contact impedance measurement (NCIM) was a newly-promoted non-destructive method to study the hydration, pore structure, chloride ion migration and permeability of cement pastes [14,18–22]. Its working principle can be found in Ref [19]. It has been shown that NCIM has sufficient precision and good reproducibility [18,20]. NCIM test does not need complicated pretreatments and reserves the original pore structure and transportation features of cement-based materials to a greatest extent [14]. In this work, the impedance response of different cement pastes described in Section 2.1 with volume of 1.7 l was measured and recorded from fresh status to hydration age of 3 days. The testing was performed in an environmental chamber with temperature of 20 ± 1 °C and 100% relative humidity.

3. Two-phase fractal model for thermal conductivity based on NCIM

In this work, a two-phase fractal model for thermal conductivity of cement pastes based on NCIM is proposed. In this model, solid phases in cement pastes are assumed to coexist with water or gas phase in the pore network, and the thermal contributions of these phases are analyzed in this work.

General speaking, the thermal resistance ($r_p(d)$) of a single water or gas phase with pore diameter d is illustrated as [23]:

$$r_p(d) = \frac{L_p(d)}{A_p(d)k_p} = \frac{4d^{1-D_t}L_0^{D_t}}{\pi d^2 k_p} \quad (2)$$

where k_p is the thermal conductivity coefficient of water or gas phase; $L_p(d)$ is the actual length of water or gas phase channel, which can be represented by a fractal law [14]; L_0 is the measured length of cement paste; D_t is the fractal dimension associated with pore tortuosity; $A_p(d)$ is the area of pore channel with diameter d.

Meanwhile, the amount of pore (δN) with size lying within d and ($d + \delta d$) in fractal cement paste is expressed as [14]:

$$\delta N = -D_f d_{\max}^{D_f} d^{-1-D_f}\,\delta d \quad (3)$$

where D_f is the fractal dimension fore pore space; $d_{\max}$ is maximal pore diameter in cement paste.