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Examination and modeling of fractality for pore-solid structure in cement paste: Starting from the mercury intrusion porosimetry test

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HIGHLIGHTS

- We examine the fractality in cement pastes.
- The MIP test reveals the most probable fractal type being the solid mass fractal.
- The fractal dimension varies with the distinct pore range.
- We introduce a generalized fractal approach to model the fractality.

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ABSTRACT

Though discussed a lot, some prominent ambiguities have not been clarified yet with respect to the fractality of pore-solid structure in cement paste, i.e., the fractal type and the scale-dependent property. In this paper, starting from the common mercury intrusion porosimetry (MIP) test, a comprehensive examination is conducted on the fractality in cement paste that might be the pore mass fractal, the pore surface fractal or the solid mass fractal. The results indicate that on one side the MIP test reveals the most probable fractal type being the solid mass fractal, and on the other side the fractal dimension varies with the scale of measurement, i.e., the distinct pore range. In addition, a generalized fractal approach is introduced that fits well for the related modeling of fractality in cement paste.

1. Introduction

The fractal characters have been well recognized among natural and artificial porous materials with complex pore-solid structures, such as limes, soils, rocks and ceramics [1–4]. Fractal describes a natural phenomenon or a mathematical set that exhibits similar pattern at different scales [5]. Usually, if the one-dimensional length of fractal is magnified, the spatial content of the fractal scales by a power that is not necessarily an integer [5]. This power is called the fractal dimension. Common examples include the Sierpinski carpet and the Menger sponge [6]. Based on the fractal concept, it is able to generate the complex pore-solid structures via simple iterations of some specific patterns. Moreover, in addition to the two general factors of porosity and pore size distribution, the fractal dimension can also be adopted as a structural parameter to correlate the macroscopic transport properties for porous materials [7–12]. By means of the fractal geometry theory, it is possible to well describe the relationship between microstructure and transport properties in terms of the fractal parameters [13–17]. As a result, though realistic porous materials are often far more complicated that deviates from the ideal fractal, the fractal concept is still widely accepted being an important characterization method.

With the critical importance to concrete, cement paste possesses the much complex pore-solid structure as well that consists of a wide scope of pores ranging from nanometers (nm) to micrometers (μm) [18]. In a pioneering work, Winslow reported the fractal nature of internal surface for cement paste [19]. Thereafter, the fractality in cement paste has been discussed frequently during past decades [20–28]. As shown in Table 1, a brief summary is made about the examined fractality of pore-solid structure in cement paste selected from literatures. It is noted that due to the different techniques and methods applied, authors have made much different conclusions. As a matter of fact, some prominent

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Nomenclature

P	intrusion pressure
d	equivalent pore diameter
γ	surface tension of mercury
θ	contact angle of imperfect wetting between mercury and pore surface
V	intrusion volume of mercury
V^*	reverse intrusion volume of mercury
D_{PM}	pore mass fractal dimension
S	internal pore surface
D_{PS}	pore surface fractal dimension
χ	solid fraction or relative density
D_{SM}	solid mass fractal dimension
L	one-dimensional length of modeling space
E	dimension of modeling Euclidean space
N	total number of identical subregions
x, y, z	respective proportion of the pore phase, the solid phase and the iterating phase in the generator
n	number of subregions in each dimension
i, j	step of iterations
a_i	size of pores, solids and iterating phases
$N_i(x)$, $N_i(y)$, $N_i(z)$	respective number of pores, solids and iterating phases with the size a_i
$V_i(x)$, $V_i(y)$, $V_i(z)$	volume of pores, solids and the iterating phases
D	fractal dimension
$\zeta_i(x)$, $\zeta_i(y)$	number of identical boxes with the size a_i to cover the pore space or solid skeleton
Ω_i	internal surface area
$\Omega_i(x)$, $\Omega_i(y)$	respective total boundary area of pores or solids

Table 1
The examined fractality in cement paste collected from literatures.

Authors	Technique	Pore range (nm)	Scale-dependence	Type	Dimension
Lange et al. [22]	Scanning electron microscope	200–2000	Negative	Pore surface fractal	1.25
Winslow et al. [23]	Small-angle X-ray scattering	3–150	Positive	Solid mass fractal, Pore surface fractal	2–3
Ji et al. [24]	Mercury intrusion porosimetry	13–34; 44–5625	Positive	Pore mass fractal	0.98; 2.98
Zeng et al. [27]	Mercury intrusion porosimetry	10–60; 3750–5000	Positive	Pore surface fractal	2.59–2.96

Table 2
Mix proportions of cement pastes.

Specimen	Composition (% in mass)			Water binder ratio	Curing age (days)
	Portland cement	Blast furnace slag	Limestone powder		
OCP	100	0	0	0.45	60
BCP	30	70	0		
LCP	90	0	10		

ambiguities remain at present with respect to the fractality of pore-solid structure in cement paste, such as the fractal type and the scale-dependent property. Herewith, the fractal type refers to that the fractality might be the pore mass fractal, the pore surface fractal or the solid mass fractal [3,10,23,24,27,28]. The scale-dependent property accounts for that the examined fractality might depend on the scale of measurement, i.e., the distinct pore range [22–24,27,28]. While these ambiguities have not been clarified yet, it is thus difficult to adopt the fractal dimension as a general structural parameter to characterize the pore-solid structure and even to correlate the macroscopic transport property for cement paste.

In this paper, starting from the mercury intrusion porosimetry (MIP) test, a comprehensive examination is conducted on the fractality of pore-solid structure in cement paste. The primary objective is to address the aforementioned two prominent ambiguities, i.e., the fractal type and the scale-dependent property. It will be shown that on one side the MIP test reveals the most probable fractal type being the solid mass fractal, and on the other side the fractal dimension varies with the scale of measurement, i.e., the distinct pore range. In addition, a generalized fractal approach will be introduced that fits well for the related modeling of fractality in cement paste. It is expected that the presented research can provide a framework towards the use of fractal dimension as a general structural parameter to characterize the pore-solid structure in cement paste.

2. MIP tests and methods for the fractality examination

2.1. MIP tests

Three groups of cement paste specimens were prepared in this paper, i.e., the ordinary cement paste (OCP), the blast furnace slag-cement paste (BCP) and the limestone powder-cement paste (LCP), as shown in Table 2. An identical water binder ratio (0.45) and curing age (60 days) were maintained for all the specimens. Upon sufficient mixing, fresh samples were cast and immersed in a curing chamber (saturated $Ca(OH)_2$ solution, 20 ± 1 °C temperature) for 24 h. Then, the demolded samples were further cured in the same chamber until the designed age. Thereafter, broken pieces were taken and subjected to the freeze-drying procedure towards the MIP test [29,30].

The MIP tests were performed on the collected small dry cement paste pieces. As shown in Fig. 1, the applied intrusion pressure was increased from 0 to 240 MPa. Each curve was averaged from three sample replicates. In common, pores are idealized as cylindrical tubes with various diameters, and thus the intrusion pressure P can be related to the pore diameter d via the Laplace equation.

$$P = \frac{4\gamma\cos\theta}{d} \tag{1}$$

where γ is the surface tension of mercury (0.48 N/m), and θ is the contact angle of imperfect wetting between mercury and pore surface (140°). The pore size distribution (PSD) is presented in terms of the incremental intrusion volume V against the pore diameter d, i.e.,