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Full Length Article

Fractal Characteristics of Pore Structures in GGBFS-based Cement Pastes

Jiyoung Kim[a], Young Cheol Choi[b], Seongcheol Choi[c,*]

[a] Department of Civil and Environmental Engineering, Chung-Ang University, Seoul 06974, South Korea
[b] Department of Architectural Engineering, Gachon University, Seongnam 13120, South Korea
[c] Department of Civil and Environmental Engineering, Chung-Ang University, 84 Heukseok-ro, Dongjak-gu, Seoul 06974, South Korea

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ABSTRACT

The present study evaluated pore surface fractal characteristics of high-strength cement pastes with different ground granulated blast-furnace slag (GGBFS) replacement ratios. Using the results of mercury intrusion porosimetry measurements, the surface fractal dimension in various pore-size ranges was calculated. Experimental results show that the fractal characteristics appeared in mesopores in range of 6–10 nm and 10–25 nm and larger capillary pores with sizes of more than 100 nm. In larger capillary pores, as the GGBFS replacement ratio increased up to 65%, the surface fractal dimension and pore volume decreased, and they increased when the GGBFS replacement ratio increased from 65% to 80%. In contrast, higher GGBFS replacement ratios in mesopore regions resulted in an increased surface fractal dimension and pore volume. Furthermore, in the regions where fractal characteristics appeared, pore volume and the surface fractal dimension exhibited a proportional relationship. The ratio of the surface fractal dimension to the volume of larger capillary pores was strongly correlated with the compressive strength of the specimens.

1. INTRODUCTION

The development of the mechanical properties and durability of cementitious materials, such as compressive strength [1–3], corrosion resistance [4], permeability [5,6], and shrinkage [7–9], are essentially influenced by their pore structures. Experimental methods for examining the pore structures of cementitious materials include mercury intrusion porosimetry (MIP), nuclear magnetic resonance, gas adsorption, and scanning electron microscopy [10], among which MIP is the most frequently used technique because its experimental procedure is simple and fast and it can measure a wider range of pore sizes than the other methods [10]. The MIP measures pore-size distributions using the volume of mercury injected at different pressures and estimates the pore structure-related parameters, such as porosity, specific surface area, critical pore diameter, and entrapment pore volume, using the results of measured pore-size distributions. Whereas the actual pore structure of cementitious materials consists of the assembly of irregular pores [11–13], the pore shapes are assumed to be cylindrical in MIP measurement, resulting in the limitation that the actual pore topography of cementitious materials cannot be represented by the parameters aforementioned [14].

The actual pore structures of cement paste are more complex than common shapes such as points, lines, planes and solids, which are defined in Euclidean geometry [15]. In an effort to characterize the irregularity of the pore surfaces of porous materials that reflects actual pore shapes, fractal geometry was introduced by Mandelbrot in the late 1970s [16], and it has been applied by several researchers since then [17–20]. As the pore structures of cementitious materials consist of complex microstructures formed by a series of binder hydration processes [21], they can be considered as fractal structures [22–25]. Fractal structures are characterized by self-similarity and recursiveness, in which small part of a structure is similar to the whole structure at every scale and repeats infinitely. In fractal geometry, the fractal structures are analyzed using such parameter as surface fractal dimension and volume fractal dimension [14,26]. Even though fractal structures comprise a chaotic system that is structurally irregular and complex in pattern [14], their surface can be characterized by the surface fractal dimension, which is the logarithmic ratio of the total length of segmented subparts to the length scale of the subparts [26]. Furthermore, as fractal structures become complex, the total length of segmented subparts increases at the same length scale of the subparts, which increases the surface fractal dimension. Thus, the surface fractal

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* Corresponding author.
E-mail address: schoi@cau.ac.kr (S. Choi).

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dimension is a parameter that can quantify the degree of irregularity of fractal structures, allowing for effective analysis of the topographical characterization of the complex pore structures of cementitious materials [14]. Extensive researches have been conducted on applying fractal geometry to investigating the actual topography of porous cementitious materials [15,27,28].

Winslow [27] experimentally investigated the pore surface fractal characteristics of cement paste using small-angle X-ray scattering and reported that fractal characteristics appeared during the hydration of cement paste, and low water-to-cement ratios lead to a high pore surface fractal dimension. Zeng et al. [15] calculated the pore surface fractal characteristics of fly ash cement pastes during hydration through the results of MIP measurements using Neimark's model [18] and Zhang's model [23] and suggested that the pore structures of cementitious materials have different fractal characteristics depending on pore size and the surface fractal dimension varies with age, water-to-binder ratios, and fly ash replacement ratios. Li et al. [28] investigated the effect of self-desiccation on the pore structures of cementitious materials incorporating a high volume (70%) of ground granulated blast furnace slag (GGBFS) under different curing conditions. They reported that self-desiccation of pores caused high capillary pressure in the pores, which increased the density of nanoscale microstructures and the surface fractal dimension.

As mentioned above, research on the application of fractal geometry to cementitious materials has been conducted extensively; however, the analysis of results has focused on the variation in the surface fractal dimension with experimental variables. As compared to the existing analyses using results of MIP, which focus on the characteristics of pore-size distributions, analysis using the surface fractal dimension can be used to examine the characteristics of pore topography, and therefore, it may be used to complement the existing analysis methods using MIP measurement and help in improving the understanding of the characteristics of the pore structures of cementitious materials during hydration. Consequently, this study analyzed the pore surface fractal characteristics of GGBFS-based high-strength cement pastes during hydration. For this purpose, cement paste specimens with GGBFS replacement ratios of 35%, 50%, 65%, and 80% were prepared. The pore-size distributions of the specimens measured using MIP were applied to Zhang's model [23], and the characteristics of the surface fractal dimension of the specimens with various GGBFS replacement ratios were assessed. In addition, the present study examined the relationship between pore volume, which is measured directly using MIP and represents the pore structures of cementitious materials in the existing methods, and the surface fractal dimension. Additionally, the compressive strength of GGBFS-based cement pastes was measured at ages of 3, 7, and 28 d to investigate the correlation between pore volume, the surface fractal dimension, and compressive strength, and a new parameter was introduced based on the relationship between pore volume and the surface fractal dimension to analyze their correlation with the strength characteristics of the specimens.

2. EXPERIMENT

2.1. Materials

In this study, GGBFS-based cement pastes were created using cement and GGBFS. Type I Portland cement, which satisfies ASTM C150 requirements, was used. Its Blaine fineness and density were 3270 cm^2/g and 3.18 g/cm^3, respectively. In the case of GGBFS, a product with a Blaine fineness of 4330 cm^2/g and a density of 2.89 g/cm^3 conforming to ASTM C989 was used. Table 1 provides the chemical compositions of the cement and GGBFS used in this study. The mineral compositions of cement calculated using Bogue's equation [29] were 58.1% C_3S, 15.0% C_2S, 8.1% C_3A, and 9.2% C_4AF. Fig. 1 shows the particle-size distributions of the cement and GGBFS used in this study. These distributions were measured using a laser diffraction particle-size analyzer (Partica LA-951V2, Japan HORIBA) in accordance with ISO 13320 [30]. As seen in Fig. 1, the Blaine fineness of GGBFS is higher than that of cement.

Table 1
Chemical compositions of cement and GGBFS. Reprinted from Constr. Build. Mater., 137, Y.C. Choi, J. Kim, S. Choi, Mercury intrusion porosimetry characterization of micropore structures of high-strength cement pastes incorporating high volume ground granulated blast-furnace slag, 96–103, 2017, with permission from Elsevier.

	Cement (mass %)	GGBFS (mass %)
SiO_2	20.80	34.00
Al_2O_3	4.93	16.40
Fe_2O_3	3.50	0.50
CaO	62.40	37.20
MgO	1.61	6.29
K_2O	0.90	0.45
Na_2O	0.33	1.33
SO_3	2.21	2.71
H_2O	–	–
LOI[a]	2.74	0.17
Sum	99.42	99.05

[a] LOI: loss of ignition.

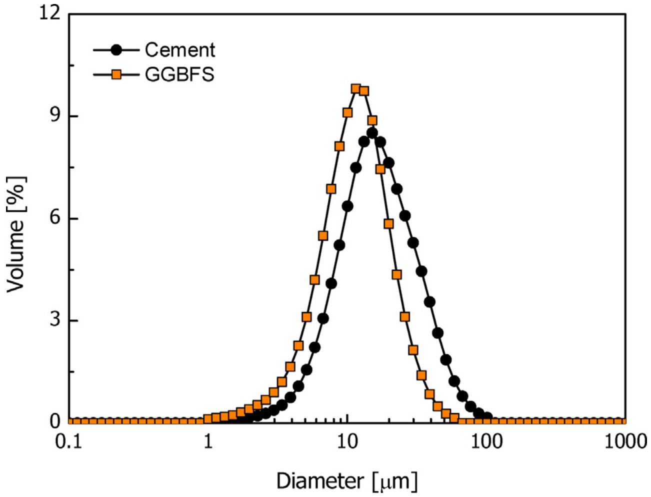

Fig. 1. Particle-size distributions of cement and GGBFS. Reprinted from Constr. Build. Mater., 137, Y.C. Choi, J. Kim, S. Choi, Mercury intrusion porosimetry characterization of micropore structures of high-strength cement pastes incorporating high volume ground granulated blast-furnace slag, 96-103, 2017, with permission from Elsevier.

Table 2
Mixture proportions of the specimens.

Specimen	Cement (g)	GGBFS (g)
S-35	7800	4200
S-50	6000	6000
S-65	4200	7800
S-80	2400	9600

2.2. Mixture proportions and test methods

Table 2 presents the mixture proportions of the specimens used in this study. Cement was partially replaced with GGBFS, comprising 35%, 50%, 65%, and 80% of the total binder weight. The water-to-binder ratio was 0.2, and a superplasticizer, which is 0.53% (63.6 g) of the total binder weight, was used. The amount of mixing water was 2400 g in all mixtures. The numbers that follow