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FRACTAL MODEL FOR SIMULATING THE SPACE-FILLING PROCESS OF CEMENT HYDRATES AND FRACTAL DIMENSIONS OF PORE STRUCTURE OF CEMENT-BASED MATERIALS

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ABSTRACT

A fractal model is established for simulating the space-filling process of cement hydrates in cement paste. Based on this model, it is predicted that the fractal dimension D of the pore structure of hardened cement paste (hcp) is between 0 and 3, and that the water-to-cement ratio, degree of hydration of cement, and the addition of pozzolanic materials will affect the value of D. With the mercury intrusion porosimetry (MIP) technique, the fractal dimensions D of the pore structure of hcp can be determined; the quantitative relationship between D, accumulative volume V^* of pores as defined in the paper, and the radius of pores ρ is established as $V^* = t\rho^{3-D}$ (where t is a constant). The experimental results of the pore size distribution of hcp from MIP were used to verify the equation, and the D value is calculated. It is experimentally found that the value of D for pores in fine diameter range is smaller than that in large diameter range. The experimental results also suggest that the higher the strength of concrete, the smaller the value of D in both the small and the large pore diameter ranges. © *1997 Elsevier Science Ltd*

Introduction

Since the pioneer application of fractal theory (1) by Winslow (2) in cement paste, the research on the fractal nature of cement-based material microstructure has received increasing attention (3–6). However, due to the difficulties in detecting the complex internal surface of pores in hardened cement paste, different experimental techniques based on different physical principles are adopted to determine the fractal dimension D of pores or microcracks in hcp. There is a great discrepancy between the reported results of fractal dimension obtained with different techniques (3).

It is not strange that different fractal dimensions of pore structure are reported because natural objects may not exhibit only one unique fractal dimension throughout the scaling range from angstroms to meters. The volume-based methods such as the small angle x-ray scattering, small angle neutron scattering, and nuclear magnetic resonance methods, which use extremely small wavelengths (so small that it could reveal extremely fine details of internal surface of pores) as yardsticks to measure or detect the delicate details of pores, usually reported higher values of D (from 2.4–3.0) than the area-based method such as the microscope method, which reported values of D ranging from 1.1–1.4. It is very important to find a suitable experimental technique using feasible yardsticks with great variable ranges from several tens of angstroms to millimeters, which can not only measure the pores at the fine end of size scale but also the pores at the coarse end of the size scale. The mercury intrusion porosimetry (MIP) technique seems to fit for this purpose because it can detect the pore diameters from tens of angstroms to millimeters. This technique is used in this paper to determine the pore size distribution of hcp and a concrete sample. Based on the pore size distribution, the fractal dimensions of pore structure are computed with the equations developed in this paper.

It is reasonable for us to expect different D values for different cement-based materials. However, only one fractal dimension of pore structure $D = 1.247$ was obtained by D.A Lange (3) for paste, paste with silica fume, and mortar. The reason may be that the yardsticks used in their image-based fractal analysis method can not be varied in great ranges, hence it detected only the pore details within certain limited scaling ranges.

Some recent efforts have been made to establish the relationship between the fractal dimension of hcp microstructure and mechanical properties (5,6). Ji (5) established one quantitative relationship between the fractal dimension of the network of microcracks in the fracture process zone and the fracture energy of concrete, and one phenomenon, i.e., the higher the strength of concrete, the lower the fractal dimension of the network of microcracks was observed. Castano et al. (6) found that the addition of polymer to the MDF mix could reduce the fractal dimension of pore structure. In this paper, the effect of the water-to-cement ratio, degree of hydration of cement, and strength of concrete on the fractal dimension of pore structure of cement-based materials was theoretically and experimentally investigated.

Establishment of a Fractal Model for Simulating the Space-Filling Process of Cement Hydrates

Three phases, i.e., solid, liquid, and air, exist in the cement paste. The solid phase consists of C-S-H gel, $Ca(OH)_2$, other cement hydrates, and unhydrated cement particles. The liquid phase includes the interlayer water in C-S-H gel, the free water in pores. The air phase includes the pores and microcracks in the cement paste. In the MIP experiment, the liquid phase (or water) is always drawn out under the effect of high vacuum, so in our fractal model, only solid phase and air phase (pore) in hcp are taken into account here.

Let us consider the simplest plane situation. Assume that in the plane there is a square of one unit area that is going to be filled in with solid phase of hcp, as shown in Figure 1. First, we divide the square into 9 small squares, as shown in Figure 2. Then assume that, due to the hydration of cement particles, there are two solid blocks of cement hydrates to fill in the two small squares, and that the two solid blocks can occupy any two of the nine small squares, for example, in Figure 2 they occupy the central small square and corner small square (shaded areas). This Figure 2 is called the generator of the fractal processes that are going to be conducted immediately. We then divide every one of the remaining seven small blank squares into nine *smaller* squares and again in every small square, two *smaller* central and corner squares (shaded areas) are filled in with cement hydrates solids, as we have done in

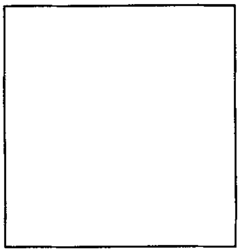

FIG. 1.
Original square of unit area (lateral length = 1).

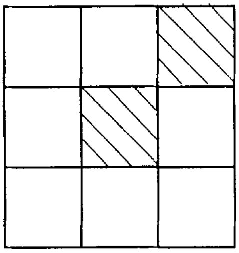

FIG. 2.
Generator of fractal process (lateral length of small square = 1/3, fractal dimension can be calculated in this process).

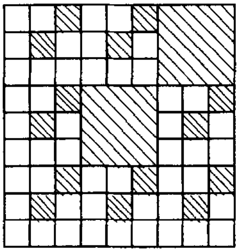

FIG. 3.
Further division of the remaining blank squares and filling process of particles of cement hydrates.

Figure 2. We can further divide every one of the blank *smaller* squares in Figure 3 into nine *even smaller* squares, and fill in the solid particles of cement hydrates into the resultant central and corner *even smaller* squares (shaded areas) resulted in this process. We can conduct the process further and further without limit.

The whole processes shown in Figures 1–3 are quite similar to the plane-filling process of particles of cement hydrates due to the continuous hydration of cement particles. However, no matter how completely the cement particles hydrate, there still remains some blank space (pores) that can not be occupied completely by the particles of cement hydrates.

According to the principle of fractal geometry (1), if a generator is composed of N small squares (Fig. 2) and the lateral length of the small square is $1/r$ of that of the original square of unit area (Fig. 1), then the fractal dimension D of the resultant blank or unshaded small squares is computed as:

$$D = \log N/\log r = \log 7/\log 3 = 1.7712 \tag{1}$$

Now let's develop the above plane fractal model into a space-fractal model. Imagine that there is a cube of unit volume. First, we divide the cube into m^3 small cubes each with lateral length $= 1/m$. Due to the hydration of cement particles, there is solid phase of cement paste to fill in n small cubes ($n < m^3$); this filling process results in $(m^3 - n)$ small cubes that remain unoccupied by solid phase of cement paste. This process is called the generator of the fractal space-filling process of solid phases of cement paste. We then divide every one of the blank $(m^3 - n)$ small cubes into m^3 *smaller* cubes each with lateral length $= 1/m^2$. As has been done in the generator process, the n *smaller* cubes in every one of the blank $(m^3 - n)$ small cubes are filled with solid particles of cement-hydrates. The division and filling process can be conducted further and further without limit. In this way, a fractal model is established for simulating the space-filling process of solid phases of cement paste due to the continuous hydration of cement particles. No matter how complete the cement particles hydrate, there remains some space that can not be taken up by the cement hydrates, and this results in the pores in the hardened cement paste.

Similar to Eq. 1, the fractal dimension of pores in this fractal model is calculated as:

$$D = \log(m^3 - n)/\log m = 3 + \frac{\log(1 - n/m^3)}{\log m} < 3 \tag{2}$$

where n is the number of small cubes that are occupied by the cement hydrates in the generator process, m^3 is the total number of small cubes in the generator process ($n < m^3$), and $m^3 - n$ is the blank cubes unoccupied by solid phase (blank cubes are analogous to pores). The term n can also be regarded as a parameter describing the space-filling capacity of cement hydrates for a specific hcp. As we can see from Eq. 2, the higher the space-filling capacity of cement hydrates, the higher the value of n and lower the D, i.e., the lower the fractal dimension of pore structure of hcp. For example, for a poorly hydrated cement paste, the production of cement hydrates is low, so n is low, hence D is high. It can be predicted from this fractal model and from Eq. 2 that the more fully hydrated hcp will result in a lower D value than the less hydrated hcp. And for hcp with high water-to-cement ratios, after the dissipation of free water in hcp, there leaves more pores for the cement hydration products to fill in, the number of blank cubes ($m^3 - n$) is high, so D is high. The prediction above about the changing tendency of D is experimentally confirmed with MIP test results in this paper.

It can also be anticipated from this fractal model that for hcp with pozzolanic materials such as silica fume, due to their pozzolanic reaction in hcp, more cement hydration products will be generated, so n in Eq. 2 will be greater than that of hcp without pozzolanic material, hence the fractal dimension of pore structure of hcp with pozzolanic material will be lower than that without silica fume. The experimental confirmation of this anticipation is under way. The fractal model also predicts that the fractal dimension of the pore structure of hcp is between 0 and 3 (i.e., $0.0 < D < 3.0$) as evidenced in Eq. 2.

Determination of the Fractal Dimensions of the Pore Structure of Cement-Based Materials with the MIP Technique

The pores or microcracks in hcp exist in great scale ranges, from angstroms to millimeters. Although the MIP technique is effective in determining the pore size distribution of hcp in the diameter range from 80 Å to 0.2 mm, it still has some demerits, for example, it can not truly reflect the size and incremental volume of ink bottle shaped pores. However, the technique can still provide overall information about the pore size distribution of hcp. The experimental results of pore size distribution are used to verify our equation (i.e., Eq. 10) describing the relationship between the fractal dimension, total pore volume, and pore diameter of hcp. Pfeifer and Avnir (4) developed a differential equation to compute the fractal dimensions of pore structure with pore size distribution experimental results from the MIP technique. The following theoretical deduction is a development from their work (4).

Assume that the network of pores (continuous and discontinuous) in hcp is composed of cylinder pores with diameter ρ, and length $h(\rho)$. We can see later that it does not matter whether the pores are cylindrical or not because $h(\rho)$ is going to be canceled.

In the MIP experiment, with the incremental pore volume we can calculate the classical cumulative pore volume V, which is accumulated in the order from great pore diameter to small pore diameter. However, a *new* cumulative pore volume V^* is defined here by accumulating the incremental pore volume in the reversed order: from small pore diameter to great diameter. The number of pores dM in the pore diameter range from ρ to $\rho + d\rho$ is:

$$dM = \frac{dV*}{\pi\rho^2 h(\rho)} d\rho/d\rho = \frac{dV*}{d\rho} \frac{d\rho}{[\pi\rho^2 h(\rho)]} \tag{3}$$

Because it is difficult to use practical yardstick to detect or measure the inner surfaces of pores in hcp, an imaginary experiment is created here using air molecules with a series of radii r as ideal yardsticks to measure the internal surfaces of pores. Monomolecule layer adsorption is assumed to form on the surface of pores. For every pore with diameter $\rho \geq r$, the number (n_a) of air molecule with radius r that one pore can accept is only:

$$n_a = \frac{2\pi\rho h(\rho)}{\pi r^2} = \frac{2\rho h(\rho)}{r^2} \tag{4}$$

The number of air molecules that dM number of pores can accept is:

$$dM \times n_a = dV^*/d\rho \frac{d\rho}{[\pi\rho^2 h(\rho)]} \frac{2\pi\rho h(\rho)}{\pi r^2} = dV^*/d\rho \frac{2d\rho}{\pi\rho r^2}$$

Assuming that the fractal dimension of pore structure is D according to the principle of fractal geometry, the total number of air molecules INN$_a$ that the whole network of pores can accept is:

$$N_a = cr^{-D} \tag{5}$$

where c is a constant and r is the radius of air molecules used as yardstick. Only the pores with radii $\rho \geq r$ can accept air molecule of radius r, the total number of air molecules N_a that can be accepted by the pore with radius $\rho \in [r, \rho_{max}]$ is:

$$N_a = \int_r^{\rho_{max}} dM \times n_a = \int_r^{\rho_{max}} \frac{dV^*}{d\rho} \frac{2d\rho}{\pi\rho r^2} \tag{6}$$

where ρ_{max} is the maximum pore radius in hcp that can be measured by the MIP technique. Substitution of N_a in Eq. 5 into Eq. 6 yields:

$$\int_r^{\rho_{max}} \frac{dV^*}{d\rho} \frac{2d\rho}{\pi p r^2} = cr^{-D} \tag{7}$$

Differentiation of Eq. 7 with respect to r leads to:

$$\frac{dV^*}{dr} = \frac{c\pi}{2}(D - 2)r^{2-D} \tag{8}$$

that is,

$$\frac{dV^*}{d\rho} = \frac{c\pi}{2}(D - 2)\rho^{2-D} \tag{9}$$

Assuming that the minimum pore radius in hcp is 0, by integrating V^* in Eq. 9 with respect to ρ from 0 to ρ, we obtain:

$$V^* = \int_0^{V^*} dV^* = \int_0^{\rho} \frac{c\pi}{2}(2 - D)\rho^{2-D} d\rho = \frac{c\pi(D - 2)\rho^{3-D}}{3 - D} = t\rho^{3-D} \tag{10}$$

where

TABLE 1
Mix Proportion and Compressive Strength of Concrete at 90 Days

		Materials (kg/m^3)					
			Aggregate				
No.	W/C	Cement	20 mm	10 mm	Sand	Water	Compressive Strength (MPa)
1	0.66	330	806	403	645	219	30
2	0.35	550	785	393	478	190	63
3	0.28	550	872	436	433	152	110

$$t = \frac{c\pi(D - 2)}{(3 - D)}$$

By taking the logarithm of Eq. 10, we have:

$$\log V^* = \log t + (3 - D)\log \rho = \log t + (3 - D)\log \frac{d}{2} = S + (3 - D)\log d \qquad (11)$$

where $S = \log t - (3 - D)\log 2$, and d is the diameter of pore, $d = 2\rho$.

If the slope of the straight line of Eq. 11 in the $\log V^*$–$\log d$ double logarithmic coordinate system is k, then:

$$D = 3 - k \qquad (12)$$

The MIP technique was used to determine the pore size distrubution of hcp, and, based on Eq. 12, the fractal dimension D of pore structure was computed.

Experimental Determination of the Fractal Dimensions of the Pore Structure of Cement-Based Materials

Hardened cement paste, normal strength, and high strength concrete were made to determine their fractal dimensions of pore structure. For hcp, the water-to-cement ratio was w/c = 0.45. The cement used was the Dunshi Brand Portland cement with strength grade #525 produced in China. For concrete, the mix proportion and compressive strength determined at the age of 91 days are given in Table 1. An Italian-made porosimeter and an American-made porosimeter were used to determine the pore size distribution of hcp at 28 days and concrete samples at 91 days, respectively. In preparing the concrete sample for the MIP test at 91 days, we first split the concrete specimens, then used a saw to cut the hcp out of the concrete; the resultant samples are in the form of pellets about 5 mm in size. Great care was taken to ensure that the pellet was made up of hcp with as little aggregate in it as possible.

For the hcp, the mean pore diameter and cumulative pore volume V^* in percentages are given in Table 2. The total mercury intrusion volume was 0.0589 mL/g.

Figure 4 is plotted according to the data in Table 2. It is shown in Figure 4 that the experimental points in the $\log V^*$–$\log d$ coordinate system can be divided into two parts, each of which can be best-fitted with two straight lines, one with a steep slope, the other with a gradual slope, respectively.

TABLE 2
The Mean Pore Diameter and Cumulative Pore Volume V* of the hcp with W/C = 0.45

Pore Diameter d (Å)	logd	Cumulative Pore Volume V* (%)	log V*	Pore Diameter d (Å)	logd	Cumulative Pore Volume V* (%)	log V*
130.5	2.1156	9.67	0.9854	1250	3.0969	94.73	1.9765
143	2.1553	18.2	1.2601	1687.5	3.2272	95.65	1.9807
158.5	2.2000	28.95	1.4617	2187.5	3.3400	96.08	1.9826
177.5	2.2492	40.72	1.6098	3125	3.4949	96.51	1.9846
201	2.3032	50.39	1.7023	4375	3.6410	96.94	1.9865
232	2.3655	60	1.7782	7187.5	3.8566	97.43	1.9887
275	2.4393	70.21	1.8464	12187.5	4.0860	97.92	1.9909
337.5	2.5283	29.28	1.8992	20000	4.3010	98.45	1.9932
437.5	2.6410	86.25	1.9358	31250	4.4949	98.98	1.9956
625	2.7959	91.54	1.9616	56250	4.750	100	2
875	2.9420	93.38	1.9703				

The range of pore diameters accounting for the steep slope line is from 130.5 Å to 337.5 Å; the range of pore diameters accounting for the gradual slope line is from 437.5 Å to 56250 Å.

For hcp, the slopes of the steep and gradual lines are, respectively, $k_1 = 2.01998$ and $k_2 = 0.02189$; from Eq. 12 the fractal dimensions of pores in small and great diameter ranges are, respectively, $D_1 = 3-k_1 = 3-2.01998 = 0.980023$ and $D_2 = 3-k_2 = 3-0.02189 = 2.9781$. Corresponding correlation coefficients by linear regression are summarized in Table 3.

The fact that, after linear regression, there exists two straight lines with distinctively different slopes in small pore diameter range and great pore diameter range respectively suggests that the pore structure of hcp exhibits multifractal dimensions characteristics.

As discussed in the fractal model above, with the hydration of cement particles, more and more cement hydrates will be produced to fill in the pores in the hcp. The pores in small

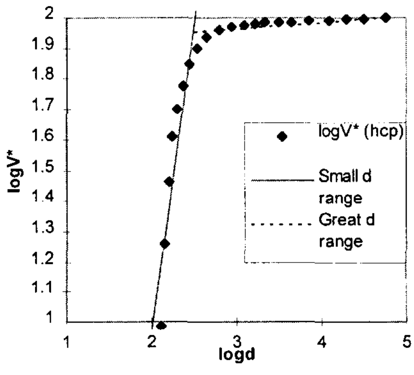

FIG. 4.
Relationship between logV^* and log$d$ of hcp with w/c = 0.45.

TABLE 3
Fractal Dimensions of Pores In Small Diameter Range and Great Diameter Range and Their Corresponding Correlation Coefficient

		Hardened Cement Paste	Concrete (30 MPa)	Concrete (63 MPa)	Concrete (110 MPa)
Small Diameter Range	Fractal Dimension of Pores in Small Diameter Range D_1	0.9800	2.3191	1.5834	1.56415
	Diameter Range (Å)	130.5–337.5	80–31084	80–641	80–402
	Correlation Coefficient	0.9155	0.9301	0.9839	0.9786
Great Diameter Range	Fractal Dimension of Pores in Great Diameter Range D_2	2.9781	2.9804	2.9678	2.9401
	Diameter Range (Å)	437.5–56250	48368–148846	805–922728	493–1560985
	Correlation Coefficient	0.8620	0.9932	0.9796	0.9540

diameter are a result of the large pores that are being filled in or "refined" by the hydration products, which means that the n in Eq. 2 is becoming greater and greater, hence the fractal dimension of pores in small diameter range is less than that of pores in great diameter range.

The experimental results of $\log V^*$–$\log d$ for high strength and normal strength concrete are plotted in Figures 5–7. The fractal dimensions calculated with Eq. 12 are summarized in Table 3. Similar to hcp, all the concretes demonstrate multifractal dimensions characteristics. The fractal dimension of pores in greater diameter range is greater than that in smaller diameter range. The comparison of fractal dimensions of pores (both in small and great diameter range) indicates that the higher the strength of concrete the smaller value of fractal dimension.

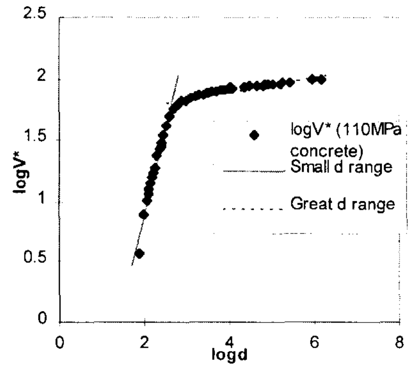

FIG. 5.
Relationship between $\log V^*$ and $\log d$ for concrete with a compressive strength of 110 MPa.

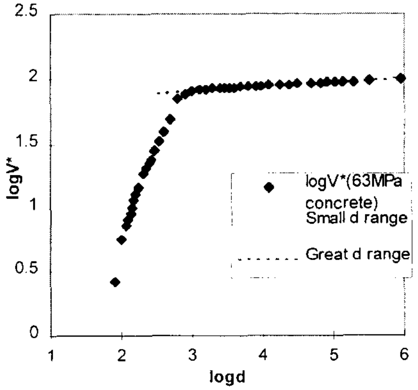

FIG. 6.
Relationship between $\log V^*$–$\log d$ for concrete with a compressive strength of 63 MPa.

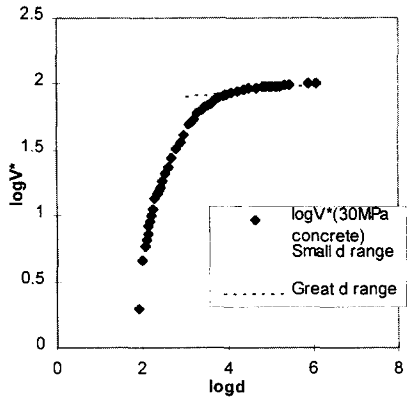

FIG. 7.
Relationship between logV^*–log$d$ for concrete with a compressive strength of 30 MPa.

Conclusions

1. A fractal model is established to simulate the space-filling process of solid phase of cement hydrates. The model predicts that the fractal dimensions of the pore structure of hcp is higher than zero but less than 3. The higher degree of hydration of cement or the reduction of w/c will result in the reduction of the fractal dimension of the pore structure of hcp.
2. The relationship between the fractal dimension D of pore structure of cement-based material, the pore diameter ρ, and the accumulative pore volume V^* defined in the paper can be expressed as $V^* = t\rho^{3-D}$ where t is a constant.
3. It is possible to determine and distinguish the fractal dimensions of pores in small diameter range from that in great diameter range with the MIP technique, and it is found that the fractal dimension of pores in small diameter range is smaller than that in great diameter range.
4. Regardless of the pore diameter ranges, experimental results showed that the higher the strength of concrete the smaller the fractal dimension of pore structure of concrete.

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